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1

ACTION OF LIGHT ON SULPHUR

BY G. A. RANKIN

Previous Work

It was first discovered by M. A. Lallemand[1] that, when sunlight concentrated with a lens is passed through a saturated solution of sulphur in carbon bisulphide, amorphous sulphur is precipitated as a fine powder along the path of the light rays. On analyzing the light after it passes through the solution it was found that all the light of the spectrum from A to G is transmitted while that from G through the ultraviolet is absorbed by the solution. Lallemand concluded that the work necessary to transform the rhombic sulphur into the amorphous state is done by the light absorbed. Berthelot[2] verified the results of Lallemand and found further that the arc light, which contains a large amount of ultraviolet light, could be used to replace the sunlight. He also found that the presence of hydrogen sulphide in the solution prevented the precipitation of the amorphous sulphur, and that when some of the amorphous sulphur was shaken with an alcoholic solution of hydrogen sulphide, it went over to the soluble form. Berthelot determined the heat of reaction when rhombic sulphur was transformed into the amorphous state. He found that a small amount of heat was evolved, and concluded that the light acted simply as an exciting agent and did not effect the work of transformation. Petersen[3] obtained an evolution of heat of 910 calories, but there seems to be a question whether his amorphous sulphur was the same as Berthelot's.

The question now arises as to what effect the use of solvents other than carbon bisulphide, the variation of concentration, temperature, and intensity of light would have on

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[1] Comptes rendus, 70, 182 (1870).

[2] Ibid., 70, 941 (1870).

[3] Zeit. phys. Chem., 8, 611 (1891).

the precipitation of the amorphous sulphur? In the present paper some attempt has been made to answer this.

Verification of Previous Work

A saturated solution of sulphur in carbon bisulphide containing an excess of sulphur was placed in the sunlight. The amorphous insoluble sulphur precipitated and the excess of soluble sulphur began to dissolve. After some time it all dissolved and the solution became unsaturated with respect to the soluble sulphur, due to the amount of insoluble sulphur thrown out of solution. To show that only light of the violet or blue end of the spectrum effected the precipitation of the amorphous sulphur the following test was made: Two bottles were taken, each containing a saturated solution of sulphur in carbon bisulphide. One was placed in a beaker containing a solution of potassium bichromate, which absorbs all the light of the spectrum from the violet to the light green, while the other bottle was placed in a similar beaker containing a solution of copper sulphate which absorbs all the light of the spectrum from the red to the light green. On placing them under the direct action of the sunlight, it was seen that the bottle in the copper sulphate solution was immediately filled with a cloud of amorphous sulphur while the other bottle remained perfectly clear. This shows clearly that it is the violet light which causes the precipitation.

Influence of Concentration

As the concentration of sulphur in carbon bisulphide is varied, the intensity of light necessary for precipitation varies. Thus with a very dilute solution the intensity of light required is very great in comparison with the intensity required for a saturated solution, the temperature being constant.

Influence of Temperature

If the concentration is held constant and the temperature varied, it is found that the intensity of light required for precipitation of the amorphous sulphur increases with rising temperature.

Influence of Solvent

If amorphous sulphur separates pure from a solution, we are dealing with the displacement of equilibrium between two solid phases, rhombic sulphur and amorphous sulphur. The nature of the solvent can therefore have no effect. When light was allowed to act on solutions of sulphur in such solvents as toluene, benzene, carbon tetrachloride, and acetone, a precipitation of amorphous sulphur was obtained in every case. Berthelot's contention that light acts only on dissolved sulphur is wrong. The reaction takes place more rapidly in the presence of a solvent because no surface film is formed.

The Reverse Reaction

The reaction between rhombic sulphur and amorphous sulphur, R. S. $\rightarrow$ A. S. takes place only under the action of light. If it is a reversible one, the reverse reaction A. S. $\rightarrow$ R. S. would take place only in total darkness or very feeble light. Such was found to be the case. A thin coating of amorphous sulphur was precipitated from solution on the sides of a vessel. The vessel was then placed in the dark for twelve hours, after which time the amorphous sulphur had entirely disappeared, showing that the reaction A. S. $\rightarrow$ R. S. had taken place. We may then represent this reversible light reaction thus:

$$\text{R. S. (Dark)} \rightleftarrows \text{A. S. (Light)}$$

The rhombic sulphur is the stable form in the dark while the amorphous insoluble form is stable in the light.

If we add to the solution some substance which accelerates sufficiently the rate of the reaction A. S. $\rightarrow$ R. S., no precipitation of amorphous sulphur will occur even in bright sunlight. Berthelot found such a substance in hydrogen sulphide which, however, does not prevent precipitation of amorphous sulphur completely in the most intense light. It has been shown by Professor Smith, of Chicago,[1] that hydrogen sulphide and ammonium hydroxide increase the rate at which

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[1] Jour. Am. Chem. Soc., 27, 993 (1905).

fused amorphous sulphur changes into the other modification, and it was to be expected that a similar catalytic action would be found at lower temperatures and in presence of a solvent. Following out this idea, experiments were also made with ammonia gas. As this reacts with carbon bisulphide, another solvent had to be used. When a solution of ethyl alcohol saturated with ammonia gas was shaken with flowers of sulphur, which had been extracted with carbon bisulphide, the amorphous sulphur went over into the soluble state in a very short time. On crystallizing from carbon bisulphide rhombic sulphur was obtained. The displacement of the equilibrium is more marked with ammonia than with hydrogen sulphide.

Equilibrium Diagram'

After the above preliminary work had been done, it was thought that it might be interesting to determine with some accuracy the conditions of concentration, temperature and light intensity at which the precipitation of the amorphous sulphur first takes place. Since the light beyond G can be treated as a new independent variable, it must be possible to obtain one isothermal curve for the solubility of rhombic sulphur and another for the solubility curve of amorphous sulphur. At the intersection of these two curves we should have rhombic and amorphous sulphur co-existing in stable dynamic equilibrium with solution and vapor. An electric arc focused with a system of lenses was used as the source of light. It answered the purpose better than any other source obtainable, as it contains large amounts of violet and ultra-violet light and can be kept constant within certain limits. The average intensity of the focus was found to be 1600 candle-power. To determine the intensity of the light at any point beyond the focus, the diameter of the beam of light at that point was measured, and knowing that the intensity varies as the square of the diameter of the beam of light, it can be determined. Table I gives the values for the intensity of the light as calculated for various distances from lens. From these data a curve was plotted as shown. The focus was 25 cm from the lens.

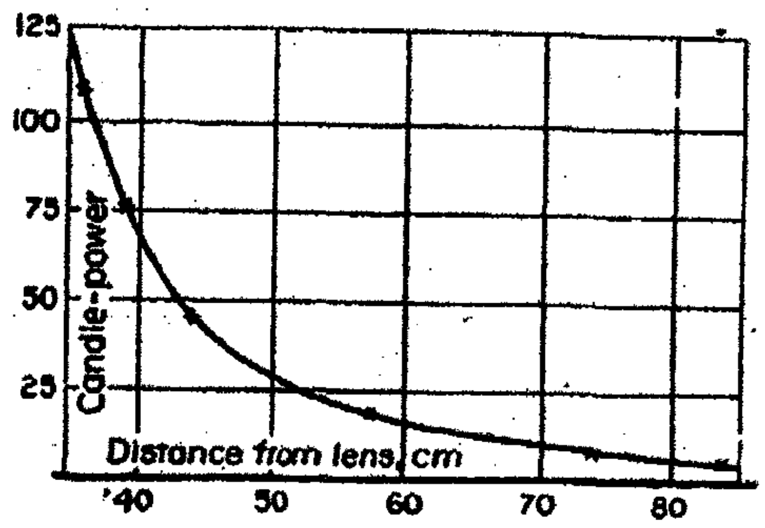

Fig. 1

TABLE I

Distance from lens cm.	Intensity in candle-power per sq. cm.
36	109
39	76.3
44	44.6
56.8	17.0
74	8.0
84	6.5

In performing the experiment the temperature was maintained constant while the concentration and light intensity were varied. Various concentrations of sulphur in carbon bisulphide were made up and the intensity of light at which each first started to precipitate was determined. By working in this way, we eliminate all difficulties as to the intensity of the light in the interior of the flask. Data for two different temperatures were obtained and are given in Tables II and III.

From the above data two curves were plotted, ordinates being taken as intensities of light and abscissas as grams of sulphur per hundred grams of carbon bisulphide. The values of the ordinates on the left refer to the 22.5° curve; those on the right to the 40° curve.

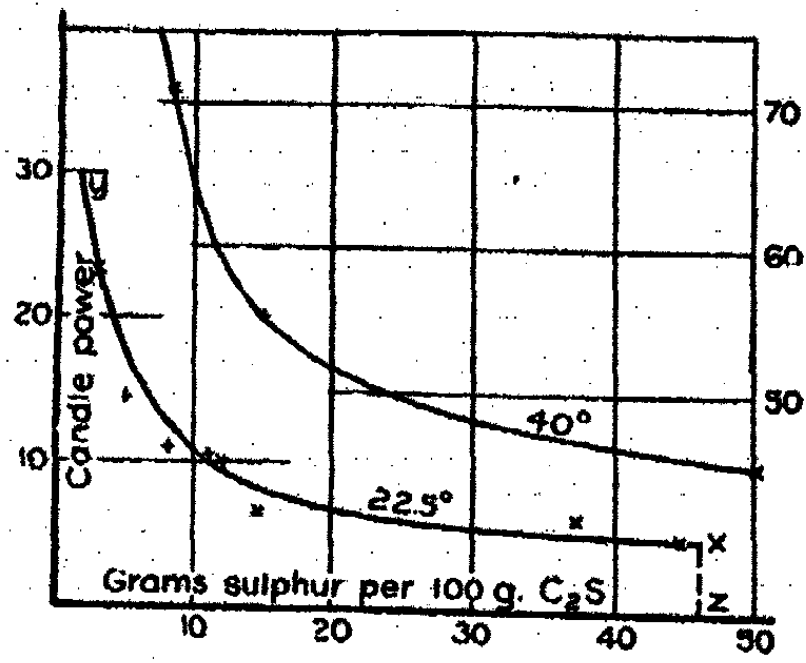

Fig. 2

TABLE II

Solvent: Carbon Bisulphide **Light: Electric Arc**

Temperature, 22.5° C

Intensity in candle-power	Grams sulphur per 100 grams carbon bisulphide
5.0	44.7
6.4	37.2
6.4	15.0
10.0	12.0
10.4	11.2
11.0	8.0
12.2	4.8
23.2	3.0

TABLE III

Temperature, 40°

70.8	8.0
54.8	15.2
45.8	49.6

Along the curve *xy* amorphous sulphur is in equilibrium with the solution and vapor. The dotted line *xz* is the solubility curve for rhombic sulphur, it being taken for granted that the solubility of the rhombic sulphur is not affected by the light. At the point *x* rhombic sulphur, amorphous sulphur, solution and vapor are in dynamic equilibrium. In the field above the curve, amorphous sulphur is the stable form while below the curve rhombic sulphur is the stable form.

The light necessary to maintain amorphous sulphur in equilibrium with the solution increases as the concentration decreases until finally the curve approaches the line of ordinates asymptotically as the concentration approaches zero. As the concentration increases, the light necessary for equilibrium decreases until the point is reached, at which, for a given temperature, the solvent is saturated with respect to both forms of sulphur. This quadruple point for a temperature of 22.5° is not at the point of total darkness as can be seen from the curve but at an intensity of about 5 candle-power.

As the temperature for any given concentration is increased, the intensity of light required for equilibrium increases rapidly, showing that the rate of change of the amorphous sulphur increases with a rise of temperature. At 40° it takes about 45 candle-power to produce the first precipitation of amorphous sulphur from a saturated solution.

No attempt has been made to calculate a formula for either curve. The values for the intensity of the light are only approximate at best and refer to the total light, whereas the effective light is that beyond G.

Summary

(1) Amorphous insoluble sulphur is precipitated from solutions of rhombic sulphur by the action of violet and ultra-violet light.

(2) As the concentration increases the intensity of light required for precipitation decreases. (Temperature constant.)

(3) If the concentration remains constant and the temperature rises, a more intense light is necessary to cause precipitation.

(4) The reaction is a reversible one, the direct action being favored by the light, the reverse by the dark.

$$\text{R. S. (Dark)} \rightleftarrows \text{A. S. (Light)}$$

(5) Ammonia and hydrogen sulphide tend to accelerate the reverse action and to prevent precipitation even in bright sunlight.

(6) Two isothermal solubility curves were obtained, which give the equilibrium conditions of concentration and intensity of light for carbon bisulphide solutions of sulphur at 22.5° and 40° C.

(7) Amorphous and rhombic sulphur are in equilibrium when acted on by a 5 candle-power light at 22.5° and by a 45 candle-power at 40°.

(8) All the phenomena are covered by the phase rule classification provided we treat the light as a new, independent variable.

The work was suggested by Professor Bancroft and carried on under his supervision.

Cornell University,
August, 1906.

ON THE MECHANISM OF INDUCED REACTIONS

BY W. LASH MILLER

The word "Induction," in the sense in which it is used in this article, was introduced into the chemical vocabulary by F. Kessler, in 1863.

"Let Rα and Rβ be two reducing agents" (wrote Kessler[1]), Oα and Oβ two oxidizing agents, such that under certain conditions Rα reacts easily with Oα while Rβ and Oβ react with difficulty or not at all. If then, on bringing all four substances together under these conditions, we find that the reaction between Rβ and Oβ is accelerated, we will regard this reaction as "induced" by that taking place between Rα and Oα. In most cases, at least so far as my knowledge goes, this general case is specialized, either by Oα being identical with Oβ, or Rα with Rβ. To distinguish these two cases, I shall call the former "induced oxidation" and the latter "induced reduction."

A large number of experimental and theoretical papers dealing with the subject of chemical induction have appeared since Kessler's time; lists are given by Manchot,[2] Engler and Weissberg,[3] Schilow,[4] Luther,[5] and Mellor.[6]

The term "induced reaction" is now generally restricted to Kessler's special case, in which only one oxidizing agent and two reducing agents are present or *vice-versa*; the name "actor" is given to the oxidizing agent in cases of induced oxidation, and to the reducing agent in cases of induced reduction, while the "inductor" is the substance which reacts quickly with the actor, and accelerates or "induces" the reaction between the

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[1] Pogg. Ann., 119, 218 (1863).

[2] Liebig's Ann., 325 (1902).

[3] Kritische Studien über die Autoxydationsvorgänge. Braunschweig, 1903.

[4] Zeit. phys. Chem., 42, 641 (1903).

[5] Ibid., 46, 777 (1903).

[6] Chemical Statics and Dynamics, London, 1904.

actor and the third reagent, or "acceptor." The "induction factor" gives the number of equivalents of acceptor which enter into reaction while one equivalent of inductor is oxidized (or reduced) by the actor.

From the theoretical point of view, the simplest cases that come under Kessler's definition are those in which the induction can be explained by the known properties of an isolable product of the reaction between actor and inductor. In order to make sure that the explanation suggested is the true one, it is only necessary to study the two reactions: actor *plus* inductor, and product *plus* acceptor, separately, and compare them with the reaction which takes place in solutions containing actor, inductor, and acceptor together. This has been done by Harcourt and Esson[1] and by Bell[2] for the system H_2O_2, HI, $Na_2S_2O_3$; by Federlin[3] for the system $K_2S_2O_8$, HI, H_3PO_3; by Schilow[4] for the system $HBrO_3$, HBr, $HAsO_3$; and by Bowman[5] for the system $HBrO_3$, HI, $HAsO_3$. Cases like these belong demonstrably to the group of consecutive reactions, none of which were included by Kessler in his tables of examples; and it seems better to employ the term "induced reaction" only where no such obvious explanation is available.

It is possible, of course, to account for the remaining cases by assuming the temporary existence of some product which could take the place of the iodine or bromine in the foregoing examples, even where all attempts to isolate such a substance have failed. The first attempt to carry this idea through in detail was made by Manchot, whose views may be gained from the following much abridged free translation from his papers "On the Process of Oxidation"[6] and "On the Formation of Peroxides of Iron,"[7] published in 1902.

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[1] Jour. Chem. Soc., 20, 476 (1867).

[2] Jour. Phys. Chem., 7, 61 (1903).

[3] Zeit. phys. Chem., 41, 565 (1902).

[4] Ibid., 42, 641 (1903).

[5] The results of this research will shortly be published.

[6] Liebig's Ann., 325, 93 (1902).

[7] Ibid., 325, 105 (1902).

Manchot's Peroxide Theory

"I was led to the following general theory of the processes of oxidation, which is completely contained in the sentence" *In every process of oxidation there is formed a primary oxide*[1] which in general has the character of a peroxide. The subsequent fate of the peroxide depends on the special circumstances of each case. The case that the final, isolable, product is identical with the peroxide seems to be the less common . . . . it is more usual for the peroxide to undergo decomposition before it can be isolated, giving up oxygen, which escapes as gas, or combines with other substances present (acceptors); among the latter may be included the substance itself which is undergoing oxidation (auto-acceptor).

"*The peroxide is formed direct* from the reagents, *intermediate states are passed over* . . . . and it is obviously only in special cases that the isolable product is more highly oxidized than the initial state (*e. g.*, ferrous—peroxide—ferric). The final state may be identical with the initial, or may be less oxidized than the latter, for instance the reduction of PbO_2 or MnO_2 by H_2O_2 in presence of acid (dioxide—peroxide—monoxide) . . . . . and in some cases the product of decomposition may be the metal itself (Au from $AuCl_3$ by H_2O_2, etc.).

"This theory necessitates the assumption in the case of many elements, of stages of oxidation which are hitherto unknown. . . . . It brings the action of all oxidizing agents under a common point of view, but I wish to state emphatically that in my opinion it is of value chiefly because it incites to experimental investigation, and, without predicting the results of the latter, is able to modify itself in accordance with them. If in any case this should clearly be shown to be impossible, the theory must be laid aside."

Granting that the "primary product" of the oxidation of ferrous sulphate, for instance, is a peroxide of iron, the composition of the latter may be ascertained "by carrying

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[1] The italics are the author's, throughout.

out the oxidation in presence of an acceptor, to which oxygen may be transferred from the peroxide. Many substances can act as acceptors, but for quantitative investigations only those of them are suitable which react fairly quickly with the ferric peroxide, so that the reduction of the peroxide is brought about *only* by the acceptor, the evolution of oxygen, or its transference to other substances (especially unused ferrous salt) being avoided. The action of the peroxide on the acceptor may be rendered more complete by increasing the concentration of the latter."

When a suitable acceptor has been found, it is only necessary to determine *n*, the number of atoms of oxygen absorbed by the acceptor for every Fe_2O_2 converted into Fe_2O_3; for the formula of the peroxide may be assumed to be Fe_2O_{3+n}.

$$2FeO \rightarrow Fe_2O_{3+n} \rightarrow Fe_2O_3 + nO$$

Thus, according to Manchot, every process of oxidation leads to the formation of a primary oxide, which in general has the character of a peroxide, and whose formula may be ascertained by determining the induction factor.

Luther and Schilow's Classification

Luther and Schilow[1] take a much broader view, and admit the existence of many types of induced reactions.

They begin by distinguishing cases of simple catalysis under conditions where the catalyzer is destroyed by independent reaction with the actor, from true copulated reactions; in the former the induction factor can be increased indefinitely by increasing the concentration of the acceptor; in the latter it reaches a limit which depends on the nature of the reaction "really" taking place in the solution.

The authors then discuss "the main question, namely, the methods of ascertaining the nature of the intermediate substance which brings about the copulation."

The upper limit, towards which the induction factor

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[1] Zeit. phys. Chem., 46, 777 (1903).

tends as the concentration of the acceptor is increased, may be employed to determine the degree of oxidation of the intermediate compound, but gives no further information as to its formula, or as to the reagents from which it has been formed. In the authors' opinion, information on this point "can be obtained only by *suitable variation of the reagents;* reagents which are necessary for the formation of the intermediate substance must have certain properties, so that they can be varied (interchanged) only within definite limits; substances which can replace one another must in certain respects be *chemically analogous,* or at least be capable of *analogous chemical changes.* On the other hand, the substances which only react with the intermediate body may belong to widely different chemical classes, the single respect in which they must resemble one another being their ability to enter into an oxidation-reduction reaction with the (hypothetical) intermediate substance."

"Observation of the occurrence or non-occurrence of induction, when the reagents are systematically varied, therefore enables one—to a certain extent—to decide which of these substances plays a *specific rôle* in the reaction . . . . and leads to a classification of the cases of induction hitherto observed. The principle underlying the following attempt at such a classification, is the dependence of copulation on the specific nature of the three reagents—actor, inductor, acceptor."

In class A, the inductor is "specific," the other two "unspecific;" the intermediate body must therefore be a derivative of the inductor; in classes B and C, actor and acceptor respectively take the place of the inductor of class A. In class D, both acceptor and inductor are "specific," and the intermediate body must be regarded as a complex derived from both of them; classes E and F complete the series, inductor and actor, or acceptor and actor respectively, being "specific."

In the authors' attempt to distribute the known cases of induction among their six classes, the weakness of the "principle" on which the classification rests becomes apparent. Ferrous salts, for instance, act as inductors in 15 reactions involving 7 actors and 9 acceptors—all are grouped in class A; but the 8 reactions in which SO_2 takes the part of inductor, and in which 6 actors and 4 acceptors are involved, are distributed among the remaining five classes. "This example shows how careful one must be in interpreting the phenomena of induction;" it also shows that much is left to individual opinion in the practical application of the authors' "principle" of classification; Luther and Schilow were quite clear on this point, "we consider our interpretations as in no case final."

A New Classification Based on Kinetic Measurements

A firmer basis for the classification may be secured by treating the problems of induction according to the methods of chemical kinetics; and comparing the rates at which the actor acts on inductor and acceptor taken each by itself, with the rates in solutions containing all three reagents together. Each case, of course, must be studied by itself, but when the effects of all the concentrations on the rates have been ascertained, a suitable hypothesis may be founded on the results of the measurements.

In the present almost total absence of experimental data, it would be premature to develope a detailed classification of the results that may be attained by future experimenters; it is sufficient to define the three classes into which all must fall, and to attract attention to an important ambiguity that must always attend attempts to assign a specific mechanism to any case of induction which falls under group II of the classification proposed.

The Three Classes

It is assumed that in every case the final products of the reactions in solutions containing all three reagents, are the same as the products of the reactions between actor and acceptor or actor and inductor separately. This excludes the obviously consecutive reactions referred to on page 10.

Class i.—The rate at which the inductor is acted on, and *the influence of the concentrations of the reagents on that rate, are unaffected by the presence and concentration of the acceptor.* The reaction comes under the head of "Catalysis combined with destruction of the catalyzer," and as pointed out by Luther (page 12) the induction factor rises indefinitely with increase in concentration of the acceptor.

Class ii.—The rate at which the actor is destroyed, and the influence of the concentrations of the reagents on that rate, are independent of the presence and concentration of the acceptor; while the rate at which the inductor is acted on, though (necessarily) slower than in absence of the acceptor, is nevertheless affected by the concentrations of the reagents in the same manner as in the absence of the acceptor. The induction may be accounted for by assuming one of Manchot's peroxides or some other product of the action of actor on inductor. This is the only case which the peroxide hypothesis is sufficient to explain; it includes Luther's classes A, B and E.

Class iii.—The effect of the concentrations of the reagents on the rate at which the inductor is destroyed is changed by adding the acceptor. The intermediate formation of some derivative of the acceptor with actor or inductor may be assumed (Luther's D and F), or resort may be had to complicated hypotheses involving equilibria; the peroxide explanation, however, is clearly excluded.

The difficulties met with in carrying out the measurements necessary for this classification are principally those of chemical analysis; up to the present, however, only two cases of induction have been studied from this point of view, *viz.*: those in which the action of chromic acid on potassium iodide is accelerated by the simultaneous oxidation of ferrous sulphate or of arsenious acid, respectively. They afford typical examples of classes iii and ii.

Chromic Acid, Ferrous Sulphate, Potassium Iodide. Type of Class iii

This reaction is particularly interesting as it is one of those discussed by Manchot, who thought it afforded striking evidence of the correctness of his theory. He considered the "primary product" of the reaction between chromic acid and ferrous sulphate to be a peroxide of the formula Fe_2O_5, which was instantaneously reduced to ferric oxide or its salts by the action of ferrous salts or of iodides. As this theory, which was subsequently adopted by Luther and Schilow, is totally at variance with the results of the kinetic measurements quoted below, it is worth while to recapitulate the arguments advanced in its support.

Manchot relied on his general theory of oxidation, outlined above (page 11), and on the observation that there is a "slight but distinct evolution of oxygen gas when ferrous sulphate is dropped into a concentrated solution of potassium bichromate in sulphuric acid;" he arrived at the formula of the peroxide by means of the induction factor. Theories of the induction based on a hypothetical ferro-hydriodic acid he dismissed on the ground that "potassium ferrocyanide[1] added to the system: chromic acid *plus* hydriodic acid, produces the same effect as ferrous sulphate, namely, sets iodine free; the liberation of iodine takes place a little more slowly, probably because the peroxide is more stable in this case; obviously there can be no talk of the formation of a ferro-hydriodic acid in this case, nor of similar complexes in the experiment on the decolorization of indigo, described below."

The considerations weighing with Luther and Schilow may be put shortly as follows: Ferrous salts act as inductors in numerous reactions involving actors and acceptors of the most varied character; these cases, therefore, all come under Group A (page 13), and are to be explained by assuming the primary formation of "an intermediate state of the inductor," that is, a peroxide of iron.

Miss Benson's measurements,[2] however, show that the effect of the concentrations of the reagents on the rate at which ferrous sulphate is oxidized by chromic acid are altogether

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[1] See, however, Miss Benson's measurements: Jour. Phys. Chem., 7, 363 (1903).

[2] Jour. Phys. Chem., 7, 356 (1903).

changed by the addition of potassium iodide. In the absence of potassium iodide the rate is proportional to the square of the concentration of the ferrous salt, in its presence to the first power; in the absence of potassium iodide, to the second power of the concentration of the acid, in its presence, to the third or fourth power; in the absence of potassium iodide to the 1.4th or 1.8th power of the concentration of the bichromate, in its presence to the first power, while the effect of continuously increasing the concentration of the iodide is first to lower, then to increase the rate at which the ferrous sulphate was oxidized.

The case therefore comes under Class iii of page 15; and *it is quite impossible to assume*, with Manchot, and with Luther and Schilow, *that the reaction between ferrous sulphate and chromic acid in the presence of potassium iodide is essentially the same as in its absence.*

Chromic Acid, Arsenious Acid, Potassium Iodide. Type of Class ii

This reaction is not included in Luther and Schilow's tables, and is not mentioned by Manchot; the kinetic investigation, which has been carried out by Mr. R. E. De Lury,[1] establishes it as the type of Class ii.

Whether potassium iodide be present or not, the rate at which arsenious acid is oxidized by chromic acid is proportional to the concentrations of the arsenious acid and bichromate, and to the 1.4th power of that of the acid. When potassium iodide is added, iodine is set free; and as the concentration of the iodide is increased the rate of liberation of iodide increases and the rate of oxidation of arsenious acid decreases, until the latter falls to one-third the rate in the absence of iodide. When this point has been reached, two equivalents of iodine are liberated for each equivalent of arsenious acid oxidized, and further increase in the concentration of the iodide has no effect on the rates. Throughout, the rate at which the chromic acid is reduced by the mixture

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[1] Trans. Roy. Soc., Canada, May, 1905.

of iodide and arsenious acid is the same as though the arsenious acid were present alone.

Thus, in contrast to the case of induction studied by Miss Benson, *the reaction involving the reduction of chromic acid is essentially the same whether iodide be added or not*; it may therefore be accounted for by assuming that a (hypothetical) peroxide of arsenic is the primary product of the reaction whose rate is measured, and that this peroxide is immediately reduced to arsenic acid by either potassium iodide or arsenious acid (Manchot's hypothesis).

Alternative Mechanisms for Reactions of Class II

From what precedes, it is clear that a study of the rates at which inductor and acceptor are acted on by the oxidizing agent (actor) is sufficient to assign each case studied to one of three classes; and in particular, that cases of induction which can be explained on Manchot's hypothesis may be distinguished by this means from those which can not.

The results of the rate measurements, on the other hand, may often be explained equally well by several different hypothetical mechanisms, within the same group. Mr. De Lury's experiments with chromic acid, arsenic, and potassium iodide, for instance, may be accounted for by assuming either As_2O_9, Cr_2O_5, or their hydrates, or some Cr–As compound of a suitable state of oxidation, as the primary product of the action of chromic acid on arsenious acid.

The method of "suitable variation of the reagents" leads to no definite conclusion as to which of these assumptions is the best. True, the reaction between chromic acid and iodides is induced by ferrous salts and by tartaric acid as well as by arsenious acid, which seems to point to the chromic acid as the "specific" and the arsenic as the "unspecific" reagent, and thus to support the Cr_2O_6 hypothesis; the As_2O_9 theory, however, is suggested by the occurrence of numerous reactions in which arsenious acid plays the part of inductor, and although iodides are not mentioned as acceptors in any of the cases recorded in Luther's tables, this may be due to the difficulty of finding another oxidizing agent which (like chromic acid) acts on arsenic quicker than on potassium iodide.

It is possible, on the other hand, that further rate measurements may lead to the adoption of one of the three theories rather than the others; although, as all three lead to the same conclusions with regard to the induction just studied, this might at first sight seem impossible.

For example, the fact that in dilute solutions the rate of oxidation of potassium iodide by chromic acid[1] is proportional to the concentrations of the iodide and bichromate, may be accounted for by assuming the reaction

$$H_2CrO_4 + HI = HOI + H_2Cr_2O_6$$

in which the hypothetical $H_2Cr_2O_6$ (a hydrate of the Cr_2O_5 of page 18) is taken as "primary product." But if this view of the reaction between chromic and hydriodic acids be combined with the Cr_2O_5 explanation of the induction by arsenious acid, it follows that hydriodic acid must act as inductor to the reaction between arsenious and chromic acids, that the two reactions must be reciprocally inductive in fact; and it is even possible to calculate the effects of the concentrations on the rates and on the induction factor in one case from a knowledge of the other.

As the rates at which chromic acid oxidizes hydriodic and arsenious acids, respectively, are different functions of the concentrations of the acid, it may be possible to increase the former and decrease the latter sufficiently to render these relations accessible to experimental investigation. Such experiments, if carried out, would remove one more degree of freedom from the imagination when inventing "mechanisms" to explain the phenomena of chemical induction.

Summary

The methods hitherto proposed for classifying cases of chemical induction are unsatisfactory.

A new classification is proposed, based on kinetic measure-

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[1] Jour. Phys. Chem., 7, 239 (1903).

ments. According to this, the induced reactions are divided into three classes: (i) cases of catalysis combined with destruction of the catalyser, (ii) cases in which the reaction between actor and inductor is the same whether acceptor be present or no, (iii) cases in which it is not.

Only two induced reactions have as yet been studied from this point of view; they furnish typical examples of classes ii and iii.

Reactions of class ii can be explained equally well by several different hypothetical mechanisms (including Manchot's peroxide hypothesis), all of which predict the same kinetic relations. The choice may be narrowed, however, by further kinetic experiments.

The University of Toronto,
December, 1906.

EQUILIBRIUM BETWEEN AMMONIA AND HYDROGEN SULPHIDE

BY J. P. MAGNUSSON

When ammonia and hydrogen sulphide are brought together in a vacuum, no reaction occurs if the pressure is below a certain value, depending on the temperature. At or above this pressure combination occurs and transparent needle-shaped crystals of NH_4SH are deposited on the walls of the containing vessel. If the pressure is still further increased more crystals will deposit, or if the pressure is reduced crystals will decompose, until a pressure is reached which is definite for each temperature. When the two gases are present in equivalent masses this pressure is termed the dissociation pressure of the solid. As we have here a vapor phase of the same composition as the solid with which it is in equilibrium, the system is univariant and we should have a definite pressure for each temperature. This is shown in the following data obtained by Isambert.[1]

TABLE I

Temp.	Pressure cm	Temp.	Pressure cm
4.2°	13.2	12.0°	21.2
6.1	14.2	15.0	25.9
7.9	15.9	18.0	32.2
9.5	17.5	22.1	41.0
10.1	18.4	25.1	50.1

When, however, we alter the composition of the vapor phase by adding ammonia or hydrogen sulphide, we pass from a one-component to a two-component system, and for each temperature we should have a series of pressures, or for each pressure a series of temperatures, at which the system is in equilibrium. On varying the concentration of one of the components at a given temperature, the concentration of the

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[1] Comptes rendus, 92, 919 (1881).

other component as well as the total pressure of the system will vary, and the functional relation connecting these quantities is given by the mass law which was first applied by Horstmann[1] to the system $CO_2 + 2NH_3 = NH_4CO_2NH_2$.

In the system

$$NH_3 + H_2S = NH_4SH$$

if C_1 and C_2 are the mass concentrations of the two gases then by the mass law

$$C_1C_2 = \text{constant} \qquad (1)$$

for a given temperature, as the active mass of the undecomposed compound is constant so long as the solid phase is present. Since, by Boyle's law, the pressure of a gas is proportional to its mass concentration, we may write

$$p_1p_2 = \text{constant}; \qquad (2)$$

where p_1 and p_2 are the partial pressures of the ammonia and hydrogen sulphide respectively. Now when ammonia and hydrogen sulphide are present in equivalent amounts, *i. e.*, when the solid NH_4SH is allowed to dissociate in a vacuum, then $p_1 = p_2 = \frac{\Pi}{2}$ and (2) then becomes

$$p_1p_2 = \text{constant} = \frac{\Pi^2}{4} \qquad (3)$$

where Π is the vapor pressure of the solid sulphydrate. This is true when the concentration of the undissociated ammonium hydrosulphide in the vapor-phase is negligible. Or

$$\log p_1 + \log p_2 = 2 \log \frac{\Pi}{2} = \text{constant} \qquad (4)$$

which is the equation of a straight line cutting the axes at an angle of 45°.

The data in Table II are taken from Ostwald's tabulation[2] of Isambert's results.[3] The pressures are given in centimeters of mercury. In the column for the products of the partial pressures, p_1 denotes ammonia and p_2 hydrogen sulphide.

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[1] Liebig's Ann., 187, 48 (1877).

[2] Lehrbuch allg. Chemie, 2, II, 517.

[3] Comptes rendus, 93, 595, 730 (1881); 94, 958 (1882).

TABLE II

Temp. 4.1°			Temp. 7.0°		
NH_3	H_2S	$p_1 \times p_2$	NH_3	H_2S	$p_1 \times p_2$
0.68	40.0	27.3	1.36	40.0	54.5
2.02	16.5	33.8	3.36	16.9	56.8
6.3	6.3	39.7	7.75	7.75	60.0
35.7	1.44	51.4	35.6	1.92	68.2
39.9	0.89	39.6	39.8	1.35	53.7
Temp. 10.1°			Temp. 12.0°		
1.80	39.9	72.0	2.50	40.3	101
4.68	17.3	81.0	5.93	18.6	110
9.2	9.2	84.4	10.6	10.6	112
35.3	2.73	96.3	36.3	3.47	126
39.4	2.16	85.0	40.5	2.87	116
Temp. 15.0°			Temp. 17.3°		
3.91	40.3	162	5.35	41.9	224
8.22	18.6	165	10.3	21.4	220
12.95	12.95	168	15.0	15.0	225
38.1	5.59	213	37.7	6.43	243
41.3	4.46	184	41.6	5.59	232
Temp. 19.3°			Temp. 22.0°		
6.42	43.3	271	9.05	43.3	392
12.6	25.5	291	15.9	25.5	406
17.45	20.5	304	20.5	20.5	420
40.7	10.8	306	40.7	10.8	439
44.3	10.1	314	44.3	10.1	447
Temp. 23.1°			Temp. 25.1°		
11.4	44.7	510	13.8	45.8	632
19.9	27.2	487	20.8	29.4	607
22.5	22.5	506	25.05	25.05	627
40.5	12.4	503	41.7	14.0	608
43.9	11.8	518	45.3	14.3	648

Owing to the lack of information as to the experimental conditions under which these results were obtained, the limited range of pressures as well as the not inconsiderable variation in the product $p_1\ p_2$, it seemed desirable to make experiments over a greater range of pressures and under more exact experimental conditions. Isambert's work was largely qualitative and no definite conclusion can be drawn from it in support of the above equation.

The original plan was to study the reaction over a wide range of pressures for a number of temperatures, but this was finally abandoned and the following data are taken at one temperature only, namely 20°. The experimental steps were: (1) The vapor-pressure of the pure compound NH_4SH was determined in a vacuum. (2) A known excess of ammonia was added, the pressures of this system determined over a range of volumes, and the partial pressures of the ammonia and hydrogen sulphide calculated. (3) Similarly, with a known excess of hydrogen sulphide. The logarithms of the partial pressures thus obtained were plotted on co-ordinate paper in order to show any deviation from the theoretical values. One of the chief sources of error in work of this kind has been the variations of the temperature in the measuring tube. Reference to Table I shows that a variation of 1° in temperature corresponds to a variation of 2.4 cm in the vapor-pressure of the compound. This is about 6 percent of the lowest pressure in these experiments. It thus became necessary to limit the possible temperature variation to within ±0.05° in order to keep the possible pressure variation below 1 percent. For this purpose the measuring tube was enclosed in a water jacket and the temperature of this regulated by means of an electric heating arrangement as shown in Fig. 1.

T is the measuring tube graduated to 0.1 cc and fixed in position in the glass casing J by means of a stout rubber stopper. Surrounding the bottom of the tube is the heating coil N of No. 24 nickel wire. This is connected up with a 110 volt alternating current source, a block of incandescent lamps, L, and a current interrupter, R, operated by a single dry cell, B. The terminals from this are connected with a mercury coil immersed in the water jacket. As the water in the bath is heated by the coil N the mercury in M expands and finally makes contact with the platinum point at C. This closes the interrupter circuit, attracting the iron bar at P and thus breaks the heating circuit. As the bath cools, the contraction of the mercury in M breaks the contact at C, thus again throwing in the heating circuit, and so on. On account of the heating produced by the stirring, it is necessary to keep the surrounding temperature at least 2° lower than that of the bath. Under these circumstances the lamps L light up about once every minute. A small incandescent lamp is shunted across C to prevent sparking when the contact is broken. When this is allowed to happen the mercury surface oxidizes and this greatly impairs the delicacy of the regulation. The bath is stirred by means of a current of air through S from two gasometers. By means of this arrangement a Beckmann thermometer could be held constant, if the stirring was con-

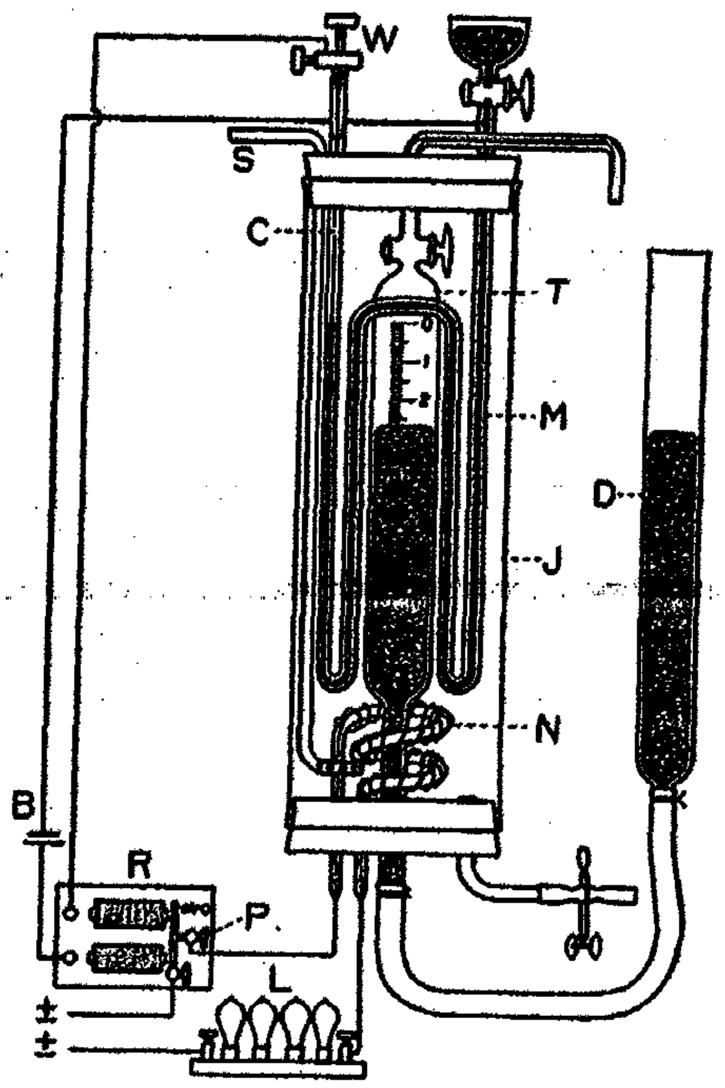

Fig. 1

stant and if the surrounding temperature did not vary much. The greatest variation of the temperature of the bath during the entire course of these experiments was ±0.005° as is seen by referring to the following tables. Efficiency and general convenience of operating commend this form of thermoregulator for general laboratory purposes.

The glass casing was enclosed in a metal jacket and the interstices filled with cotton wool to minimize heat conduction. Two oblong openings in this jacket permitted the mercury level in the enclosed tube to be read. The mercury levels in the tube T and the leveling tube D were read by means of a cathetometer placed at a distance of about five feet from the apparatus. In order to bring out a clean-cut edge of the mercury meniscus, a metal strip was clamped on the leveling tube as well as on the metal jacket. When this is moved down close to the mercury surface, the meniscus edge comes out sharp against a white background and can be read accurately. The gases were measured in from small Hempel burettes graduated to 0.1 cc and surrounded by water jackets. At each reading this water was stirred and its temperature read on a thermometer inserted at the top. The levels in these burettes were also read by means of the cathetometer so as to avoid parallax.

The burettes and jacketed tube were calibrated by means of a side-arm pipette whose volume was calculated from the weight of water contained as follows:

Weight of crucible (*a*)...........	12.0085 grams	(*b*)	9.1700 grams
Weight of crucible and water....	13.9900		11.1520
Weight of water.................	1.9815		1.9820

Density of water at 20.5° = 0.998126

$$\text{Therefore volume of pipette} = \frac{1.9817}{0.998126} = 1.9856 \text{ cc.}$$

The calibrations and corrections for the jacketed tube and burettes were as follows:

TABLE III
Calibration of Burettes

Jacketed tube			NH_3 burette			H_2S burette		
Obs. cc	Calc. cc	Cor. cc	Obs. cc	Calc. cc	Cor. cc	Obs. cc	Calc. cc	Cor. cc
2.02	1.99	—0.03	3.98	3.97	—0.01	3.97	3.97	0.00
4.03	3.97	0.06	7.92	7.94	+0.02	7.94	7.94	0.00
6.03	5.96	0.07	11.90	11.91	0.01	11.91	11.91	0.00
8.02	7.94	0.08	15.90	15.88	—0.02	15.90	15.88	—0.02
10.01	9.92	0.09	19.89	19.86	0.03	19.89	19.86	0.03
12.01	11.91	0.10	23.87	23.82	0.05	23.89	23.82	0.07
14.00	13.90	0.10	27.83	27.80	0.03	27.88	27.80	0.08
15.99	15.88	0.11	31.79	31.77	0.02	31.83	31.77	0.06
17.97	17.87	0.10	35.78	35.74	0.04	35.79	35.74	0.05
19.94	19.86	0.08	39.75	39.71	0.04	39.76	39.71	0.05
21.95	21.84	0.11	43.73	43.70	0.03	43.73	43.70	0.03
23.95	23.83	0.12						
25.93	25.81	0.12						
27.90	27.79	0.11						
29.89	29.78	0.11						
31.88	31.77	0.11						
33.87	33.75	0.12						
35.86	35.74	0.12						
37.85	37.73	0.12						
39.84	39.71	0.13						

The volume of the portion of the measuring tube from the glass stop-cock to the o mark was determined by measuring in a known volume of dry air, calculating its new volume from the existing pressure and temperature and subtracting the volume as read on the tube corrected by above calibration. The data and results are given in Table IV, L being the mercury level in the measuring tube and R the mercury level in the leveling tube.

The accuracy of the cathetometer adjustment is shown by the table below. Four different positions of the mercury in the leveling tube were read, each three times. In this and in other readings in this work the meniscus was always approached from above and the position read where the lower edge of the middle point of the horizontal cross-hair seemed

TABLE IV

Value in cc of 0 mark on jacketed tube

(A)					
	Burette	22.48 14.62			
	Volume taken	7.86 cc	Temp. 20°		Bar., 74.00 cm
	" calc	8.27 "	L	R	P
	" read	6.26 "	61.43	57.72	70.29 cm
	" to 0 mark	2.01 "			
(B)					
	Burette	22.48 13.50			
	Volume taken	8.98 cc	Temp. 20°		Bar. 73.98 cm
	" calc	9.28 "	L	R	P
	" read	7.28 "	60.57	58.18	71.59 cm
	" to 0 mark	2.00 "			
(C)					
	Burette	22.50 12.59			
	Volume taken	9.91 cc	Temp. 20°		Bar. 73.98 cm
	" calc	10.36 "	L	R	P
	" read	8.35 "	59.68	56.44	70.74 cm
	" to 0 mark	2.01 "			

Therefore volume to 0 mark = 2.01 cc.

TABLE V

Limit of error of the cathetometer adjustment

Position	(a)	(b)	(c)	(d)
Readings	83.37 83.36 83.36	60.49 60.50 60.50	31.38 31.39 31.38	4.47 4.49 4.48
Limit of error	±0.005 cm	0.005 cm	0.005 cm	0.01 cm

just to touch the highest point of the mercury meniscus. It should also be said that the scale engraved on the cathetometer was found to match accurately with a metal scale belonging to the department.

The ammonia gas used in these experiments was prepared by heating concentrated ammonia water, and drying the gas through a train consisting of two ten-inch soda-lime cylinders, two eight-inch U-tubes filled with crushed KOH sticks and finally a six-inch U-tube filled with fine shavings of metallic sodium. After the displacement of air from the apparatus as shown by the absorption of the escaping gas in an acid solution, the gas was slowly collected over mercury in a small gasometer of about 300 cc capacity. It should be said that the gas thus obtained would not completely absorb in acids even after prolonged passing. A small residue always remained which, however, did not amount to more than 0.5 percent of the total volume of gas evolved.

The hydrogen sulphide was prepared by the method described by Divers and Shimidzu.[1] About 50 grams of magnesia were suspended in a liter of water and hydrogen sulphide from a Kipp generator passed in under pressure for several hours, allowing the impurities to escape through a side tube dipping into an alkaline liquid. On heating the magnesium hydrosulphide thus obtained, a regular evolution of hydrogen sulphide takes place at 60°. According to these authors the gas thus obtained is free from hydrogen and arsine. A small residue was, however, always left over on absorption in ammonium hydroxide solution, but the volume percent of this was not greater than in the case of the ammonia. The gas was then passed through a series of calcium chloride tubes and finally through a U-tube of phosphorus pentoxide.

The mercury used in these experiments was purified by prolonged contact with concentrated sulphuric acid and mercurous sulphate, after which it was heated to 200°, allowed to cool and filtered through a small opening in a filter until no

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[1] Jour. Chem. Soc., 45, 699 (1884).

oxide was left on the paper. It was then stored in a Hempel desiccator containing a few sticks of caustic potash. The gases stored over mercury purified in this way did not tarnish the mercury surface on long standing.

When the two gases were brought together in the measuring tube a slight film of sulphide formed on the mercury surface and this adhered to the walls of the tube, but after the excess of gas had been expelled no more film was formed, and the readings could be made accurately. At first the microscopic crystals of the salt formed an opaque coating on the walls of the tube, but on long standing or by slowly moving the leveling tube up and down, these small crystals disappeared and large transparent ones were formed so that readings could be made. On mixing equal volumes of the two gases it was found that an excess of uncombined gas always remained even at high pressures. On expelling this from the tube its odor indicated that it was hydrogen sulphide. Walker and Lumsden,[1] in their work on the alkyl hydrosulphides, noticed the same phenomenon. This is what would be expected as the two gases would combine by equal volumes only in case they both obeyed Boyle's law or deviated from it in the same way. Another and probably more important reason for this will be brought out later on in this paper. After this excess of gas had been expelled the leveling tube was lowered until a portion of the sulphydrate was vaporized and pressure readings taken as indicated in the following table.

The notation in the following tables is as follows: T, reading on the Beckmann thermometer; V, volume corrected from the reading on measuring tube; L, cathetometer reading for mercury level in measuring tube; R, cathetometer reading for mercury level in leveling tube; P, observed pressure; P′, calculated pressure; p_1, partial pressure of ammonia; p_2, partial pressure of hydrogen sulphide; Π, vapor-pressure of the compound in vacuum; Bar., barometer reading; Temp., temperature of the gas in the burette before it is run into the measuring tube.

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[1] Jour. Chem. Soc., 71, 428 (1897).

TABLE VI

Vapor-pressure of NH_4SH at 20°

(A)	Bar cm	V cc	L	R	P cm
	74.14	2.61	65.85	27.18	35.47
	74.14	15.65	55.10	16.49	35.53
	74.14	22.57	49.68	11.04	35.50
	74.14	34.95	39.96	1.30	35.48
				Mean,	35.49
(B)					
	73.95	2.21	66.38	27.94	35.51
	73.94	11.59	57.89	19.48	35.52
	73.93	21.48	50.70	12.28	35.52
	73.93	33.06	40.09	1.33	35.18
				Mean (omitting 4th rdg.),	35.52

Therefore vapor-pressure of $NH_4SH = 35.51$ cm $= \Pi$.

The vapor-pressure of the compound is thus seen to be independent of the volume or of the amount of solid present. A value obtained by Isambert at a somewhat lower temperature, 19.3°, is 34.9 cm. Assuming that the compound dissociates on vaporization into equal volumes of ammonia and hydrogen sulphide,

$$p_1 = \frac{\Pi}{2} = p_2.$$

On increasing the concentration of one of the gases, that of the other will have to decrease in order that the equation

$$C_1C_2 = \text{constant}$$

shall hold. This can only take place by the increase of the mass of the solid phase at the expense of equal volumes of the two gases. This was expressed by Isambert by saying that the vapor-pressure of the solid in the presence of an excess of one of the constituent gases is less than in a vacuum. At equilibrium, then, the total pressure of the system is made up of the pressure of the gas added, the pressure of the dissociated vapor of the solid and a slight pressure due to the undissociated vapor. If this latter is neglected, the partial pressures of the two constituents may be calculated by subtracting the pressure of the added gas, P′, calculated as if the gas occupied the entire volume read, from the total observed pressure, and dividing the difference by two. This gives the partial pressure of the gas not in excess, while the total minus this is, of course, the partial pressure of the excess constituent. Or expressed in symbols

$$p_1 = \frac{P - P'}{2} + P',$$

$$p_2 = \frac{P - P'}{2},$$

where the letters have the meaning given them above.

P_1 was calculated in the following way:

$$P' = \frac{V_1 \text{ Bar } T_1}{V \text{ (Temp.} + 273)}$$

where V_1 is the excess volume added under "Bar" cm pressure and "Temp." + 273° absolute temperature, the other letters having the meaning given them above. Three runs were made with each gas, one with about 5 cc, one with 10 cc, and one with 15 cc in excess. In this way a wide range of pressures was covered and more points were obtained on the curve. Following are the data and results:

TABLE VII

Ammonia in excess (1)

(A) Data:

Burette.........	36.05 30.88		
Volume NH_3...	5.17 cc	Temp. 16.6° C	Bar 74.81 cm

T	Bar cm	V cc	L	R	P cm	P′ cm
1.498°	74.81	4.02	62.14	88.55	101.22	97.34
1.498°	74.79	4.35	61.91	82.20	95.08	89.96
1.498°	74.79	5.04	61.32	71.30	84.77	77.64
1.498°	74.80	5.88	60.59	60.78	74.99	66.55
1.498°	74.78	7.85	59.05	45.43	61.16	49.85
1.498°	74.78	16.23	52.24	19.74	42.28	24.11
1.498°	74.78	25.43	44.93	7.16	37.01	15.29

TABLE VII—(*Continued*)

(B) Calculated results:

NH_3 (p_1) cm	H_2S (p_2) cm	Log p_1 + Log p_2	$p_1 \times p_2$
99.28	1.94	2.2847	192.6
92.52	2.56	2.3745	236.9
81.20	3.56	2.4610	289.1
70.77	4.22	2.4752	298.6
55.44	5.65	2.4920	313.5
33.19	9.08	2.4791	301.4
26.10	10.81	2.4505	282.2

$$\frac{\Pi^2}{4} = 315.0$$

TABLE VIII

Ammonia in excess (2)

(A) Data:

Burette.........	29.91 19.90		
Volume NH_3....	10.01 cc	Temp. 18.9° C	Bar 74.62 cm

T	Bar cm	V cc	L	R	P cm	P′ cm
1.505	74.57	7.48	59.28	88.90	104.19	100.25
1.500	74.60	8.09	58.80	82.17	97.97	92.68
1.491	74.60	9.63	57.54	68.04	85.10	77.86
1.491	74.62	11.38	56.12	56.22	74.72	65.88
1.505	74.57	16.62	51.88	35.02	57.71	45.12
1.505	74.55	22.85	46.92	20.74	48.37	32.81
1.505	74.55	29.11	41.99	10.65	43.21	25.76

(B) Calculated results:

NH_3 (p_1) cm	H_2S (p_2) cm	Log p_1 + Log p_2	$p_1 \times p_2$
102.22	1.97	2.3040	201.4
95.32	2.64	2.4008	251.6
81.48	3.62	2.4698	294.9
70.30	4.42	2.4924	310.8
51.41	6.29	2.5097	323.3
40.59	7.78	2.4994	315.8
34.48	8.72	2.4781	300.7

$$\frac{\Pi^2}{4} = 315.0$$

TABLE IX
Ammonia in excess (3)

(A) Data:

Burette.........	19.01 3.41		
Volume NH_3....	15.60 cc	Temp. 18.7° C	Bar 74.55 cm

T	Bar cm	V cc	L	R	P cm	P′ cm
1.510	74.52	11.42	56.09	88.67	107.10	102.29
1.510	74.52	12.51	55.24	80.10	99.38	93.38
1.510	74.53	14.59	53.49	66.63	87.67	80.07
1.510	74.55	18.01	50.77	50.54	74.32	64.86
1.510	74.49	23.80	46.15	33.83	61.17	49.08
1.510	74.49	28.90	42.11	21.60	53.98	40.42
1.510	74.52	33.38	38.58	13.86	49.80	35.00

(B) Calculated result:

NH_3 (p_1) cm	H_2S (p_2) cm	Log p_1 + Log p_2	$p_1 \times p_2$
104.69	2.40	2.4001	251.3
96.38	3.00	2.4611	289.2
83.87	3.80	2.5034	318.7
69.59	4.73	2.5174	329.2
55.12	6.04	2.5223	333.0
47.20	6.78	2.5052	320.0
42.40	7.40	2.4966	313.8

$$\frac{\Pi^2}{4} = 315.0$$

TABLE X

Hydrogen in excess (1)

(A) Data:

Burette.........	41.48 36.48		
Volume H_2S....	5.00 cc	Temp. 17.8° C	Bar 74.28 cm

T	Bar cm	V cc	L	R	P cm	p′ cm
1.497	74.33	3.98	62.27	88.18	100.24	94.24
1.497	74.49	4.29	61.97	81.17	93.96	87.23
1.497	74.30	4.89	61.53	71.48	84.25	76.53
1.497	74.32	5.73	60.87	60.91	74.36	65.31
1.497	74.42	8.24	58.75	42.18	57.85	45.41
1.490	74.44	15.70	52.68	21.61	42.77	23.84
1.490	74.44	25.84	44.61	7.86	37.69	14.48

(B) Calculated results:

NH_3 (p_1) cm	H_2S (p_2) cm	Log p_1 + Log p_2	$p_1 \times p_2$
3.00	97.24	2.4650	291.7
3.36	90.59	2.4834	304.4
3.86	80.39	2.4918	310.3
4.52	69.83	2.4992	315.6
6.22	51.63	2.5067	321.1
9.46	33.30	2.4983	315.0
11.60	26.08	2.4808	302.5
		Mean,	308.6

$$\frac{\Pi^2}{4} = 315.0$$

TABLE XI

Hydrogen sulphide in excess (2)

(A) Data:

Burette.........	31.35 21.07		
Volume H_2S....	10.28 cc	Temp. 20.6°	Bar 73.79

T	Bar cm	V cc	L	R	P cm	P′ cm
1.501	73.79	8.23	62.50	87.50	98.79	91.98
1.501	73.79	9.47	61.43	75.15	87.51	79.94
1.501	73.79	11.82	59.47	59.04	73.36	64.04
1.504	73.78	20.22	52.65	30.81	57.95	37.44
1.504	73.78	30.17	44.86	14.66	43.58	25.09
1.504	73.79	42.53	35.11	1.09	39.77	17.80

TABLE XI—(*Continued*)

(B) Calculated results:

NH_3 (p_1) cm	H_2S (p_2) cm	Log p_1 + Log p_2	$p_1 \times p_2$
3.40	95.38	2.5010	316.9
3.78	83.72	2.5003	316.5
4.66	68.70	2.5053	320.1
7.25	44.69	2.5105	324.0
9.24	34.33	2.5013	317.2
10.98	28.78	2.4997	316.0
		Mean,	317.3

$$\frac{\Pi^2}{4} = 315.0$$

TABLE XII

Hydrogen sulphide in excess (3)

(A) Data:

Burette........	20.08 4.50		
Volume H_2S....	15.58 cc	Temp. 18.5° C	Bar 73.82 cm

T.	Bar cm	V cc	L	R	P cm	P′ cm
1.490	73.82	12.04	59.32	88.06	102.56	96.02
1.490	73.82	14.61	57.20	70.44	87.06	79.13
1.490	73.82	17.80	54.55	55.04	74.31	64.91
1.490	73.82	25.51	48.40	32.49	57.91	45.32
1.490	73.86	33.60	42.15	17.85	49.56	34.41
1.490	73.86	47.31	31.39	0.53	43.00	24.43

(B) Calculated results:

NH_3 (p_1) cm	H_2S (p_2) cm	Log p_1 + Log p_2	$p_1 \times p_2$
3.27	99.29	2.5114	324.6
3.96	83.09	2.5172	329.0
4.70	69.61	2.5148	327.1
6.29	51.61	2.5114	324.6
7.57	41.98	2.5021	317.8
9.28	33.71	2.4953	312.9
		Mean,	321.0

$$\frac{\Pi^2}{4} = 315.0$$

With log p_1 as abscissas and log p_2 as ordinates the accompanying graph Fig. 2 was obtained. To distinguish between the different runs the points on the curve are marked as shown, + representing the smaller volume, ⊕ the next larger and O the largest. The large circle on the center of the curve is the value for the vapor-pressure of the pure compound. The dotted line shows the prolongation of the straight line.

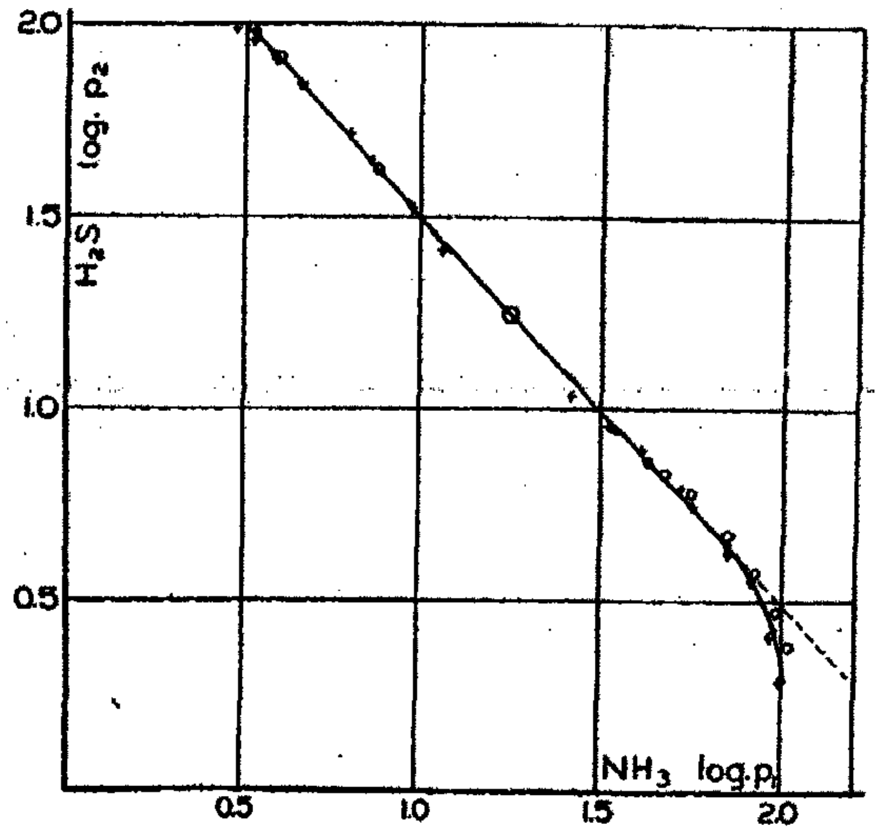

Fig. 2

An examination of the different series of points on the curve brings out the following facts: (1) The values for the smaller volumes show an unmistakable bend with the concave side toward the origin. This also appears in the values for the larger volumes of ammonia. (2) The points on the ammonia end are more scattered than those on the hydrogen sulphide end, and at the ends of the curve they bend sharply downward toward the abscissa axis. This can hardly be due to experimental error, for, by actual calculation, an error of 0.01 cc in V corresponds to a change of 0.07 cm in P' and of 2.9 in $p_1 p_2$ while it shifts the corresponding point on the curve one-half of a small division. While this and the possible corresponding errors in the pressure readings are sufficient to account for the minor irregularities along the curve, yet this will not explain the deviations at the ammonia end.

In calculating the results the assumption was made that the two gases combine volume for volume, *i. e.*, that one-half the vapor-pressure of the pure compound is due to ammonia and one-half to hydrogen sulphide, an assumption which is probably not justifiable for reasons given. Secondly, it was assumed that the gases obey Boyle's law which we know they do not, the only question being whether the deviation is great enough to account for the above results. Furthermore, it was noticed, especially in the case of ammonia, that on lowering the pressure in a burette which had been filled with the gas for some time, large bubbles appeared between the mercury and the glass, showing that considerable quantities of the gas had been adsorbed on the glass surface. This would make P′ too high as calculated and consequently p_1 and p_2 as well as $p_1 p_2$ too low. This is seen to be the case, especially at the end of the curve where the pressure was high and consequently where more adsorption would result. Thus a deviation from Boyle's law and an adsorption of gas on the walls of the tube would both tend to produce a bend in the curve as observed. To determine the effect on the value of P′ from these two causes, the following runs were made with the pure gases, P′ being calculated as stated above.

TABLE XIII

Adsorption of ammonia (4.89 cc)

T	Bar cm	V cc	L	R	P cm	P′ cm	Correction
1.500	74.36	3.78	66.22	88.17	96.31	96.34	—0.03
1.500	74.36	4.06	66.01	81.17	89.51	89.69	0.18
1.500	74.36	4.21	65.83	77.60	86.13	86.50	0.37
1.500	74.35	4.89	65.32	65.44	74.47	—	—
1.498	74.37	7.54	63.12	37.32	48.58	48.30	+ 0.28
1.498	74.37	11.66	59.67	16.70	31.40	31.23	0.17
1.498	74.37	15.54	56.48	5.93	23.84	23.43	0.41
Adsorption of ammonia (9.94 cc)							
1.504	74.37	7.48	63.15	88.12	99.34	99.04	+ 0.30
1.504	74.37	7.94	62.77	81.66	93.26	83.30	— 0.04
1.504	74.37	8.94	61.89	70.50	82.98	82.87	+ 0.11
1.500	74.37	9.94	61.09	61.25	74.53	—	—
1.504	74.41	13.35	58.31	39.72	55.85	55.49	0.36
1.502	74.41	17.95	54.52	21.70	41.59	41.27	0.32
1.502	74.43	22.70	50.70	9.19	32.90	32.63	0.27

TABLE XIV

Adsorption of hydrogen sulphide (5.09 cc)

T	Bar cm	V cc	L	R	P cm	P′ cm	Correction
1.502	74.74	3.96	65.87	87.70	96.57	96.44	+ 0.13
1.500	74.73	4.12	65.74	83.64	92.63	92.69	— 0.06
1.500	74.73	4.63	65.32	73.08	82.49	82.48	+ 0.01
1.500	74.73	5.09	64.95	65.24	75.03	—	—
1.500	74.73	6.79	63.49	45.03	56.28	56.24	0.04
1.503	74.73	10.96	60.07	20.12	34.80	34.84	— 0.04
1.510	74.73	15.99	55.92	5.36	24.17	23.88	+ 0.29
Adsorption of hydrogen sulphide (15.51 cc)							
1.502	74.77	11.13	59.96	88.09	102.91	102.82	+ 0.09
1.502	74.75	11.96	59.25	80.18	95.68	95.70	0.02
1.502	74.75	13.48	58.03	68.43	85.10	84.91	0.19
1.505	74.75	15.51	56.32	55.37	73.80	—	—
1.510	74.77	19.29	53.28	38.12	59.61	59.34	0.27
1.506	74.77	23.37	50.06	24.37	49.08	48.98	0.10
1.504	74.78	28.07	46.35	12.54	40.97	40.78	0.19

These data show that while there are appreciable differences between the values of P and P′ yet these show no regularity and, furthermore, most of them are within the limit of experimental error. They are insufficient to explain the bend in the curve.

When casting about further for an explanation it was suggested that, if the discrepancy is due to adsorption of gases on the walls of the tube, this effect would be increased by the deposition of a solid on the walls of the tube, thus increasing the exposed surface. This was of course the condition of affairs in the above measurements; the crystals of the sulphydrate accumulate rapidly as the pressure is increased, thus exposing a larger and larger surface.[1] An attempt was made to duplicate this condition by causing HCl gas and NH_3 to combine in the upper part of the measuring tube. The opaque deposit of ammonium chloride crystals was made transparent by washing a few times with a mixture of alcohol and ether.

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[1] This can only be an adsorption phenomenon. If a compound were formed, $NH_4SH.xNH_3$, there would be an interval over which the pressure would be constant, and nothing of this sort is to be noticed.

Enough of the salt was dissolved out so that the layer seemed to be of about the same thickness as that of the sulphydrate at the higher pressures. Runs were then made first with pure hydrogen sulphide, then with pure ammonia, similar to those given in Tables XIII and XIV. Two runs were made with hydrogen sulphide with different initial volumes, and three with ammonia. The results are given in Tables XIV, XV, XVI, XVII and XVIII.

TABLE XV

Adsorption of hydrogen sulphide

(A) Small volume (NH$_4$Cl in tube)

T	Bar cm	V cc	L	R	P cm	P′ cm	Correction
1.501	73.80	4.63	62.35	87.20	98.65	99.00	+ 0.35
1.501	73.79	5.09	61.99	77.92	89.72	90.05	0.33
1.501	73.77	5.62	61.52	68.83	81.08	81.56	0.48
1.501	73.77	6.20	61.08	61.24	73.93	—	—
1.501	73.78	7.58	59.94	46.44	60.28	60.47	0.19
1.501	73.78	10.89	57.23	25.53	42.08	42.09	0.01
1.501	73.78	16.30	52.81	7.25	28.22	28.12	— 0.10
(B) Larger volume							
1.500	73.84	8.94	58.82	86.75	101.77	101.40	+ 0.37
1.500	73.84	9.74	58.16	77.49	93.17	93.06	0.11
1.500	73.84	10.74	57.33	67.81	84.32	84.40	0.08
1.500	73.84	12.27	56.05	56.08	73.87	—	—
1.500	73.80	15.20	53.69	39.79	59.90	59.63	0.27
1.500	73.80	19.81	49.98	22.00	45.82	45.75	0.07
1.500	73.80	23.50	47.09	12.01	38.72	38.57	0.15

TABLE XVI

Adsorption of ammonia (4.79 cc)

(NH$_4$Cl in tube)

T	Bar cm	V cc	L	R	P cm	P′ cm	Correction
1.503	73.22	3.51	65.04	87.81	95.97	99.32	— 3.35
1.504	73.22	3.73	64.84	82.60	90.98	93.46	2.48
1.504	73.24	4.26	64.44	73.04	81.84	82.81	0.97
1.506	73.24	4.79	63.93	63.47	72.78	—	—
1.501	73.22	5.97	62.98	49.16	59.40	58.39	+ 1.01
1.498	73.18	7.79	61.47	34.88	46.59	44.81	1.71
1.498	73.18	10.82	58.95	20.07	34.30	32.22	2.08
1.498	73.18	14.40	56.04	9.37	26.51	24.21	2.30

TABLE XVII

Adsorption of ammonia (9.70 cc)

(NH_4Cl in tube)

T	Bar cm	V cc	L	R	P cm	P′ cm	Correction
1.510	73.20	6.98	62.05	88.44	99.59	101.88	— 2.29
1.510	73.20	7.75	61.45	78.42	90.17	91.76	1.59
1.510	73.20	8.74	60.66	68.25	80.79	81.36	0.57
1.510	73.20	9.70	59.85	59.96	73.31	—	—
1.500	73.22	12.25	57.74	43.25	58.73	58.05	+ 0.68
1.500	73.22	16.32	54.43	26.21	45.00	43.58	1.42
1.501	73.24	20.88	50.74	13.33	35.83	34.06	1.77

TABLE XVIII

Adsorption of ammonia (15.27 cc)

(NH_4Cl in tube)

T	Bar cm	V cc	L	R	P cm	P′ cm	Correction
1.503	73.55	10.71	58.93	88.46	103.08	105.19	— 2.11
1.503	73.57	11.66	58.12	79.54	94.98	96.64	1.66
1.504	73.57	13.06	57.02	69.07	85.62	86.28	0.66
1.505	73.57	15.27	55.10	55.35	73.73	—	—
1.490	73.55	18.49	52.64	40.84	61.75	60.94	+ 0.81
1.493	73.55	22.56	49.36	26.96	51.15	49.95	1.20
1.497	73.55	26.06	46.67	17.70	44.58	43.24	1.34

As before, no considerable deviation is noticed in the values for P and P′ for hydrogen sulphide, which was to be expected from the excess runs; but ammonia deviates considerably at the higher and lower pressures and furthermore the deviation is in the right direction, *i. e.*, P′, the calculated pressure, is too high as stated above. These corrections were plotted as follows: Abscissas are volumes and ordinates are the corresponding pressure corrections, the positive values being above and the negative values below a zero line in the middle of the paper. From the curve thus obtained (Fig. 3) corrections were applied to the values of P′ in the previous excess runs, Tables VII, VIII and IX. The corresponding corrected partial pressures and their products are given in Table XIX. The third column shows that the corrections are too great, *i. e.*, the bend of the curve on the ammonia end is turned in the other direction. A thinner layer of ammonium chloride crystals was then deposited on the tube and correction measurements made, but it seemed impossible to get the crystals of the right size and number to give the desired correction. The values were either too small or too large. The reason for this is obvious. The exact conditions in the measuring tube can not be exactly duplicated in this way as

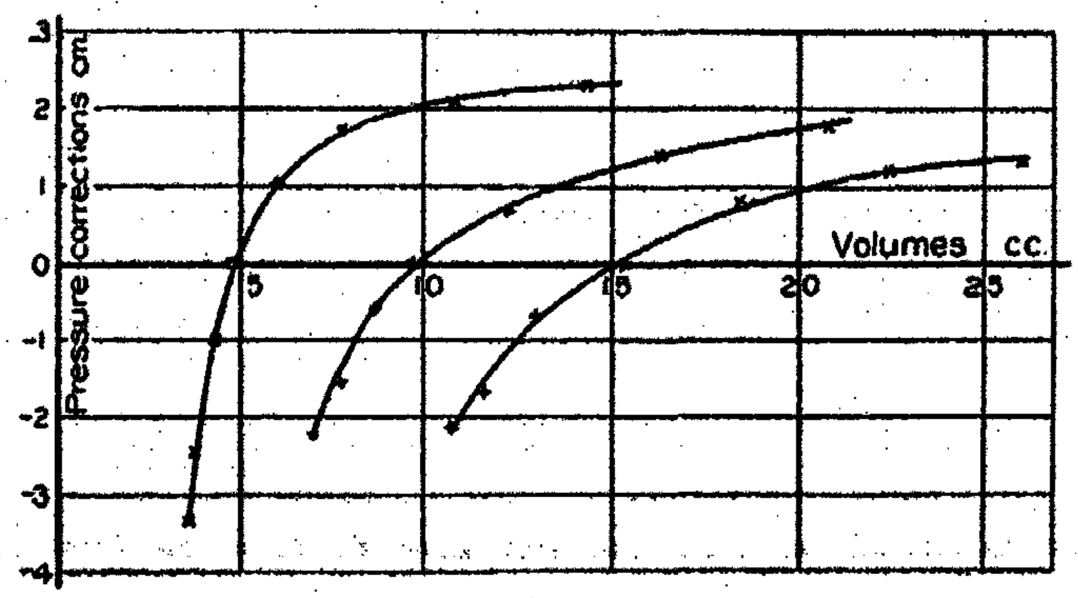

Fig. 3

TABLE XIX

Corrected partial pressures, ammonia in excess

NH_3 (p) cm	H_2S (p_1) cm	$p_1 \times p_2$
	(4.79 cc)	
97.03	4.19	406.6
90.52	4.56	412.7
80.35	4.41	354.3
70.77	4.22	298.6
56.18	4.98	279.7
34.37	7.91	272.0
27.40	9.61	263.3
	(15.27 cc)	
102.69	4.40	451.8
94.88	4.50	426.9
83.19	4.47	380.1
69.59	4.73	329.2
55.67	5.49	305.6
47.87	6.10	292.0
43.10	6.60	284.5

the sulphydrate crystals accumulate at the higher pressures and disappear at the lower pressures, so that the exposed surface varies greatly. But the result does show that the deviation of ammonia from the theoretical value is due to the adsorption of the gas on the exposed surface, so that so far as the actual prevailing pressures are concerned, the mass law holds.

For the purpose of comparison the numerical results of the above experiments are summarized in Table XX.

TABLE XX

Summary of Results

Temperature, 20° C

1. Vapor-pressure (Π) of NH_4SH—35.52 cm. $\frac{\Pi^2}{4} = 315.0$

2. Ammonia in excess

Run *a*, 5.17 cc NH_3 in excess

Total pressure cm	Partial pressure ammonia (p_1) cm	Partial pressure Hydrogen sulphide (p_2) cm	$p_1 \times p_2$
101.22	99.28	1.94	192.6
95.08	92.52	2.56	236.9
84.77	81.20	3.56	289.1
74.99	70.77	4.22	298.6
61.16	55.44	5.65	313.5
42.28	33.19	9.08	303.4
37.01	26.10	10.81	282.2
Run *b*, 10.01 cc NH_3 in excess			
104.19	102.22	1.97	201.4
97.97	95.32	2.64	251.6
85.10	81.48	3.62	294.9
74.72	70.30	4.42	310.8
57.71	51.41	6.29	323.3
48.37	40.59	7.78	315.8
43.21	34.48	8.72	300.7
Run *c*, 15.60 cc NH_3 in excess			
107.10	104.69	2.40	251.3
99.38	96.38	3.00	289.2
87.67	83.87	3.80	318.7
74.32	69.59	4.73	329.2
61.17	55.12	6.04	333.0
53.98	47.20	6.78	320.0
49.80	42.40	7.40	313.8

TABLE XX—(*Continued*)

3. Hydrogen sulphide in excess

Run *a*, 5.00 cc H_2S in excess

100.24	3.00	97.24	291.7
93.96	3.36	90.59	304.4
84.25	3.86	80.39	310.3
74.36	4.52	69.83	315.6
57.85	6.22	51.63	321.1
42.77	9.46	33.30	315.0
37.69	11.60	26.08	302.5

Run *b*, 10.28 cc H_2S in excess

98.79	3.40	95.38	316.9
87.51	3.78	83.72	316.5
73.36	4.66	68.70	320.1
57.95	7.25	44.69	320.4
43.58	9.24	34.33	317.2
39.77	10.98	28.78	316.0

Run *c*, 15.58 cc H_2S in excess

102.56	3.27	99.29	324.6
87.06	3.96	83.09	329.0
74.31	4.70	69.61	327.1
57.91	6.29	51.61	324.6
49.56	7.57	41.98	317.8
43.00	9.28	33.71	312.9

In order to render the above table more convenient for reference the three separate runs under (2) were brought together in Table XXI by taking the mean of the three corresponding total pressures in the three runs as the total pressure, and the mean of the three corresponding partial pressures of each gas as the partial pressure. Thus the last value in column 1, 104.17, is the mean of 101.22, 104.19, and 107.10; the last figure in column 2, 102.06, is the mean of 99.28, 102.22, and 104.96; and so on. Similarly for (3). In column 4 are given the products of these new partial pressures. In calculating the mean value of these products the figures marked (*) were omitted. These last values would also coincide if the proper correction were made for the adsorption.

Tables XIII and XIV show that under the conditions of the experiment ammonia and hydrogen sulphide obey Boyle's law over the range of pressures measured and with no solid deposited on the inside glass surface of the measuring tube.

TABLE XXI

Total pressure cm	Partial pressure (p_1) NH_3	Partial pressure (p_2) H_2S	$p_1 \times p_2$
100.53	3.22	97.30	313.3
86.27	3.87	82.40	318.8
74.01	4.63	69.38	321.2
55.90	6.59	49.31	325.0
45.30	8.76	36.54	320.1
40.15	10.62	29.52	313.5
43.34	34.34	8.99	308.8
48.21	40.33	7.88	317.7
60.01	54.01	5.99	323.5
74.68	70.22	4.46	313.2
85.84	82.18	3.66	300.8
97.47	94.74	2.73	258.6*
104.17	102.06	2.10	214.3*
			Mean, 314.0
			$\frac{\Pi^2}{4} = 315.0$

During these experiments it was noticed that if readings were taken at once after each adjustment of the leveling tube, more concordant results were obtained for the calculated and observed pressures than when some time elapsed before readings were taken. In the measurements given in the following table readings were taken fifteen minutes after adjustment. V is the observed volume, P the observed pressure, and P′ the calculated pressure as before.

TABLE XXII

V cc	P cm	P′ cm	P — P′ cm
10.84	101.98	102.20	—0.22
11.73	94.32	94.44	0.12
15.01	73.80	—	—
17.82	62.42	62.26	+0.16
23.27	47.77	47.60	0.17
27.58	40.44	40.16	0.28

At pressures above atmospheric the values of P′ are distinctly higher than those of P, while at lower pressures P′ is too low. In another experiment 4.49 cc ammonia were allowed to stand for two hours under a pressure of 88.78 cm. The calculated pressure was 89.44 cm. For another volume, 13.69 cc allowed to stand for the same length of time P = 83.02 cm and P′ 83.38 cm. This, together with the values of P and P′ in Table XIII, indicates that the difference between the observed and calculated pressures depends on the length of time the gas is allowed to remain under a given pressure, *i. e.*, that the apparent deviation from Boyle's law is due, not to a too great compressibility of the gas, but to a gradual adsorption of the gas on the walls of the containing vessel. It also explains the excess of hydrogen sulphide remaining on mixing equal volumes of the two gases as noted at the beginning of this paper. Of course, the above data are too meager to warrant any general conclusion on this point; but the question is of special interest in connection with our conception of the so-called imperfect gases, and therefore offers an interesting problem for further study.

Briefly stated the results of these experiments are as follows:

(1) The equilibrium between ammonia and hydrogen sulphide has been studied at one temperature, namely 20°, and over a range of 95 cm partial pressures.

(2) The mass law describes the relation between the partial pressures of the ammonia and hydrogen sulphide over the pressure range studied when corrections are made for adsorption.

(3) The deviations observed when ammonia is present in excess are due to adsorption of the gas on the surfaces with which it is in contact, chiefly on the solid ammonium hydrosulphide.

(4) The deviations from Boyle's law in the case of ammonia have been shown to depend on a time factor, thus showing an interesting bearing of the above experiments on our conception of the so-called imperfect gases.

In conclusion, I desire to thank Professor Bancroft for his kindly interest and many valuable suggestions during the course of this work.

Cornell University,
June, 1906.

THE RATE OF OXIDATION OF ARSENIOUS ACID BY CHROMIC ACID

BY RALPH E. DE LURY

The following measurements together with those on the rate of oxidation of iodide by chromic acid[1] constitute a necessary preliminary investigation to the study of the rates of the reactions in solutions containing arsenious acid, iodide, bichromate and sulphuric acid.[2]

In all of these experiments the concentration of the arsenious acid was small and the sulphuric acid and potassium bichromate concentrations relatively large, so that the results might be directly comparable with the measurements in which iodide was present. It was consequently possible to consider the concentrations of the sulphuric acid and bichromate as constant in the experiments of each table.

Method of Experimenting

A supply of distilled water and dilute solutions of potassium bichromate, sulphuric acid and arsenious acid were kept at 0° *C* in a thermostat. The bichromate and sulphuric acid and some of the water were measured into a beaker clamped down in the bath; the arsenious acid mixed with the rest of the water necessary to make up the required total volume, was thrown into the beaker from a large test-tube, the reacting mixture violently stirred and the time noted. To stop the reaction a quantity of ammonium bicarbonate solution more than sufficient to neutralize the acid present was added to the beaker and the contents were thoroughly stirred. The residual arsenious acid was then determined by titration with volumetric iodine and arsenious acid.

Solutions Employed

The following stock solutions were prepared :

Potassium Bichromate, $K_2Cr_2O_7$, 0.1 *F*, or 0.6 *N*, prepared

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[1] De Lury: Jour. Phys. Chem., 7, 239 (1903).

[2] Ibid., immediately following the present paper.

by dissolving 58.9 grams of the pure salt in 2 litres of distilled water.

Sulphuric Acid, H_2SO_4, 0.967 *N*, standardized gravimetrically with barium.

Arsenious Acid, As_2O_3, 0.025 *F*, or 0.1 *N*, prepared by dissolving 9.90 grams of pure "lump white arsenic" in hot water and diluting to 2 liters with distilled water; before use the solution was diluted to ten times its volume with boiled distilled water (to prevent slow oxidation by oxygen).

Iodine, approximately 0.1 *N*, prepared by dissolving resublimed iodine in potassium iodide solution and diluting. For titrating, this solution was diluted to ten times its volume and compared frequently with the volumetric arsenious acid solution.

Ammonium Bicarbonate, "restrainer," prepared by passing carbon dioxide into a saturated solution of commercial ammonium carbonate, diluting with its own volume of water and again saturating with carbon dioxide.

Starch Solution, "indicator," prepared frequently by dissolving a gram or two of starch in 500 *cc* of boiling water, cooling and allowing to settle.

Explanation of the Tables

After *Cr* and *Ac* at the head of the tables are given the amounts expressed in 10^{-5} gram-formula-weights (*i. e.*, in *cc* of 0.01 *F* solution) of $K_2Cr_2O_7$ and H_2SO_4 respectively; after *As* the amount of As_2O_3, the unit being 0.25×10^{-5} gram-formula-weights (*i. e.*, 1 *cc* of 0.01 *N* solution); after *Vol.* is given the volume of the reacting mixture in cubic centimeters. The constant *k* is defined by the equation, $k = \frac{1}{t} . \log._{10} \frac{As}{As - x}$, where *x* is the amount (expressed in *cc* of 0.01 *N* solution) of arsenious acid oxidized in *t* minutes. After *Avg.* at the end of the tables is given the average of the constants; in taking the average, bracketed numbers were omitted.

TABLE I

As, 9.94; *Cr*, 149; *Ac*, 484; *Vol.*, 500

t	$As - x$	x	k
2	7.54	2.40	0.060
3	6.53	3.41	0.061
4	6.04	3.90	0.054
5	5.20	4.74	0.056
7	3.91	6.03	0.058
			Avg. 0.058

TABLE II

As, 9.94; *Cr*, 298; *Ac*, 484; *Vol.*, 500

t	$As - x$	x	k
1	7.51	2.43	0.122
2	6.05	3.89	0.108
3	5.00	4.94	0.100
4	3.93	6.01	0.108
			Avg. 0.110

TABLE III

As, 9.94; *Cr*, 447; *Ac*, 484; *Vol.*, 500

t	$As - x$	x	k
1	6.46	3.48	0.187
2	4.54	5.40	0.170
			Avg. 0.178

TABLE IV

As, 4.95; *Cr*, 149; *Ac*, 484; *Vol.*, 500

t	$As - x$	x	k
1	4.45	0.50	(0.046)
2	3.92	1.03	0.051
3	3.44	1.51	0.053
4	3.02	1.93	0.054
5	2.72	2.23	0.052
			Avg. 0.052

TABLE V

As, 9.94; *Cr*, 149; *Ac*, 968; *Vol*, 500

t	$As - x$	x	k
1	6.61	3.33	(0.177)
1.5	5.56	4.38	0.168
2	4.70	5.24	0.163
2.5	3.93	6.01	0.161
3	3.17	6.77	0.166
			Avg. 0.164

TABLE VI

As, 9.94; *Cr*, 149; *Ac*, 725; *Vol.*, 500

t	$As - x$	x	k
1	7.58	2.36	(0.118)
1.5	6.79	3.15	0.110
2	5.96	3.98	0.111
2.5	5.40	4.54	0.106
3	4.83	5.11	0.105
4	3.80	6.14	0.104
			Avg. 0.107

In the measurements of Tables I–VI the residual arsenious acid was not always titrated immediately after adding the restrainer; this introduced an error due to oxidation of arsenious acid in alkaline solution.[1] In the measurements of Tables VII–XVI the arsenious acid was titrated with iodine

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[1] Kessler: Pogg. Ann, 113, 142 (1861). In an average case (Table XIV), it was found that about 0.05 *cc* of 0.01 *N* arsenious acid solution was oxidized in one minute after adding the restrainer.

in the ice bath immediately after stopping the reaction; to make the end-point distinct, a light and reflector and beakers coated with white enamel were used. The constants of these tables are more uniform than those of the above six tables.

TABLE VII (under CO_2)

As, 10.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As — x*	*x*	*k*
5	8.77	1.23	0.0114
10	7.67	2.33	0.0115
15	6.69	3.31	0.0116
20	5.90	4.10	0.0115
		Avg.	0.0115

TABLE VIII

As, 10.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As — x*	*x*	*k*
5	8.79	1.21	0.0112
10	7.66	2.34	0.0116
15	6.72	3.28	0.0115
20	6.01	3.99	0.0111
25	5.20	4.80	0.0114
30	4.75	5.25	(0.0108)
		Avg.	0.0114

TABLE IX

As, 20.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As — x*	*x*	*k*
5	17.32	2.68	0.0121
10	15.27	4.73	0.0117
15	13.50	6.50	0.0114
20	11.95	8.05	0.0112
		Avg.	0.0116

TABLE X

As, 5.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As — x*	*x*	*k*
5	4.37	0.63	0.0117
10	3.84	1.16	0.0115
15	3.32	1.68	0.0112
20	2.97	2.03	0.0113
25	2.59	2.41	0.0114
30	2.29	2.71	0.0113
		Avg.	0.0114

TABLE XI

As, 10.00; *Cr*, 20; *Ac*, 484; *Vol.*, 300

t	*As — x*	*x*	*k*
5	6.83	3.17	0.0332
10	4.83	5.17	0.0316
14	3.71	6.29	0.0307
		Avg.	0.0318

TABLE XII

As, 5.00; *Cr*, 20; *Ac*, 484; *Vol.*, 300

t	*As — x*	*x*	*k*
5	3.48	1.52	0.0315
10	2.47	2.53	0.0306
15	1.77	3.23	0.0301
20	1.30	3.70	0.0293
25	0.96	4.04	0.0287
		Avg.	0.0300

Table XIII

As, 10.00; *Cr*, 40; *Ac*, 242; *Vol.*, 300

t	*As – x*	*x*	*k*
5	7.77	2.23	0.0219
10	6.07	3.93	0.0217
15	4.78	5.22	0.0214
			Avg. 0.0217

Table XIV

As, 5.00; *Cr*, 40; *Ac*, 242; *Vol.*, 300

t	*As – x*	*x*	*k*
5	4.05	0.95	(0.0183)
10	3.24	1.76	0.0188
14	2.55	2.45	0.0209
15	2.51	2.49	0.0202
20	1.92	3.08	0.0208
25	1.76	3.24	(0.0181)
30	1.37	3.63	0.0188
			Avg. 0.0200

Table XV

As, 10.00; *Cr*, 20; *Ac*, 121; *Vol.*, 300

t	*As – x*	*x*	*k*
10	9.00	1.00	0.0046
20	8.20	1.80	0.0043
22.5	7.99	2.01	0.0043
30	7.38	2.62	0.0043
			Avg. 0.0044

Table XVI (*10° C*)

As, 10.00; *Cr*, 20; *Ac*, 242; *Vol.*, 300

t	*As – x*	*x*	*k*
10	7.15	2.85	0.0146
15	6.10	3.90	0.0146
20	5.18	4.82	0.0143
			Avg. 0.0144

The oxygen of the air, while it affects the oxidation of arsenite in alkaline solution, has no effect on the oxidation of arsenious acid by chromic acid. This is seen by comparing Tables VII and VIII. The measurements of VII were made, using solutions free from air and protecting the reacting mixture with carbon dioxide; those of VIII were made, taking no precautions to exclude air. The constants and *As–x* readings agree closely.

I further satisfied myself that arsenic acid of the concentration formed in the experiments has no effect on the rate of oxidation of arsenious acid.

Discussion of the Results

Effect of the Arsenious Acid.—The fair constancy of *k* throughout the tables, more particularly in Tables VII–XVI where special precautions were taken, leads to the conclusion that the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid; conclusive proof of this is furnished by the fact that *k* is unaffected by changing the concentration of the arsenious acid (Tables I and IV; VII, VIII and IX; XI and XII).

Effect of the Bichromate.—Doubling the concentration of the bichromate nearly doubles the constant, or halves the time necessary for the oxidation of the same amount of arsenious acid (Tables I and II; VII, VIII and XIII; X and XIV). Trebling *Cr* trebles *k* or divides by three the time necessary for the oxidation of a fixed amount of arsenious acid (Tables I and III). The rate of oxidation of arsenious acid is thus nearly proportional to the first power of the concentration of the bichromate. This deviation from an exact first power may be attributed to incomplete dissociation of $H_2Cr_2O_7$. To account for the fall in the constant it is necessary to assume that the dissociation of the chromic acid in mixture VIII is about 7 percent greater than in XIII.[1]

Effect of the Sulphuric Acid.—If the concentration of the sulphuric acid be doubled the constant is nearly trebled, or the time needed to oxidize the same amount of arsenious acid is divided by three (Tables I and V, VII, VIII and XI). The results of Table VI are in accord with this. The rate may thus be set proportional to the 1.4*th* or 1.5*th* power of the concentration of the sulphuric acid. The deviation from a sharp second power is probably due to the influence of the hydrogenion on the dissociation of the arsenious acid; it is quite possible that arsenious acid in more than one form (ions or undissociated acid) reacts with chromic acid, and the rates of these reactions involve different powers of the concentration of the hydrogenion, the resultant power being the 1.4*th* in the above experiments.

Effect of the Temperature.—For an increase of 10° *C* in the temperature the constant is increased from 0.0114 to 0.0144 (Tables VIII and XVI); that is, the rate is increased only 26 percent, a very low temperature effect indeed.

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[1] See also Jour. Phys. Chem., 7, 248 (1903).

The experimental results of this investigation are summarized in Table XVII. K is defined by the equation (*Vol.* 300 *cc.*),

$$\frac{dx}{dt} = K(As - x).Cr^{0.9}.Ac^{1.4},$$

and hence,

$$K = \frac{2.30\,k}{Cr^{0.9}.Ac^{1.4}} \cdot \left\{\frac{Vol}{300}\right\}^{2.3}.$$

It will be seen that the value of K is fairly constant throughout.

TABLE XVII

Table	*As*	*Cr*	*Ac*	*Vol.*	*k*	$K \times 10^8$
I	9.94	149	484	500	0.058	84
II	9.94	298	484	500	0.110	85
III	9.94	447	484	500	0.178	95
IV	4.95	149	484	500	0.052	75
V	9.94	149	968	500	0.164	89
VI	9.94	149	726	500	0.107	87
VII	10.00	20	242	300	0.0115	82
VIII	10.00	20	242	300	0.0114	82
IX	20.00	20	242	300	0.0116	83
X	5.00	20	242	300	0.0114	82
XI	10.00	20	484	300	0.0318	86
XII	5.00	20	484	300	0.0300	81
XIII	10.00	40	242	300	0.0217	83
XIV	5.00	40	242	300	0.0200	77
XV	5.00	20	121	300	0.0044	83

Summary

The rate of oxidation of arsenious acid (dilute solutions) by bichromate and sulphuric acid, is proportional to the first power of the concentration of the arsenious acid, the 0.9*th* power of the concentration of the bichromate and the 1.4*th* power of the concentration of the sulphuric acid, that is,

$$\frac{dx}{dt} = K(As - x).Cr^{0.9}.Ac^{1.4}.$$

The effect of temperature on this reaction is unusually small; for an increase of 10° *C* the rate is increased only 26 percent.

University of Toronto,
May, 1905

THE INDUCTION BY ARSENIOUS ACID OF THE REACTION BETWEEN CHROMIC AND HYDRIODIC ACIDS

BY RALPH E. DE LURY

It has long been known that the process of oxidation in solution can often be hastened by the presence of a small quantity of some easily oxidizable substance. This phenomenon is called *induced oxidation*: the name *acceptor* is given to the substance whose oxidation is accelerated and the reagent causing the acceleration is called the *inductor*. Ferrous salts, arsenious acid and nitric oxide act as inductors and iodide as acceptor for the oxygen of chromic acid.

About the middle of the last century many cases of induced oxidation, occurring chiefly in the development of methods of analysis, were noted and classified by Schönbein, Kessler and others. By selecting various combinations of reducing and oxidizing agents the number of similar cases might be multiplied indefinitely. Many of these cases have been studied qualitatively and to a certain degree quantitatively, and the attempts to explain the results of these investigations have led to the development of the *peroxide theory* so ably championed by Manchot.[1]

The peroxide theory is based on a considerable amount of qualitative and some quantitative data, and on the fact that some peroxides are known to be formed in the process of oxidation, such as hydrogen peroxide and benzoyl hydroperoxide: these peroxides may be regarded as the primary products of the oxidation of hydrogen and benzaldehyde respectively.

However, if a *non-isolable* peroxide, regarded as the cause of induced oxidation, be formed, its formation can be ascertained only by a careful study of the rates of all the reactions involved, since it is as an explanation of these rates

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[1] Lieb. Ann., 325, 95 (1902).

that the peroxide theory is advanced. This obvious method of attacking the problem has been neglected, no doubt on account of the difficulties of analysis which such a method in general presents; hence the quantitative investigation of such cases has been chiefly confined to the measurement of the ratio of the amounts of inductor and acceptor oxidized when the reaction is complete.[1] Such a method will often give the oxidizing value of the intermediate product but the results are not reliable or sufficient.

The only case of which I am aware to which the method of studying all the rates involved has been applied as yet, is the reactions in solutions containing chromic acid, iodide and ferrous salt[2] investigated by Miss C. C. Benson, and curiously enough the results are not in accord with the peroxide theory.

In the present paper I communicate the results of measurements of the rates of the reactions in solutions containing chromic acid, iodide and arsenious acid and am able to show that the assumption of the formation of a peroxide explains the induction in this case. The rates of oxidation of iodide[3] and of arsenious acid[4] by chromic acid have already been studied by myself.

Plan of the Investigation

In solutions containing potassium iodide, arsenious acid, potassium bichromate and sulphuric acid the following reactions may occur:

A. Oxidation of the iodide by chromic acid,

$$9KI + K_2Cr_2O_7 + 7H_2SO_4 = 3KI_3 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O,$$

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[1] Manchot: loc. cit.; Schilow: Zeit. phys. Chem. 42, 641 (1903).

[2] Jour. Phys. Chem., 7, 356 (1903).

[3] Ibid., 7, 239 (1903).

[4] Ibid., 11, 47 (1907).

whose rate at 0° C, may be represented[1] approximately by the kinetic equation:[2]

$$\frac{dI_3}{dt}(c) = Ric = 1 \times 10^{-12}.Cr.(Ac)^2\left[KI + 0.002(KI)^2\right] \qquad (1)$$

B. Oxidation of arsenious acid by chromic acid,

$$3As_2O_3 + 2K_2Cr_2O_7 + 8H_2SO_4 = 3As_2O_5 + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 8H_2O.$$

In the absence of potassium iodide the rate of this reaction at 0° C, may be represented by the equation:[3]

$$\frac{d\overset{v}{As}}{dt}(c) = Rac = 83 \times 10^{-8}.As.(Cr)^{0.9}.(Ac)^{1.4} \qquad (2)$$

C. Oxidation of the iodide by arsenic acid formed in the reaction,

$$6KI + As_2O_5 + 2H_2SO_4 = 2KI_3 + As_2O_3 + 2K_2SO_4 + 2H_2O,$$

and the rate of this reaction at 0° C, may be represented[4] thus:

$$\frac{dI_3}{dt}(a) = Ria = 4 \times 10^{-12}.\overset{v}{As}.KI.Ac \qquad (3)$$

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[1] KI, Cr and Ac denote the amounts of potassium iodide, potassium bichromate and sulphuric acid respectively, expressed in 10^{-5} gram-formula-weights (i. e. in *cc.* of 0.01 F solution): the same unit as employed in the measurements on the rate of oxidation of iodide by chromic acid (*loc. cit.*). As and $\overset{v}{As}$ denote respectively the amounts of arsenious acid and arsenic acid expressed in 0.25×10^{-5} gram-formula-weights (i. e. in *cc.* of 0.01 N solution); this unit is selected in order to facilitate comparison between the iodine and arsenious acid readings in the Tables which follow. I_3 denotes the "free iodine" in 0.5×10^{-5} gram-formula-weights (i. e. in *cc.* of 0.01 N solution). The letter R denotes rate; Ric denotes the rate of oxidation of iodide by chromic acid; Rac denotes the rate of oxidation of arsenious acid by chromic acid, etc. In the subscripts *ic*, *ac*, etc. the letters *i*, *a*, *c*, suggest iodide (or tri-iodide), arsenious acid (or arsenic acid), and chromic acid respectively: the letter which goes first denoting the substance oxidized and the second letter the substance oxidizing.

The constants are calculated for a volume of 300 *cc.*

[2] De Lury: loc. cit.

[3] The paper just preceding the present paper.

[4] Roebuck: Jour. Phys. Chem., 6, 365 (1902). In concentrated solutions the indices of the power of KI and Ac are greater than 1.

D. Oxidation of the arsenious acid by the triiodide formed in the reaction,

$$As_2O_3 + 2KI_3 + 2K_2SO_4 + 2H_2O = As_2O_5 + 6KI + 2H_2SO_4$$

whose rate at 0° *C*, is expressed by:[1]

$$\frac{d\overset{v}{As}}{dt}(i) = -\frac{dI_3}{dt}(a) = Rai = 1 \times 10^{-6}.I_3.As.(KI)^{-2}.(Ac)^{-1} \quad (4)$$

E. Oxidation of the iodide due to the influence of the arsenious acid; the symbol *Rip* denotes the rate of this reaction.[2]

In order to simplify the study of the rate of reaction *E* the concentrations of the reagents were selected so as to reduce the rates of reactions *A*, *C* and *D* as much as possible. Of these, reaction *C* (*Ria*) gave no trouble at all since the rate constant is very small and no arsenic acid was present except that formed in reactions *B* (*Rac*) and *D* (*Rai*). The loss of I_3 by reaction *D* could not be prevented by high concentrations of *KI* and *Ac* without unduly increasing *Ric*, and in the end it was found necessary to remove the iodine as soon as it was liberated by the use of thiosulphate (see page 58).

Thus in my experiments *Ria* and *Rai* were negligibly small, and therefore,

$$\frac{d\overset{v}{As}}{dt} = Ra = Rac + M\text{[3]} \quad (5)$$

$$\frac{dI_3}{dt} = Ri = Ric + Rip \quad (6)$$

and *Ric* being determined by blank experiments *Rip* is obtained by difference.

EXPERIMENTAL PART

It was necessary to determine the quantities of iodide and arsenious acid oxidized at any stage of the reaction. Three methods of analysis were tried.

First Method.—When a suitable interval had elapsed the

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[1] Roebuck: Loc. cit.

[2] *p*, for peroxide in anticipation of the theory (see p. 78).

[3] *M* is the modification in *Rac* due to the iodide (see p. 73).

concentration of the acid was reduced by addition of sodium bicarbonate, the iodine quickly titrated with sodium thiosulphate, excess of ammonium bicarbonate added and the residual arsenious acid titrated with iodine. This method was not successful.

Second Method.—After the reaction had proceeded for some time excess of ammonium bicarbonate was added and the arsenious acid titrated with iodine. In a duplicate experiment after the same interval, a measured quantity of 0.002 *N* thiosulphate solution, slightly in excess of the iodine present, was thrown into the reacting mixture, with violent stirring just before the ammonium bicarbonate which served as restrainer. Starch was then added and the arsenious acid and residual thiosulphate titrated with iodine, the iodine added being the sum of the arsenious acid and a *function* of the remaining thiosulphate. From these two measurements the arsenious acid oxidized and the iodine present could be determined if this function were known. Experiments showed that it depended on so many variables that no reliable determinations could be made, and the method was abandoned.

Third Method.—In the end a modification of Harcourt and Esson's compensation method was found to serve, and was adopted in all the measurements of this paper. The details of the method are as follows:

Method of Making the Measurements

Distilled water and dilute solutions of potassium bichromate, sulphuric acid, potassium iodide and arsenious acid were kept at 0° *C* in a thermostat. The bichromate, sulphuric acid and water were mixed in a beaker coated on the outside with white enamel. In a large test-tube the iodide and arsenious acid were mixed and a little starch solution added. At a suitable time the contents of the test-tube were thrown into the beaker with violent stirring, and a stop-watch set going by pressure of the foot.

Over the beaker was clamped a 10 *cc* burette from which 0.01 *N* sodium thiosulphate solution was added drop by drop as the reaction proceeded, care being taken to keep the solution in the beaker as near as possible free from both iodine and thiosulphate. A number of readings of the burette were made during each experiment, and finally after a definite interval the reaction was stopped with excess of ammonium bicarbonate, and the residual arsenious acid titrated immediately[1] with iodine.

To test the method of analysis the measurements recorded in Tables I, II and III were made. In these tables, "*yellow*" denotes "slight excess of thiosulphate," and "*green*" denotes "slight excess of iodine," that is, just enough to keep the reacting mixture bluish green with the starch present; "*close*" means "as near as possible free from both thiosulphate and iodine."

TABLE I

As, 10.00; *KI*, 9.8; *Cr*, 20; *Ac*, 484

Minutes	*cc* thiosulphate
5.1	1.59 *yellow*
5.1	1.31 *close*
5.1	1.09 *green*

TABLE II

As, 10.00; *KI*, 245; *Cr*, 20; *Ac*, 242

Minutes	*cc* thiosulphate
9.5	2.00 *yellow*
9.5	2.00 *close*
9.6	2.00 *green*

TABLE III

As, 10.00; *KI*, 98; *Cr*, 20; *Ac*, 242

cc thiosulphate	*yellow* *Minutes*	*close* *Minutes*	*green* *Minutes*
0.50	3.2	3.5	3.3
1.00	6.0	6.2	6.2
1.50	9.0	9.1	8.8
2.00	11.9	12.0	12.0

In Table I where the concentration of the iodide was low the amount of thiosulphate needed to neutralize the iodine liberated in a fixed interval, depends on the method of working. This is due to the absorption of iodine by arsenious acid, and as the rate of this reaction[2] is inversely proportional

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[1] To prevent oxidation of the arsenite in the alkaline solution of chromate and oxygen.

[2] See equation (4).

to the square of the concentration of the iodide, the difference in the thiosulphate readings becomes less when the concentration of the iodide is increased and disappears when the iodide concentration is equal to (or greater than) ten times the concentration of the arsenious acid (Tables II and III). The fact that in these last two tables, the readings made when the mixture was "*yellow*" and "*green*" are the same is proof that the oxidation of thiosulphate by chromic acid[1] is negligible. In those of my measurements where the concentration of the iodide was small, I was careful to keep the reacting mixture slightly "*yellow*" until near the end of the interval desired; this involved an approximate knowledge of the rate at which the iodine was being liberated and in some cases necessitated the duplication of the experiments.

A number of blank experiments carried out for the purpose, showed that neither the oxygen of the air, nor the arsenic acid[2] and tetrathionate[3] formed in the reaction, affected the rates.

Solutions Employed

In addition to the solutions, $K_2Cr_2O_7$, 0.1 F or 0.6 N; H_2SO_4, approximately 0.1 N; As_2O_3, 0.025 F or 0.1 N; ammonium bicarbonate and starch, employed in the measurements on the rate of oxidation of arsenious acid by chromic acid, a solution of potassium iodide 0.098 F (standardized by silver) and approximately 0.01 N solutions of thiosulphate and iodine (standardized by comparison with the arsenious acid), were used.

Explanation of the Tables

After KI, Cr and Ac at the head of the tables are given the amounts, expressed in 10^{-5} gram-formula-weights (*i. e.*, in *cc* of 0.01 F solution) of KI, $K_2Cr_2O_7$ and H_2SO_4 respectively

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[1] See Bell: Jour. Phys. Chem., 7, 61 (1903).

[2] See equation (3) above, et seq.

[3] The concentration of the tetrathionate is not large enough to cause any error due to decomposition in the alkaline solution during the short interval between adding the bicarbonate and the completion of the titration.

(the same unit as employed in the measurements of the oxidation of iodide); after *As*, the amount of As_2O_3, the unit being 0.25×10^{-5} gram-formula-weights (*i. e.*, 1 *cc* 0.01 *N* solution), this unit is selected so as to facilitate comparison between the iodine and arsenious acid readings.

Under *t* are entered the durations of the reaction in minutes. Under *h* are given the amounts of thiosulphate ("*hypo*"), added from the small burette during the reaction expressed in *cc* of 0.01 *N* solution. Under $As-x'$ are entered the amounts of arsenious acid remaining unoxidized after *t* minutes, expressed in *cc* of 0.01 *N* solution; x' thus represents the amount of arsenious acid oxidized: this symbol is used only when iodide is present in the reacting mixture. The symbol x denotes the amount of arsenious acid oxidized in the absence of iodide.

Under *ic* in Table XXI are given the amounts of iodine (in *cc* of 0.01 *N* solution) liberated by the oxidation of iodide in the absence of arsenious acid. The experiments were carried out just like those in which arsenite was present (page 58), and the *ic* readings were obtained from the readings of the small thiosulphate burette. The numbers under *ic* in Tables IV–X and XII–XX were obtained from these by interpolation. In Table XI where the reaction was allowed to proceed until the arsenious acid was completely oxidized, the numbers under *ic* (*calc*) were calculated from the equation, $ic(calc) = 0.60 \frac{t}{5} \cdot \frac{20 \times 6 - 0.5(h + x')}{20 \times 6}$, thus allowing for the decrease in the concentration of the bichromate.

In all of the experiments the initial volume was as near as possible $300 - \frac{h}{2}$ *cc*, so that the average volume during the reaction was 300 *cc*. The temperature was always 0° *C* except in Table XX and in one series of Table XXI where the temperature was 10° *C*.

The difference between the amounts of iodine liberated in the presence and absence of arsenious acid is entered under

$h—ic$. The constant, k', is defined by the equation, $k' = \frac{1}{t}.log_{10}\frac{As}{As-x'}$. When no iodide is present k' becomes k of the tables on the oxidation of arsenious acid by chromic acid, and at the same time x' becomes x of those tables (i. e., k and x are the limiting values of k' and x' when $KI = 0$).

In Tables V–IX, *Ra* and *Rip* (see page 56) represent the rates of oxidation of arsenious acid, and of iodide in the presence of arsenious acid after correcting for the direct action of chromic acid. Since the concentrations of the bichromate and sulphuric acid are so large that they may be regarded as constant, the rate, *Ra*, may be calculated by the equation:

$$Ra = 2.30k'.As.$$

Rac is the limiting value of *Ra* when $KI = 0$.

A rough approximation to the rate, *Rip*, is given by the quotient, $\frac{h-ic}{t}$; in this expression, however, the decrease in the concentration of the arsenious acid during the reaction is neglected. In the experiments of Tables V–IX this decrease is at most 25 *percent*, and hence the average amount of arsenite present during the interval is closely represented by $As—0.5x'$. On page 74 I show that the rate is proportional to the concentration of the arsenious acid, and have therefore employed the following expression for calculating the values of *Rip*:

$$Rip = \frac{h-ic}{t}.\frac{As}{As-0.5x'}.$$

TABLE IV

As, 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 121; *t*, 22.5

n	h	$As-x'$	x'	ic	$h-ic$	$r=\frac{h-ic}{x'}$	k'
30	1.60	9.25	0.69	0.18	1.42	2.06	0.0014
40	1.75	9.30	0.64	0.31	1.44	2.25	0.0013
50	1.93	9.26	0.68	0.52	1.41	2.07	0.0013
60	2.03	9.33	0.61	0.70	1.33	2.18	0.0012
70	2.25	9.28	0.66	0.90	1.35	2.04	0.0013
80	2.40	9.27	0.67	1.10	1.30	1.94	0.0013

TABLE V

As, 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 242; *t*, 10

n	h	$As-x'$	ic	$r = \frac{h-ic}{x'}$	k'	Rip	Ra	$Rip+Ra$
0	—	—	—	—	—	0.000	0.263	0.263
1	0.43	7.97	0.01	0.21	0.0096	0.046	0.221	0.267
2	0.70	8.32	0.02	0.42	0.0077	0.073	0.178	0.251
4	1.33	8.79	0.04	1.12	0.0053	0.137	0.122	0.259
6	1.53	8.81	0.06	1.30	0.0052	0.156	0.120	0.276
8	1.60	8.86	0.08	1.41	0.0050	0.160	0.116	0.276
10	1.74	9.00	0.10	1.75	0.0043	0.172	0.099	0.271
10	1.98	9.16	0.10	(2.41)	0.0036	0.195	0.083	0.278
12	1.80	9.07	0.14	1.91	0.0040	0.173	0.092	0.265
15	1.83	9.12	0.19	2.00	0.0037	0.170	0.085	0.255
20	1.88	9.00	0.26	(1.71)	0.0043	0.169	0.099	0.268
30	2.00	9.18	0.43	2.07	0.0035	0.163	0.081	0.244
30	2.17	9.12	0.43	2.12	0.0037	0.182	0.085	0.267
40	2.24	9.25	0.63	2.33	0.0031	0.167	0.071	0.238
50	2.58	9.29	0.95	(2.51)	0.0029	0.168	0.067	0.235
60	2.70	9.18	1.15	2.04	0.0035	0.160	0.081	0.241
70	3.02	9.25	1.45	2.27	0.0031	0.162	0.071	0.233
80	3.30	9.26	1.75	2.26	0.0031	0.160	0.071	0.231

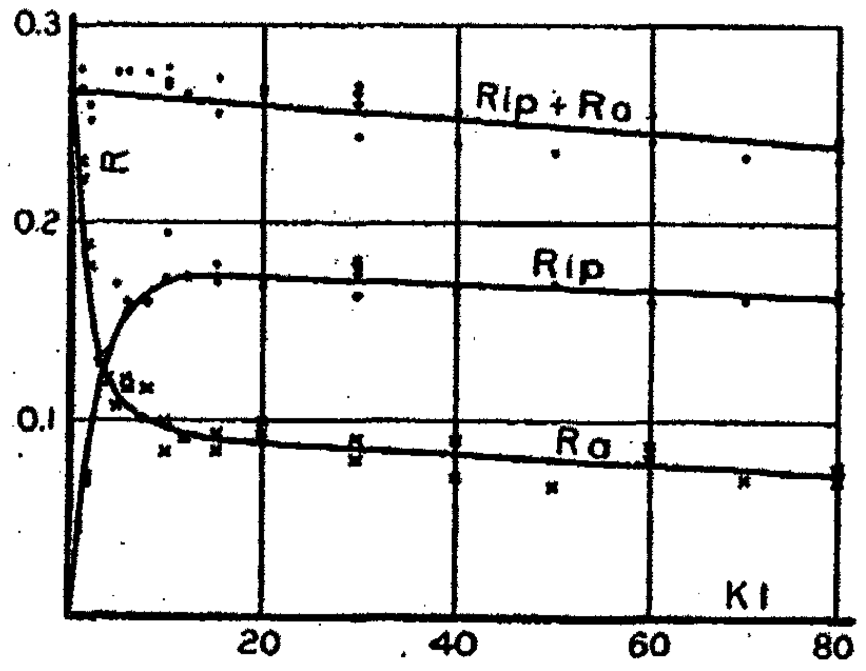

Fig. 1 (Cf. Tables V and VI)

NOTE.—In Figs. 1–4, the unit in which *KI* is represented is 9.8×10^{-5} gram-formula-weights.

Table VI

As. 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 242; *l*, 15

n	*h*	*As—x′*	*ic*	$r=\frac{h-ic}{x'}$	*k′*	*Rip*	*Ra*	*Rip + Ra*
0	—	—	—	—	—	0.000	0.263	0.263
1	0.63	7.03	0.01	0.21	0.0100	0.047	0.230	0.277
2	0.95	7.48	0.02	0.38	0.0082	0.069	0.189	0.258
3	1.87	8.15	0.03	1.03	0.0057	0.134	0.131	0.265
5	2.40	8.46	0.05	1.59	0.0047	0.169	0.108	0.277
6	2.27	8.33	0.06	(1.37)	0.0051	0.160	0.117	0.277
10	2.52	8.56	0.15	1.68	0.0043	0.170	0.099	0.269
15	2.72	8.63	0.28	1.86	0.0041	0.179	0.094	0.273
20	2.78	8.63	0.39	1.82	0.0041	0.171	0.094	0.265
30	3.15	8.67	0.64	1.98	0.0040	0.178	0.092	0.270
30	3.11	8.74	0.64	2.06	0.0037	0.175	0.085	9.260
40	3.34	8.69	0.95	1.91	0.0039	0.166	0.090	0.256
60	4.00	8.73	1.66	1.93	0.0038	0.166	0.088	0.253
80	5.00	8.84	2.62	2.14	0.0033	0.166	0.076	0.242

Table VII

As, 19.90; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 242; *l*, 10

n	*h*	*As—x′*	*ic*	$r=\frac{h-ic}{x'}$	*k′*	*Rip*	*Ra*	*Rip + Ra*
0	—	—	—	—	—	0.000	0.536	0.536
4	2.85	17.63	0.04	1.24	0.0053	0.296	0.243	0.539
6	3.05	17.79	0.06	1.41	0.0049	0.314	0.224	0.538
8	3.10	17.77	0.08	1.41	0.0049	0.317	0.227	0.544
10	3.20	17.83	0.10	1.50	0.0048	0.325	0.220	0.545
12	3.30	18.03	0.14	1.51	0.0043	0.330	0.198	0.534
15	3.44	18.07	0.19	1.77	0.0042	0.340	0.194	0.534
20	3.57	18.12	0.26	1.86	0.0041	0.346	0.188	0.534
30	3.76	18.26	0.43	2.05	0.0037	0.347	0.172	0.519
50	4.40	18.27	0.95	2.12	0.0037	0.359	0.172	0.531
70	4.80	18.31	1.45	2.11	0.0036	0.348	0.167	0.515

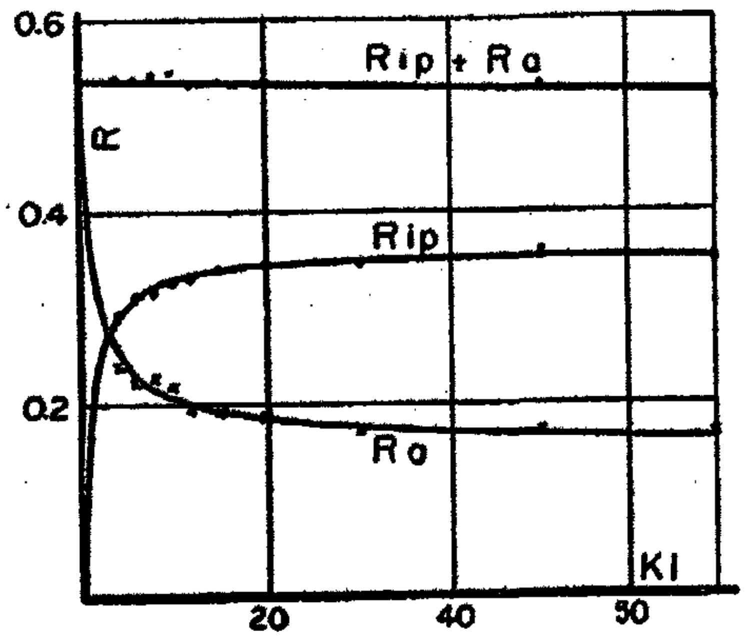

Fig. 2 (Cf. Table VII)

TABLE VIII

As, 9.94; *KI*, *n*.9.8; *Cr*, 40; *Ac*, 242; *t*, 10

n	*h*	$As - x'$	*ic*	$r = \frac{h - ic}{x'}$	*k'*	*Rip*	*Ra*	*Rip* + *Ra*
0	—	—	—	—	—	0.000	0.500	0.500
5	2.87	8.12	0.09	1.53	0.0088	0.303	0.202	0.505
10	3.10	8.28	0.18	1.76	0.0079	0.315	0.183	0.498
15	3.26	8.34	0.33	1.83	0.0076	0.316	0.176	0.492
20	3.55	8.35	0.48	1.93	0.0075	0.331	0.175	0.506
30	3.85	8.35	0.80	1.93	0.0076	0.329	0.175	0.504
50	4.82	8.40	1.80	2.00	0.0073	0.326	0.168	0.494

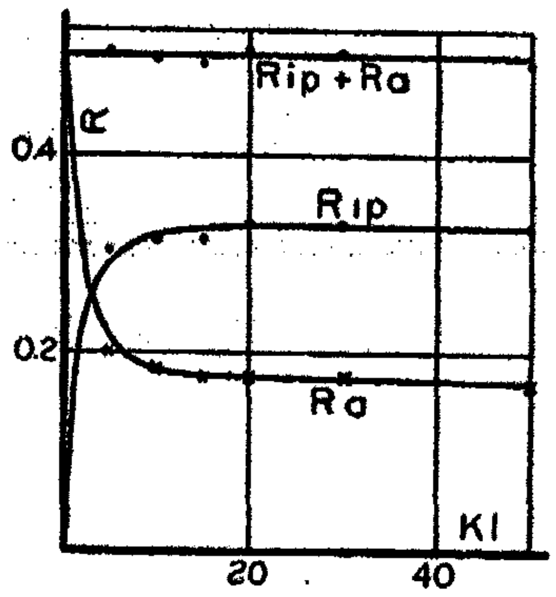

Fig. 3 (Cf. Table VIII)

TABLE IX

As, 9.94; *KI*, *n*.9.8; *Cr*, 20; *Ac*, 484; *t*, 10

n	*h*	$As - x'$	*ic*	$r = \frac{h - ic}{x'}$	*k'*	*Rip*	*Ra*	*Rip* + *Ra*
0	—	—	—	—	—	0.000	0.765	0.765
5	4.59	7.12	0.28	1.54	0.0183	0.487	0.306	0.793
10	5.06	7.32	0.56	1.72	0.0133	0.509	0.306	0.815
10	5.23	7.53	0.56	1.94	0.0121	0.525	0.279	0.804
15	5.54	7.58	0.84	2.00	0.0118	0.525	0.272	0.797
20	6.00	7.81	1.20	2.25	0.0105	0.531	0.242	0.773
20	5.67	7.57	1.20	1.89	0.0118	0.500	0.272	0.772
40	7.50	7.85	2.74	2.23	0.0103	0.526	0.237	0.763
40	7.44	7.50	2.74	1.93	0.0122	0.527	0.281	0.808
60	9.68	8.18	4.80	(2.83)	0.0085	0.531	0.196	0.727
60	9.13	7.77	4.80	1.83	0.0107	0.484	0.247	0.731

Note.—Thiosulphate solution 0.04 *N* was used in the measurements of this table to avoid a too great change in volume.

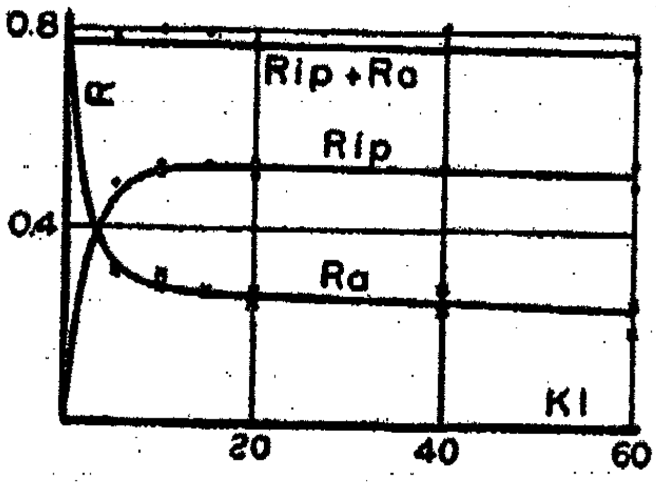

Fig. 4 (Cf. Table IX)

TABLE X

$t = 9.5$

As	10.00	20.00	10.00	10.00	10.00
KI	245	245	490	245	245
Cr	20	20	20	40	20
Ac	242	242	242	242	484
h	2.00	3.60	2.60	3.60	6.00
$As - x'$	9.15	18.30	9.18	8.50	7.70
x'	0.85	1.70	0.82	1.50	2.30
ic	0.35	0.35	0.88	0.68	1.40
$h - ic$	1.65	3.25	1.72	2.92	4.60
$r = \frac{h - ic}{x'}$	1.94	1.91	2.10	1.95	2.00
k'	0.0040	0.0040	0.0037	0.0074	0.0119
k	0.0114	0.0116	0.0114	0.0217	0.0318
$r = \frac{k - k'}{k}$	1.9	1.9	2.1	2.0	1.7

TABLE XI

As, 5.00; *KI*, 196; *Cr*, 20; *Ac*, 484

t	h	ic (calc.)	$h - ic$ (calc.)	t	h	ic (calc.)	$h - ic$ (calc.)
3	1.20	0.35	0.85	55	13.92	5.85	8.07
5	1.92	0.58	1.34	60	14.64	6.38	8.26
9	3.36	1.04	2.32	65	15.28	6.90	8.38
10	3.80	1.15	2.65	70	15.96	7.40	8.56
15	5.40	1.72	3.68	75	16.56	7.90	8.66
20	6.72	2.28	4.44	80	17.24	8.40	8.84
25	8.00	2.82	5.18	85	17.92	8.90	9.02
30	9.20	3.32	5.98	95	19.16	9.90	9.26
35	10.32	3.81	6.51	100	19.76	10.40	9.36
40	11.28	4.30	6.98	105	21.16	10.88	9.28
45	12.32	4.82	7.50	140	23.68	14.20	9.48
50	13.16	5.34	7.82	160	25.28	15.80	9.48

Note.—In making the iodine titrations 0.04 thiosulphate was used to avoid a too great change in volume.

Fig. 5 is plotted from the results of Table XI together with the values of x from Table XII of my paper on the oxidation of arsenious acid, and the values of x' from Table XVIII of the present paper.

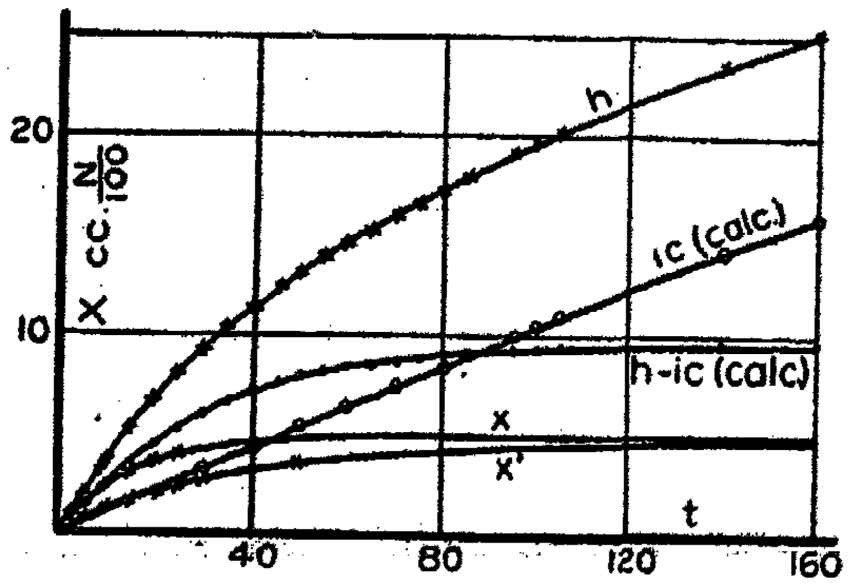

Fig. 5 (Cf. Table XI)

TABLE XII

As, 9.94; *KI*, 98; *Cr*, 20; *Ac*, 242

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
10	1.74	9.00	0.94	0.10	1.64	1.75	0.0043
10	1.93	9.16	0.78	0.10	1.88	(2.41)	(0.0036)
15	2.52	8.56	1.38	0.15	2.37	1.72	0.0043
20	3.40	8.23	1.71	0.20	3.20	1.87	0.0041
30	4.75	7.52	2.42	0.30	4.45	1.84	0.0040
						Avg. 1.80	*Avg.* 0.0041

TABLE XIII

As, 9.94; *KI*, 196; *Cr*, 20; *Ac*, 242

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
5	0.98	9.48	0.46	0.14	0.84	1.83	0.0041
10	1.88	9.00	0.94	0.27	1.61	1.71	0.0043
15	2.78	8.63	1.31	0.40	2.38	1.83	0.0041
15	2.74	8.55	1.39	0.40	2.34	1.69	0.0044
20	3.66	8.23	1.71	0.54	3.12	1.82	0.0041
25	4.40	7.84	2.10	0.67	3.73	1.78	0.0041
30	5.14	7.58	2.36	0.81	4.33	1.84	0.0039
						Avg. 1.80	*Avg.* 0.0041

TABLE XIV

As, 9.94; *KI*, 294; *Cr*, 20; *Ac*, 242

t	h	$As - x'$	ic	$r = \frac{h - ic}{x'}$	k'	x	x (*calc.*)	$h - ic + x'$
10	2.00	9.18	0.43	2.07	0.0035	—	—	—
10	2.17	9.12	0.43	2.12	0.0037	2.34	2.56	2.56
15	3.15	8.67	0.64	1.98	0.0040	3.28	3.75	3.78
15	3.11	8.74	0.64	2.08	0.0037	3.28	3.75	3.67
20	4.00	8.42	0.85	2.07	0.0036	3.99	4.76	4.67
30	5.67	7.74	1.28	2.00	0.0036	5.35	6.68	6.59
40	7.26	7.12	1.70	1.97	0.0038	6.50	8.86	8.38

Note.—The values of x of this table are taken from Table VIII of the paper on the oxidation of arsenious acid; x(*calc.*) is calculated as described in the foot-note on page 73.

TABLE XV

As, 5.00; *KI*, 196; *Cr*, 20; *Ac*, 242,

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
10	1.15	4.57	0.43	0.27	0.88	2.05	0.0039
15	1.62	4.40	0.60	0.40	1.22	2.03	0.0037
20	2.10	4.19	0.81	0.54	1.56	1.93	0.0038
25	2.58	4.04	0.96	0.67	1.91	1.99	0.0037
30	3.04	3.85	1.15	0.81	2.23	1.94	0.0038
						Avg. 1.99	*Avg.* 0.0038

TABLE XVI

As, 5.00; *KI*, 196; *Cr*, 40; *Ac*, 242

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
5	1.10	4.69	0.31	0.24	0.86	(2.77)	(0.0056)
10	2.02	4.24	0.76	0.48	1.54	2.03	0.0072
15	2.83	3.85	1.15	0.72	2.11	1.94	0.0076
20	3.63	3.58	1.42	0.96	2.67	1.88	0.0073
30	5.09	3.05	1.95	1.44	3.65	1.87	0.0072
						Avg. 1.93	*Avg.* 0.0073

TABLE XVII

As, 9.94; *KI*, 196; *Cr*, 40; *Ac*, 242

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
5	1.84	9.14	0.80	0.25	1.59	1.99	0.0073
10	3.46	8.44	1.50	0.50	2.96	1.97	0.0071
15	4.87	7.79	2.15	0.75	4.12	1.92	0.0071
						Avg. 1.95	*Avg.* 0.0072

TABLE XVIII

As, 5.00; *KI*, 196; *Cr*, 20; *Ac*, 484

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
5	1.90	4.30	0.70	0.60	1.30	1.86	(0.0131)
10	3.59	3.80	1.20	1.20	2.39	1.99	0.0119
15	5.16	3.37	1.63	1.80	3.36	2.06	0.0114
20	6.48	2.95	2.05	2.40	4.08	1.99	0.0115
						Avg. 1.98	*Avg.* 0.0116

TABLE XIX

As, 9.94; *KI*, 196; *Cr*, 20; *Ac*, 484

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
5	3.05	8.61	1.33	0.60	2.45	1.84	(0.0125)
10	5.67	7.57	2.37	1.20	4.47	1.89	0.0118
15	8.03	6.64	3.30	1.80	6.25	1.89	0.0117
						Avg. 1.87	*Avg.* 0.0118

TABLE XX

As, 9.94; *KI*, 196; *Cr*, 20; *Ac*, 242 (*Temperature 10° C*)

t	h	$As - x'$	x'	ic	$h - ic$	$r = \frac{h - ic}{x'}$	k'
10	2.55	8.90	1.04	0.35	2.20	2.1	0.0048
15	3.53	8.26	1.68	0.52	3.01	1.8	0.0054
20	4.56	7.84	2.10	0.70	3.86	1.8	0.0052
25	5.55	7.33	2.61	0.87	4.68	1.8	0.0055
						Avg. 1.9	*Avg.* 0.0054

TABLE XXI

KI, 98; *Cr*, 20; *Ac*, 242		*KI*, 196; *Cr*, 20; *Ac*, 242				*KI*, 294; *Cr*, 20; *Ac*, 242.			
ic	t	ic 0° C	t 0° C	ic 10° C	t 10° C	ic	t	ic	t
0.20	11	0.25	9.2	0.30	10	0.48	11	2.00	46
0.28	30	0.50	18.7	0.50	15	0.81	19	2.40	57
0.83	86	1.10	42	0.85	25	1.40	31	3.20	75
1.23	120	1.20	45.5	1.10	30	1.48	35	3.84	90

KI, 392; *Cr*, 20; *Ac*, 242.				*KI*, 245; *Cr*, 20; *Ac*, 242.				*KI*, 686; *Cr*, 20; *Ac*, 242			
ic	*t*	*ic*	*t*	*ic*	*t*	*ic*	*t*	*ic*	*t*	*ic*	*t*
0.24	4.2	0.87	14.5	0.31	9.5	1.33	38	0.40	2.5	2.00	13.5
0.30	5.0	1.00	17.0	0.50	14.0	1.68	47.5	0.80	5.5	3.55	26
0.58	10.0	1.21	20.2	0.67	19.0	2.00	57	1.10	7.5	3.75	27
0.80	13.2	1.20	20.7	1.02	28.5	2.64	76	1.45	10	4.10	30.4

KI, 196; *Cr*, 40; *Ac*, 242.		*KI*, 196; *Cr*, 20; *Ac*, 484.		*KI*, 490; *Cr*, 10; *Ac*, 242	
ic	*t*	*ic*	*t*	*ic*	*t*
0.27	5	0.60	5	0.29	6
0.44	7.5	1.20	10	0.52	13
0.57	10	1.82	15	0.66	17
0.78	15	2.43	20	0.76	19.5
1.03	20	3.00	25	0.95	25.5
1.75	35	3.60	31	1.19	32
1.98	40	4.20	35	1.42	40
2.40	50	—	—	—	—

TABLE XXII

Table XII r'	Table XIII r'	Table XIV r'	Table XV r'	Table XVI r'	Table XVII r'	Table XVIII r'	Table XIX r'
1.7	1.7	1.5	(2.6)	(2.8)	1.7	1.4	2.4
(2.5)	1.6	2.0	1.7	2.0	1.4	2.3	1.4
1.5	1.5	1.7	1.5	1.5	—	1.5	—
1.6	1.5	1.7	—	—	—	—	—
—	1.5	1.5	—	—	—	—	—
r''	r''	r''	r''	r''	r''	r''	r''
1.9	1.9	1.9	(2.5)	(2.7)	1.9	(3.5)	2.3
2.1	1.8	2.1	1.9	2.2	1.8	(3.0)	2.1
1.8	1.8	2.1	2.0	2.1	1.6	2.4	1.9
1.9	1.8	2.0	1.8	1.9	—	2.3	—
1.7	1.8	1.9	1.7	1.8	—	—	—
—	1.7	1.8	—	—	—	—	—
—	1 6	1.6	—	—	—	—	—

TABLE XXIII

Table	IV	V	VI	VII	VII	IX
As	10	10	10	20	10	10
KI	300+	150+	150+	300+	150+	150+
Cr	20	20	20	20	40	20
Ac	121	242	242	242	242	484
k	0.0044	0.0114	0.0114	0.0116	0.0217	0.0318
k'	0.0013	0.0037	0.0038	0.0037	0.0076	0.0112
$r+1=\frac{k}{k'}$	3.4	3.1	3.0	3.1	2.9	2.9
$r=\frac{k-k'}{k'}$	2.4	2.1	2.0	2.1	1.9	1.9

Table	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX
As	10	10	10	5	5	10	5	10
KI	98	196	294	196	196	196	196	196
Cr	20	20	20	20	40	40	20	20
Ac	242	242	242	242	242	242	484	484
k	0.0114	0.0114	0.0114	0.0114	0.0200	0.0217	0.0300	0.0318
k'	0.0041	0.0041	0.0037	0.0038	0.0073	0.0072	0.0116	0.0118
$r+1=\frac{k}{k'}$	2.8	2.8	3.1	3.0	3.0	3.0	2.6	2.7
$r=\frac{k-k'}{k'}$	1.8	1.8	2.1	2.0	2.0	2.0	1.6	1.7

Note.—See also Table X.

Discussion of the Experimental Data

The measurements recorded above together with those of my previous papers on the action of chromic acid on iodide[1] and arsenious acid[2] constitute all the experimental data on which the theory developed in the following pages is based. In order to collect all the facts together the generalizations deduced in the last-mentioned papers are quoted in the following paragraphs along with the general conclusions drawn from the tables of the present paper.

Effect of the Concentration of the Iodide

Tables IV–IX (in each of which t is constant) show that increasing the concentration of the iodide causes a gradual

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[1] See equation (1).

[2] See equation (2).

increase in the value of $h - ic$ (the iodine liberated due to the presence of the arsenious acid), and a gradual decrease in the value of x' (the arsenious acid oxidized in the presence of iodide), a maximum value of $h - ic$ and a minimum value of x' being reached when the concentration of the iodide is about fifteen times that of the arsenious acid, that is, when $KI = 15As$. Further increase in the concentration of the iodide does not appreciably affect these limiting values of $h - ic$ and x'.

When the iodide is in excess the value of the ratio, $\frac{h - ic}{x'}$, is 2.00 within the limit of the experimental error, no matter what the concentrations of the other reagents are. Thus in Tables XII–XX the average values of this ratio are, 1.80, 1.80, 2.04, 1.99, 1.93, 1.95, 1.98, 1.87 and 1.9 (at 10° *C*); in Table IV the values are, 2.06, 2.25, 2.07, 2.18, 2.04 and 1.94; and in Table X, 1.94, 1.91, 2.10, 1.95 and 2.00. Additional evidence is afforded by the measurements of Tables V–IX (Figs. 1–4) and the curves of Fig. 5.[1] The slight deviations in both directions, from the number 2.00 must be ascribed to experimental error, for the ratio in question is the quotient of two small numbers, each of which is the difference between two small readings of the burette, and owing to the nature of the method of analysis it usually happens that when one of these numbers (say $h - ic$) is too small the other (x') is too large.

Tables V–IX and the curves of Figs. 1–4, show that addition of potassium iodide lessens the rate of oxidation of arsenious acid by chromic acid, the retardation increasing with the concentration of the iodide up to a certain point from which on (Ra, when $KI = 0$, being equal to Rac),

$$Ra, (KI\ excess) = \frac{1}{3} \cdot Rac. \qquad (7)$$

Additional evidence of relation (7) is afforded by Table XXIII in which k is seen to closely equal 3 k'.

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[1] The curve, $h - ic$, approaches the line, $X = 10 = 2As$, asymptotically, and simultaneously the curve, x', approaches the line, $X = 5 = As$.

Tables V–IX and Figs. 1–4 further show that the rate at which iodine is liberated in solutions containing arsenious and chromic acids, after correcting for the direct oxidation of iodide by chromic acid, increases with the concentration of the iodide up to a certain point from which on,

$$Rip,\ (KI\ excess) = 2Ra,\ (KI\ excess) = \frac{2}{3}\cdot Rac. \qquad (8)$$

The last columns of Tables V–IX and the upper curves of Figs. 1–4, show that the sum, $Ra + Rip$, that is, the rate of reduction of chromic acid[1] after correcting for the direct action of the chromic acid on the iodide, is the same for all concentrations of iodide from zero up, or,

$$Ra + Ri - Ric = Rac \qquad (9)$$

that is,

$$Ra + Rip = Rac. \qquad (10)$$

Thus M of equation (5) is $-Rip$.

In the absence of arsenious acid the rate of oxidation of iodide by chromic acid is connected with the concentration of the iodide by a quadratic relation (see equation 1).

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[1] On comparing the above Tables of results with those on the oxidation of arsenious acid in the absence of iodide, it will be noticed, however, that for any fixed interval of time the total oxidation is greater in the presence than in the absence of the iodide, that is, $h - ic + x'$ is greater than x for a fixed time. This is due to the fact that in the former case the concentration of the arsenious acid (on which the $h - ic$ reading depends) does not fall off so rapidly as in the latter case. If the average concentration of the arsenious acid had remained the same as it did in the experiments in which iodide was present, we would have for the value of x:

$$x(calc) = x.\frac{As.t - \int_0^t x'.dt}{As.t - \int_0^t x.dt};$$

and as shown by Table XIV, $x(calc)$ is equal to the experimentally determined value, $h - ic + x'$. For the method of computation, see Jour. Phys. Chem., 10, 423 (1906).

Effect of the Concentration of the Arsenious Acid

In the absence of iodide the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid. This suggested computing the constant of the "first order" in the tables of the present paper. The constancy of k' in each of the Tables XII–XX, and more particularly the fact that changing the concentration of the arsenious acid in these tables as well as in Tables V, VI and VII, does not effect the value of k', shows that in the presence as well as in the absence of iodide the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid.

Since in the presence of excess of iodide, $h - ic = 2x'$ (see page 72), the rate Rip is twice the rate Ra, (*KIexcess*), and is therefore, like the latter, proportional to the concentration of the arsenious acid. The fact that $Rip + Ra = Rac$ for all concentrations of iodide from zero up, is also proof that Rip is proportional to the first power of the concentration of the arsenious acid.

Effect of the Concentration of the Bichromate

Comparison of Tables V and VIII, XV and XVI, XIII and XVII, shows that doubling the concentration of the bichromate almost doubles the value of k', that is, almost doubles the rate of oxidation of arsenious acid, Ra, when iodide is present; or the rate Ra is proportional to about the 0.9*th* power of the concentration of the bichromate.

In the absence of iodide the same relation was found to hold; that is, Rac is proportional to the 0.9*th* power of the concentration of the bichromate.

Since in the presence of excess of iodide $h - ic = 2x'$, the rate Rip is twice the rate Ra, (*KI excess*), and is therefore like the latter proportional to the same (0.9*th*) power of the concentration of the bichromate; and the fact that $Rip + Ra = Rac$ is also proof that the rate Rip is proportional to the 0.9*th* power of the concentration of the bichromate.

In the absence of arsenious acid the rate of oxidation of iodide (*Ric*) was found to be proportional to a power of the bichromate slightly less than the first (except when very dilute solutions of bichromate were employed, when the power was the first exactly). In the above tables *ic* is scarcely doubled for a fixed interval by doubling the concentration of the bichromate.

Thus the rates *Rac Ra*, *Rip* and *Ric* are each proportional to a power of the concentration of the bichromate slightly less than the first.

Effect of the Concentration of the Sulphuric Acid

Doubling the concentration of the sulphuric acid nearly trebles the rates *Ra* and *Rip* in Tables V and IX, and the constants k' in Tables XV and XVIII, XIII and XIX. Thus the rates *Ra* and *Rip* are proportional to the 1.4*th* power of the concentration of the sulphuric acid.

The rate of oxidation of arsenious acid in the absence of iodide is also proportional to the 1.4*th* power of the concentration of the sulphuric acid. This unusual fractional power is thus common to the kinetic formulae for the rates *Rac*, *Ra* and *Rip*, while the rate of oxidation of iodide in the absence of arsenious acid (*Ric*) is proportional to the square of the concentration of the sulphuric acid.

Effect of the Temperature

Changing the temperature from 0° *C* to 10° *C* causes a change in the constant k' of 29 *percent* (0.0041 to 0.0053, Tables XIII and XX). Since in these tables $h - ic = 2x'$, the rate *Rip* is also increased by the same amount.

Changing the temperature has practically the same effect on the rate of oxidation of arsenious acid in the absence of iodide (*Rac*); the experiments showed that changing the temperature from 0° *C* to 10° *C* causes a change of 26 *percent* in the constant k (0.0114 to 0.0144).

Thus the rates *Rac*, *Ra* and *Rip* have the same unusually low temperature coefficient, *viz.*, less than 1.3.

The temperature coefficient of the rate of oxidation of iodide by chromic acid is also very low, *viz.*, 1.4.

Short Statement of the Results

The following are the general results of the experiments:

$$Rac = k.As\,(Cr)^{0.9}.(Ac)^{1.4} \qquad (11)$$

$$Ra = k'.As\,(Cr)^{0.9}.(Ac)^{1.4} \qquad (12)$$

$$Ric = K.(m.KI + n.(KI)^2).Cr.(Ac)^2,$$

Compare equation (1)

$$Ri - Ric = Rip = k''.As.(Cr)^{0.9}.(Ac)^{1.4} \qquad (13)$$

and $Rac = Ra + Rip.$

The constants k' and k'' depend on the amount of iodide present: as the concentration of the iodide increases, k' decreases from k, for $KI = 0$, to $\frac{k}{3}$, for KI, *excess*; and simultaneously k'' increases from 0 to $2k'$ or $2\frac{k}{3}$.

When the iodide is in excess the ratio $\frac{h - ic}{x'}$ is equal to 2.

The rates *Rac*, *Ra*, (*KI excess*) and *Rip*, (*KI excess*) have the same unusually low temperature coefficient, *viz.*, less than 1.3 (from 0° *C* to 10° *C*); the temperature coefficient for the rate *Ric* is about 1.4.

THEORETICAL PART

The above results show that:

(*a*) The rate of reduction of chromic acid in solutions containing arsenious acid and iodide is equal to the sum of the rates of reduction of chromic acid by arsenious acid and by iodide taken separately, or, in other words, the acceleration of the rate of oxidation of iodide is just equal to the retardation in the rate of oxidation of arsenious acid.

(*b*) The effects of temperature and the concentrations of the various reagents are the same for the three rates:

(*i*) Oxidation of arsenious acid by chromic acid in the absence of iodide (*Rac*).

(*ii*) Oxidation of arsenious acid by chromic acid in the presence of excess of iodide (*Ra*, *KI excess*).

(*iii*) Oxidation of iodide in the presence of arsenious acid, when the iodide is in excess (*Rip*, *KI excess*).

(*c*) The ratio *Ra*:*Rip* is independent of the concentrations of the bichromate and sulphuric acid for all concentrations of iodide.

(*d*) In the absence of arsenious acid the rate of oxidation of iodide is proportional to powers of the concentrations of the reagents somewhat different from those of rates (*i*), (*ii*) and (*iii*) of (*b*).

These facts suggest the theory of the formation of a primary oxide when chromic acid acts on arsenious acid, and the succeeding paragraphs will show that the above experimental results may be satisfactorily accounted for by the following assumptions.

Assumptions

(*a*) That arsenious acid acting on chromic acid forms slowly a primary oxide.

(*b*) That this oxide is completely and instantaneously reduced by either arsenious acid or iodide.

(*c*) That the fractions of the primary oxide reduced by arsenious acid and iodide respectively, in solutions containing both, depend on their relative concentrations; when the iodide is in large excess the amount of the primary oxide reduced by the arsenious acid is negligible.

The primary oxide may be one of the following:[1]

(1) *A peroxide of arsenic represented by the formula,* As_2O_9, *or one of its hydrates, e. g.,* H_3AsO_6, the reactions being as follows:

(*i*) Slow formation of the peroxide,

$$As_2O_3 + 2K_2Cr_2O_7 + 3H_2SO_4 = As_2O_9 + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 3H_2O;$$

or,

$$\overset{---}{AsO_3} + \overset{--}{Cr_2O_7} + 2\overset{+}{H} = \overset{---}{AsO_6} + Cr_2O_3 + H_2O. \qquad (14)$$

(*ii*) Rapid reduction by arsenious acid or iodide,

$$As_2O_3 + 2As_2O_3 = 3As_2O_5;\ \text{or,}\ \overset{---}{AsO_6} + 2\overset{---}{AsO_3} = 3\overset{---}{AsO_4} \qquad (15)$$

and

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[1] For methods of determining the degree of oxidation of the primary oxide, see p. 83.

$As_2O_9 + 8HI = As_2O_5 + 4I_2 + 4H_2O$; or,

$$\overset{---}{AsO_6} + 4\overset{-}{I} + 4\overset{+}{H} = \overset{---}{AsO_4} + 2I_2 + 2H_2O. \qquad (16)$$

(2) *An intermediate oxide*[1] *of chromium of the formula* Cr_2O_5, *or one of its hydrates, e. g.,* $H_2Cr_2O_6$, the reactions being as follows:

(*i*) Slow formation of the intermediate oxide (peroxide),

$As_2O_3 + 2K_2Cr_2O_7 = As_2O_5 + 2K_2Cr_2O_6$; *i. e.*,

$$As_2O_3 + 4CrO_3 = As_2O_5 + 2Cr_2O_5;$$

or,

$$\overset{---}{AsO_3} + \overset{--}{Cr_2O_7} = \overset{---}{AsO_4} + \overset{--}{Cr_2O_6}. \qquad (14a)$$

(*ii*) Rapid reduction by arsenious acid or iodide,

$Cr_2O_5 + As_2O_3 = Cr_2O_3 + As_2O_5$; or,

$$\overset{--}{Cr_2O_6} + 2\overset{---}{AsO_3} = \overset{--}{Cr_2O_4} + 2\overset{---}{AsO_4} \qquad (15a)$$

and

$Cr_2O_5 + 4HI = Cr_2O_3 + 2I_2 + 2H_2O$; or,

$$\overset{--}{Cr_2O_6} + 4\overset{-}{I} + 4\overset{+}{H} = \overset{--}{Cr_2O_4} + 2I_2 + 2H_2O \qquad (16a)$$

(3) *A mixed peroxide of arsenic and chromium of the same degree of oxidation as* (1) *and* (2).

Development of the Theory

It has been found convenient to introduce the symbol *Rp*, for the rate of formation of the hypothetical oxide, according to equations (14) or (14*a*), the unit being 0.25×10^{-5} formula-weights if the oxide As_2O_9 be assumed, or 0.5×10^{-5} formula-weights if the oxide Cr_2O_5 be assumed, and the symbol *Rap* for the rate of oxidation of arsenious acid by peroxide, according to equations (15) and (15*a*). *Rip* has already been introduced (page 57): it may now be defined as the rate of oxidation of iodide by peroxide, as in equations (16) and (16*a*).

If the solution contains chromic and arsenious acids only, then for every unit of arsenious acid oxidized in the first stage

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[1] Although the formula Cr_2O_5 contains less oxygen than the formula CrO_3 I shall speak of it as a peroxide of chromium.

(formation of peroxide, equations (14) and (14*a*)) two more are oxidized in the second stage (reduction of peroxide, equations (15) and (15*a*)), the final result being the formation of three units of arsenic acid. As, by hypothesis, the second stage takes place instantaneously, the time required for the formation of this amount of arsenic acid is practically that involved in the formation of a unit of peroxide, or,

$$Rp = \frac{1}{3} \cdot Rac. \tag{17}$$

If, however, the solution contains iodide as well as arsenious acid, both will be oxidized on the reduction of the peroxide, the total quantity of iodine and arsenic acid formed in the second stage amounting to two units in all. As before, for one unit of peroxide formed and reduced three units of arsenic acid and iodine taken together are generated, and

$$Rp = \frac{1}{3}(Ra + Rip). \tag{18}$$

Whether iodide be present or not, however, for every unit of peroxide formed one unit of arsenious acid must be oxidized to arsenic acid;[1] any additional arsenic acid formed is due to the oxidation of arsenious acid by the peroxide. Thus,

$$Ra = Rp + Rap \tag{19}$$

It has been pointed out in the paragraph preceding equation (18), that two units of iodine and arsenic acid counted together are formed by the reduction of one unit of peroxide; the share of these two units, however, that falls to each, depends upon the relative concentrations of the iodide and arsenious acid. As the concentration of the iodide is increased, the reaction represented by equation (15) or (15*a*), falls more and more into the background until in the presence of large excess of iodide,

$$Rap, (KI\ excess) = 0 \tag{20}$$

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[1] If the peroxide be Cr_2O_5, this unit of arsenic acid is formed in the first stage, equation (14*a*); if As_2O_9, from the peroxide on reduction, equations (15) and (16).

whence by equation (19),

$$Ra, (KI\ excess) = Rp \qquad (21)$$

and by equation (18),

$$Rip, (KI\ excess) = 2\,Rp. \qquad (22)$$

Comparison of the Theory with Results of the Experiments

By eliminating the hypothetical Rp from equations (17) to (22) the relations deduced from the assumptions of page 77, may be compared with the experimental results.

The elimination gives:

From equations (17) and (18),

$$Ra + Rip = Rac,$$

which is the same as equation (10); from equations (17) and (21),

$$Ra, (KI\ excess) = \frac{1}{3} \cdot Rac,$$

which is the same as equation (7); also from equations (21) and (22),

$$Rip, (KI\ excess) = 2Ra, (KI\ excess) = \frac{2}{3} \cdot Rac$$

which is the same as equation (8).

That is to say, the main quantitative relations between the rates of oxidation of acceptor and inductor are in accordance with the postulates of the theory set forth on page 77. These relations are clearly shown in Fig. 6, which is in obvious agreement with Figs. 1 to 5, where the curves were plotted from the experimental data.

Further Development of the Theory

A graphic representation of the theoretical relations is given in Fig. 6, where the dotted line shows the general form of the Rip curve for increasing concentration of iodide.

Conclusions as to the relative *effects of the reagents on the rates, Rap and Rip* might be drawn from the form of the *Rap* and *Rip* curves before they become horizontal; unfortunately, the experimental errors incident to the method of analysis are greatest when the concentration of the iodide is small and this renders any detailed study of the curves useless.

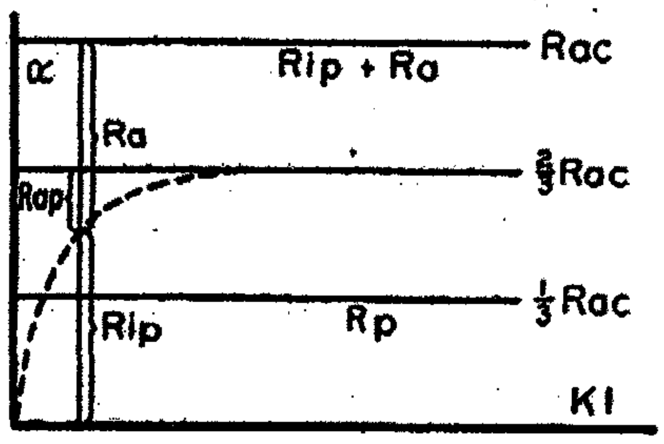

Fig. 6

However, from Tables V and VI it appears that in solutions containing *As* 10, *Cr* 20, *Ac* 242, the rates *Rip* and *Rap* are equal when *KI* is about 25. If *Rip* were proportional to the first power of the concentration of the iodide then for $KI = 150$, $\frac{Rip}{Rap}$ would be 6; and if to the second power of the iodide, 36. The first is certainly far too low to be in agreement with the results while the second is not.

Again, comparison of Tables VI and VII shows that when the concentrations of both the arsenic and iodide are doubled the ratio $\frac{Rip}{Rap}$ is increased; or in other words the arsenious acid has less effect on the rate *Rap* than the iodide has on the rate *Rip*; if *Rip* be set proportional to the second power of the concentration of the iodide (in accordance with the conclusion reached in last paragraph), then *Rap* must be set proportional to some lower power of the concentration of the arsenious acid—perhaps the first.

Nature of the Primary Oxide

As has been shown on page 77 the experimental results of the present paper accord equally well with either of the following assumptions:

(1) A peroxide of arsenic.

(2) A peroxide of chromium.

(3) A complex peroxide of chromium and arsenic.

If one is to choose between these assumptions, additional evidence is necessary. Such evidence may possibly be obtained in the following ways:

(*a*) *By comparison of the powers of the reagents corresponding to the various hypotheses, with those obtained by experiment*—as suggested by Van't Hoff.

Equations (14) and (14*a*), corresponding to the assumptions of a peroxide of arsenic and one of chromium respectively both agree with the fact that the rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid and to the 0.9*th* power of the concentration of the bichromate (regarding the chromic acid as not being completely dissociated); and equation (14), together with the view that an ion[1] of arsenious acid reacts with chromic acid, satisfactorily accounts for the effect of the sulphuric acid concentration, while equation (14*a*) offers no explanation of the effect of the concentration of the acid. We thus have an argument in favor of assumption (1) or (3), and against assumption (2).

(*b*) *By "systematic variation of the three reagents,"* as suggested by Luther and Schilow.[2]

Many qualitative experiments were made substituting for chromic acid other oxidizing agents, such as, H_2O_2, $K_2S_2O_8$, $KBrO_3$, $KClO_3$, $KClO_4$, using starch as indicator for the iodine liberated, and keeping the concentrations of the iodide and sulphuric acid sufficiently large to prevent the arsenious acid from acting on the liberated iodine. In no case was the oxidation of iodide found to be accelerated by the addition of arsenious acid. Thus we have evidence that the primary oxide is a compound of chromium (assumptions (2) and (3)).

Also when certain reducing agents are substituted for

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[1] See the paper on the rate of oxidation of arsenious acid by chromic acid.

[2] Zeit. phys. Chem. 46, 816 (1903).

arsenious acid the rate of oxidation of iodide by chromic acid is accelerated; this is noticeable in the case of some organic acids as tartaric and oxalic acids[1] and in the case of ferrous salts[2] in this last case, however, the acceleration cannot be ascribed to the formation of a peroxide, as Miss Benson has shown. So too, in any given case, to account for the acceleration, different types of intermediate compounds may be assumed in the absence of definite knowledge of the kinetics of the reactions, and it is in this particular that the method suggested by Luther and Schilow fails.

Summing up the evidence brought forward by the application of the above two methods, (*a*) and (*b*), we find arguments for and against the assumptions that the primary oxide is one of arsenic or one of chromium, (1) and (2), but none contrary to the view that the primary product is a complex peroxide of arsenic and chromium (3).

Determination of the Degree of Oxidation of a Hypothetical Primary Oxide

The problem of determining the degree of oxidation of an assumed primary oxide is of general interest, and some methods of doing so will now be given, using the present case in illustration.

(*a*) *From the ratio of the quantities of acceptor and inductor oxidized in any interval (induction factor), when the concentration of the acceptor is so great that this ratio has become constant* (as employed by Manchot, Luther and Schilow and others).

Let the composition of the peroxide be represented by the general formula, As_2O_{5+2r}. Then the reaction between the peroxide and arsenious acid must be written:

$$As_2O_{5+2r} + rAs_2O_3 = (r+1)As_2O_5 \qquad (23)$$

and that between the peroxide and the iodide,

$$As_2O_{5+2r} + 4rHI = 2rI_2 + As_2O_5 + 2rH_2O. \qquad (24)$$

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[1] I have made some measurements on this subject, and these I hope soon to complete and publish.

[2] Manchot: loc. cit.; Miss C. C. Benson: loc. cit.

When the iodide is in excess reaction (23) is negligible, and hence for every equivalent of arsenic acid formed r equivalents of iodine are liberated, or,

$$\frac{h-ic}{x'}\ (KI\ excess) = r, \qquad (25)$$

where $h-ic$ and x' are the amounts of iodide and of arsenious acid oxidized in the same time (both quantities being expressed in *cc* of 0.01 N solution) see page 61.

As shown on page 72, $r=2$, and hence the peroxide is As_2O_9.

If a primary oxide of chromium be assumed the treatment is similar. Regarding CrO_3 and Cr_2O_3 as the initial and final oxides in the reduction of chromic acid, let the general formula of the peroxide be Cr_2O_{3+s}. Then for the formation of this oxide we have:

$$2CrO_3 + \frac{3-s}{2} As_2O_3 = Cr_2O_{3+s} + \frac{3-s}{2} As_2O_5; \qquad (26)$$

for the oxidation of arsenious acid by peroxide,

$$Cr_2O_{3+s} + \frac{s}{2} As_2O_3 = Cr_2O_3 + \frac{s}{2} As_2O_5; \qquad (27)$$

and for the reaction between peroxide and iodide,

$$Cr_2O_{3+s} + 2sHI = Cr_2O_3 + sI_2. \qquad (28)$$

When the iodide is in excess, reaction (27) is negligible, hence,

$$\frac{h-ic}{x'}\ (KI\ excess) = \frac{s}{3-s}. \qquad (29)$$

As shown on page 72 the value of the ratio $(h-ic):x'$, when the iodide is in excess, is 2, hence $s=2$, and the formula of the peroxide is Cr_2O_5.

(*b*) *From the ratio of the rates of oxidation of the inductor in the absence of the acceptor to that in the presence of excess of the acceptor.*

If the peroxide be one of arsenic, As_2O_{5+2r}, we have from equations (23) and (24):

$$\frac{Rac}{Ra_1\,(KI\ excess)} = r+1, \text{ or, } \frac{Rac - Ra_1\,(KI\ excess)}{Ra_1\,(KI\ excess)} = r. \qquad (30)$$

Hence from the definitions of k and k' given on page 62.

$$\frac{k}{k'} = r + 1, \text{ or, } \frac{k - k'}{k'} = r. \tag{31}$$

Or if a peroxide of chromium, Cr_2O_{3+s}, be assumed, we have from equations (26) and (27):

$$\frac{Rac}{Ra, (KI\ excess)} = \frac{3}{3-s} \text{ or, } \frac{Rac - Ra, (KI\ excess)}{Ra, (KI\ excess)} = \frac{s}{3-s} \tag{32}$$

hence also,

$$\frac{k}{k'} = \frac{3}{3-s}, \text{ or, } \frac{k-k'}{k'} = \frac{s}{3-s}. \tag{33}$$

In Tables V–IX it is seen that the value of the ratio $Rac : Ra$, $(KI\ excess)$ is very close to 3; hence from equation (30), $r = 2$, and from equation (32), $s = 2$. In the summary, Table XXIII, the value of the ratio, $k : k'$ is seen to be 3; hence again r and s have the value 2 (equations (31) and (33)). Thus the formula of the peroxide must be written, As_2O_5 or Cr_2O_5.

(*c*) ***From the amounts of the acceptor oxidized in known intervals, assuming that the law of the oxidation of the inductor in the absence of acceptor is known.***

It is generally very difficult to determine the amounts of each of two reducing agents in the presence of an oxidizing agent, and quite often impossible to find accurately the induction factor (when the reaction is over); in such cases if it is possible to make near the beginning of the reaction a few measurements of the amount of acceptor oxidized when this reagent is in excess, the degree of oxidation of the primary product may be calculated by the following methods.

The rate of oxidation of arsenious acid by chromic acid is proportional to the first power of the concentration of the arsenious acid; thus using the symbols defined on page 62, we have,

$$k = \frac{1}{t} \cdot \log_{10} \frac{As}{As - x} \tag{34}$$

and when the acceptor is present in excess,

$$k' = \frac{1}{t} \cdot \log_{10} \frac{As}{As - x'}. \tag{35}$$

When the acceptor is in excess, we have, assuming the formula of the peroxide to be As_2O_{5+2r}

$$\frac{h-ic}{x'}\,(KI\ \text{excess}) = r$$

whence, writing a for $h - ic$ to economize space,

$$x' = \frac{a}{r}$$

and we have,

$$\frac{1}{t_1}.\log_{10}\frac{As}{As-\frac{a_1}{r}} = \frac{1}{t_2}.\log_{10}\frac{As}{As-\frac{a_2}{r}} = \frac{1}{t_3}.\log_{10}\frac{As}{As-\frac{a_3}{r}} = \ldots \qquad (36)$$

where t_1, a_1; t_2, a_2; t_3, a_3; etc., are experimentally determined values of t and a.

(i) This equation may be solved for r, most simply by testing in turn, the numbers, 1, 2, etc.

If the rate of oxidation of the inductor had been proportional to any other power of its concentration than the first, an equation somewhat similar to (36) could be written, to be solved for r.

(ii) If it be assumed that the value of k in equation (34) be known, r can be found from the following equation (which is obtained from (31) and (33)):

$$k' = \frac{k}{r+1} = \frac{1}{t}.\log_{10}\frac{As}{As-\frac{a}{r}} \qquad (37)$$

by putting it in the form,

$$\frac{2.30\,k}{r+1} = -\frac{1}{t}.\log_e\left(1-\frac{a}{r.As}\right)$$
$$= \frac{1}{t}\left\{\frac{a}{r.As}+\frac{1}{2}\left(\frac{a}{r.As}\right)^2+\frac{1}{3}\left(\frac{a}{r.As}\right)^3+\ldots\right\}. \qquad (38)$$

If the fraction $\frac{a}{r.As}$ be very small we have as a first approximation,

$$\frac{2.30\,k}{r+1} = \frac{1}{t}.\frac{a}{r.As} \qquad (39)$$

and since $a = h - ic$ we have,

$$r = \frac{0.4343(h - ic)}{k.t.As - 0.4343(h - ic)} = r' \text{ of Table XXII.} \qquad (40)$$

Using this approximation the values of r' given in Table XXII were calculated. It will be noticed that the value of r' diminishes as a (*i. e.*, $h - ic$) increases, because the neglected terms of equation (38) become larger and larger. Hence a closer approximation is to be desired:

$$\frac{2.30\,k}{r+1} = \frac{1}{t}\left(\frac{a}{r.As} + \frac{1}{t}\left(\frac{a}{r.As}\right)^2\right) \qquad (41)$$

and hence,

$$r = \frac{a}{4.As} \cdot \frac{\sqrt{(a+2.As)^2 + 8.As(2.30k.t.As - a)} + (a + 2.As)}{2.30k.t.As - a} = r''$$

of Table XXII. (42)

The values of r'' in Table XXII were calculated by means of formula (42).

These values do not fall off so noticeably on increasing the value of a (*i. e.*, $h - ic$) as do the values of r' in the same table. Both r' and r'' point to the number 2 as the value of r. A slight error in k or a will cause a considerable error in the value of r''; this is noticeable in initial values of some of the tables.

(*iii*) The value of r may be found also in the following manner:

We have

$$\frac{dx'}{dt} = 2.30k'(As - x'),$$

and since $a = r.x'$, it follows that

$$\frac{da}{dt} = 2.30k'(r.As - a), \qquad (43)$$

whence,

$$a = 2.30k'\int_0^t (r.As - a).dt = 2.30k'\left(r.As.t - \int_0^t a.dt\right),$$

and therefore,

$$\frac{a}{t} = 2.30k'\left(r.As - \frac{1}{t}\int_0^t a.dt\right). \qquad (44)$$

Now the values of $\int_0^t a.dt$ can be found easily and accurately from the plotted curve, a, t, and hence the values of k' and of $r.As$ can be found by means of equation (44) for any two pairs of values of a and t.
Thus, we have

$$\frac{r.As}{As} = \frac{h-ic}{x'}\ (\text{for } t = \infty) = r\text{[1]}, \qquad (45)$$

If in addition the value of k of equation (34) be known, the value of r can be determined from the above calculated value of k' as in equation (31).

SUMMARY

A method of analysis, which may be of use in the study of other complicated cases of induced oxidation, is described.

Addition of potassium iodide lessens the rate of oxidation of arsenious acid by chromic acid, the retardation increasing with the concentration of the iodide up to a certain point from which on the rate of oxidation of arsenious acid is equal to one-third the rate when no iodide is present; or symbolically,

$$Ra\,(KI\ excess) = \frac{1}{3} . Rac.$$

The rate at which iodine is liberated in solutions containing arsenious acid, iodide and chromic acid, after correcting for the direct oxidation of iodide by chromic acid, in-

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[1] As an example of this method the following table calculated from the data of Table XI, by methods described in Jour. Phys. Chem., 10, 423 (1906) is given.

	t	$\frac{1}{t}\int_0^t a.dt$	$r.As$
(1)	20	2.55	—
(2)	25	2.96	—
(3)	30	3.42	10.0, from (1) and (3)
(4)	35	3.83	10.4, from (2) and (4)
(5)	40	4.19	10.4, from (3) and (5)

In this table $a = h - ic$ (*calc.*) of Table XI. The value of As is 5.00 and hence $r = 2$ very closely.

creases with the concentration of the iodide up to a certain point from which on the rate of liberation of iodine is twice the rate of oxidation of arsenious acid (expressing both iodide and arsenious acid in equivalents), or,

$$Rip = 2Ra, \ (KI\ excess).$$

The rate of reduction of chromic acid (after correcting for the direct action of the iodide) is the same for all concentrations of iodide from zero up, or,

$$Ra + Ri - Ric = Ra + Rip = Rac.$$

Expressing each of the three rates, *Rac* (rate of oxidation of arsenious acid by chromic acid in the absence of iodide), *Ra* (rate of oxidation of arsenious acid in the presence of iodide) and *Rip* (rate of liberation of iodine after correcting for the direct action of the chromic acid on iodide), in terms of the concentrations of the reagents, we have

$$Rac = k.As.(Cr)^{0.9}.(Ac)^{1.4}$$
$$Ra = k'.As.(Cr)^{0.9}.(Ac)^{1.4}$$
$$Rip = k''.As.(Cr)^{0.9}.(Ac)^{1.4}$$

where k' and k'' depend on the concentration of the iodide. When the iodide is in excess,

$$k = 3k' = \frac{3}{2}.k''.$$

The effect of the temperature on the rates *Rac*, *Ra* (*KI excess*) and *Rip*, (*KI excess*) is the same, the coefficient being unusually small (somewhat less than 1.3).

The results may be accounted for by assuming:

(*a*) *That arsenious acid acting on chromic acid forms slowly a primary oxide.*

(*b*) *That this oxide is completely and instantaneously reduced by either arsenious acid or iodide.*

(*c*) *That the fractions of the primary oxide reduced by arsenious acid and iodide respectively, in solutions containing both, depend on their relative concentrations*: when the iodide is in large excess the amount of the primary oxide reduced by the arsenious acid is negligible.

The primary oxide may be one of the following:

(1) A peroxide of arsenic represented by the formula, As_2O_6, or one of its hydrates, *e. g.*, H_3AsO_6.

(2) An intermediate oxide of chromium of the formula, Cr_2O_6, or one of its hydrates, *e. g.*, $H_2Cr_2O_6$.

(3) A complex peroxide of arsenic and chromium of the same degree of oxidation as (1) and (2).

Other evidence is in support of the view that the peroxide is one of arsenic; and still other evidence favors the assumption that the primary oxide is a compound of chromium; ***the view that the primary oxide is a complex peroxide of arsenic and chromium is, however, in best accord with all the facts.***

Methods are described by which the degree of oxidation of a hypothetical primary oxide may be determined.

The above experimental work was completed in the Chemical Laboratory of the University of Toronto in May, 1905.

I wish here to express my thanks to Professor W. Lash Miller at whose suggestion this research was undertaken, for his kind advice and assistance throughout.

CONTENTS

NEW BOOKS

Theorien der Chemie. *Nach Vorlesungen gehalten an der Universität von Kalifornien zu Berkeley. By Svante Arrhenius. Mit Unterstützung des Verfassers aus dem englischen Manuskript übersetzt von Alexis Finkelstein. 17 × 24 cm; pp. vii + 177. Leipzig: Akademische Verlagsgesellschaft, 1906.*—These lectures were given at the University of California during the summer of 1904. It is the author's belief that the theory of osmotic pressure and the electrolytic dissociation theory are the normal developments of the work of Lavoisier, Dalton, Faraday, Bunsen and Helmholtz. This is a point of view which will be shared by every one who takes the trouble to consider the historical development. Van't Hoff's relation between chemical affinity and electromotive force is avowedly a special case of Helmholtz's formula for the free energy. The theory of osmotic pressure was the normal outcome of the work of v. Babo, Wüllner, Pfeffer and Raoult. The electrolytic dissociation theory was made possible by the work of Faraday, Daniell, Hittorf and Kohlrausch. What has made the development of physical chemistry so remarkable during the last twenty years has been the simultaneous development of the theories of osmotic pressure and electrolytic pressure, the re-appearance of the mass law—and the wonderful leadership of Ostwald.

The fact that Arrhenius thinks and works in terms of the atomic theory of course makes the connection between the past and the present more close than it might seem if he shared all of Ostwald's views. *Wilder D. Bancroft*

Theorie der Verdampfung und Verflüssigung von Gemischen und der fraktionierten Destillation. *By J. P. Kuenen. (Handbuch der angewandten physikalischen Chemie. Herausgegeben von Prof. Dr. G. Bredig). Band IV. 16 × 25 cm; pp. xii + 244. Leipzig: Johann Ambrosius Barth, 1906. Price: paper, 12 marks; bound, 13 marks.*—This treatise on the theory of the evaporation and condensation of mixtures, and on the theory and practice of fractional distillation, is a volume of Bredig's handbook of applied physical chemistry. The topics of its nine chapters are: experimental methods, graphic representation, theory of mixtures, coexistent liquid and vapor, special problems, partially miscible liquids, solid phases, distillation, ternary systems. The bulk of the space is devoted to binary mixtures in coexistent fluid phases. Solid phases, especially as concerns their behavior in the critical region, and ternary mixtures are studied in one chapter each. Very properly, the special case of dilute solutions is only cursorily considered. Distillation under constant pressure is extensively gone into. A bibliography is appended to the discussion of each topic. It is a good feature of Kuenen's treatment that all general thermodynamic deductions are kept distinct from conditions involving the form of van der Waals's characteristic equation. The book, as was to be anticipated, is a very interesting and instructive summary of the recent advances in its field, and one that no physical chemist can afford to neglect. It is appropriately dedicated to H. Kamerlingh Onnes. *J. E. Trevor*

A History of Chemistry *from Earliest Times to the Present Day. Being also an Introduction to the Study of the Science. By Ernst von Meyer. Translated* *with the Author's Sanction by George McGowan. Third English Edition, Translated from the Third German Edition, with Various Additions and Alterations. 14 × 23 cm; pp. xii + 691. New York: The Macmillian Company, 1906. Price: bound, $4.25 net.*—As the first German edition appeared in 1888, it is not necessary to say anything about the early history as given in the third English edition, based on the third German edition. The chapter on the history of physical chemistry in recent times is one which did not appear in the first edition. The subject is treated under the following headings: determination of vapor density; dissociation; the liquefaction of gases; the kinetic theory of gases; spectrum analysis; atomic volumes of solids and liquids; laws regulating the boiling temperature; specific heat of substances; optical behavior of substances; diffusion, etc.; theory of solution and electrolytic dissociation; electrolysis of liquid or of dissolved substances; isomorphism, etc.; thermochemistry; photochemistry; radio-activity; development of the doctrine of affinity since the time of Bergmann; Bergmann's doctrine of affinity; Berthollet's doctrine of affinity; the supplanting of Berthollet's opinions by other doctrines; the revival of Berthollet's doctrines; the latest development of the doctrine of affinity.

With forty-two pages devoted to the history of physical chemistry, some might feel that the reference to the phase rule was either too short or too long. "The conception of chemical equilibrium was given definite expression by Willard Gibbs in the phase rule, which has proved a valuable guide in numerous experimental researches of recent years. This theorem is mainly of value in representing clearly on a diagram the results of experiment, but it cannot be discussed here; the reader is referred to the literature on the subject." After this one is not surprised to read, p. 394, that Gibbs's "most important book, Thermodynamic Studies, was translated into German—as one of the *Klassiker*—by Ostwald."

This book of von Meyer's is the only book of its kind that there is and it rises superior to criticism for that reason. Each one of us pictures to himself a better book perhaps; but the years come and go, and this volume holds the field. It is often easier to see the merits of a book which has not been written than of one that has; but it is only the latter which is of value to the reader.

Wilder D. Bancroft

ERRATA.

In Mr. Sammis's article, Jour. Phys. Chem., 10, 593 (1906), the following corrections are to be made:

Page 603, first line, for "about 2.6," read "about 1.7."
Page 603, Table VIII Expt. (7), for "6.0" read "1.6."
Page 603, Table VIII Expt. (8), for "7" read "1.7."

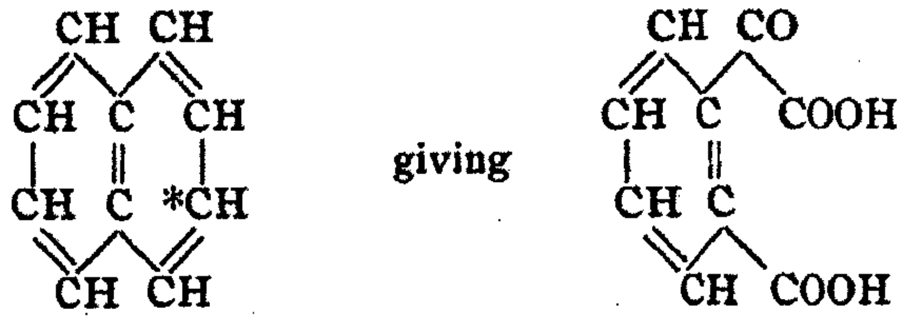
[THE MECHANISM OF THE OXIDATION OF NAPHTHALENE. I.]

THE OXIDATION OF NAPHTHALENE TO PHTHALONIC ACID BY ALKALINE SOLUTIONS OF PERMANGANATE

BY R. ARTHUR DALY

In 1894 Tcherniac[1] showed that naphthalene may readily be oxidized to phthalonic acid by the action of a boiling solution of potassium permanganate; and this reaction, which gives a yield of about 80 percent of the theoretical amount, has ever since been used as the best method of preparing that acid.[2]

The molecule of phthalonic acid contains but nine of the ten carbon atoms present in naphthalene, the tenth (marked with a star in the formula), being oxidized to CO_2 by the permanganate:



Naphthalene Phthalonic acid

It is natural to suppose, however, that the phthalonic acid, although the product of the oxidation under the conditions of the method of preparation, is only the last of a number of compounds which have been formed and oxidized in turn. This supposition is supported by the fact that both α- and β-naphthol on treatment with potassium permanganate are converted into phthalonic acid;[3] and further by the existence of a large number of substances intermediate in composition between naphthalene and phthalonic acid, some of which—like α-naphtho-quinone[4]—may be prepared direct

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[1] German patent 79693, March 23, 1894.

[2] Graebe und Trümpy: Ber. chem. Ges., Berlin, 31, 369 (1898).

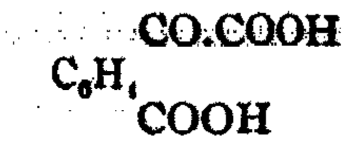
[3] Henriques: Ibid., 21, 1608 (1888).

[4] Groves: Jour. Chem. Soc., 26, 209 (1873).

from the naphthalene by treatment with suitable oxidizing agents.

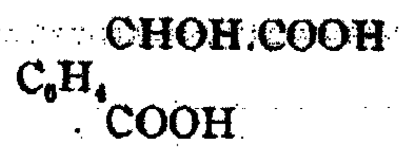
The experiments described in the following pages were undertaken in order to ascertain, if possible, which of the numerous intermediate compounds whose formulas suggest themselves may be regarded as actual stages in the formation of the phthalonic acid from the naphthalene, and which may not.

As phthalonic acid is a ketone, it seemed proper to begin the investigation with the corresponding secondary alcohol, and hydrocarbon. These are known as carboxy-mandelic acid (existing in the free form as the inner anhydride, phthalid-carbonic acid), and homophthalic acid, respectively.



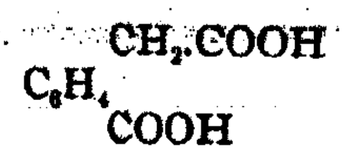
$C_6H_4\begin{matrix}CO.COOH\\COOH\end{matrix}$

Phthalonic acid.



$C_6H_4\begin{matrix}CHOH.COOH\\COOH\end{matrix}$

Carboxy-mandelic acid.



$C_6H_4\begin{matrix}CH_2.COOH\\COOH\end{matrix}$

Homophthalic acid.

Neither of these has been detected in the product of the action of permanganate on naphthalene—it would indeed be difficult if not impossible to detect small quantities of them—but this is no proof that they were not first formed and then oxidized further.

Measurements of the rates at which naphthalene, homophthalic acid, and carboxy-mandelic acid are oxidized by potassium permanganate were accordingly undertaken, the idea being that if the two last named were really intermediate stages in the formation of phthalonic acid, they must be much more quickly oxidized than naphthalene itself, under the conditions which lead to a good yield of phthalonic acid.

The formation of phthalonic acid from naphthalene and potassium permanganate may be represented by the following gross chemical equation:

$$C_{10}H_8 + 16/3\ KMnO_4 = C_9H_6O_5 + CO_2 + H_2O + 16/3\ MnO_2 + 8/3 K_2O.$$

As will be seen from this equation, the carbon dioxide formed in the reaction is not enough to neutralize the potash, so that the oxidation takes place in a solution which gradually becomes more alkaline as the reaction proceeds, and whose alkalinity is apt to be affected by the formation of carbon dioxide in subsidiary reactions, for as noted above, the yield of phthalonic acid is only about 80 percent of the theoretical amount.

It was necessary, therefore, to see whether the degree of alkalinity affects the rate of oxidation of the naphthalene; and preliminary experiments were undertaken with this object in view.

Five grams of naphthalene and 25 cc of a decinormal solution of potassium permanganate were placed in each of four glass-stoppered bottles, which contained, respectively,

a 40 cc of decinormal potassium hydrate
b 40 cc decinormal sodium bicarbonate (8.4 grams per liter)
c 40 cc water
d 40 cc decinormal sulphuric acid

All the solutions were at the temperature of the room; the bottles were shaken for five hours and a half, and then the residual permanganate was determined. The analyses showed that in

a 14.9 cc permanganate had been reduced
b 11.5 cc " " " "
c 5.7 cc " " " "
d all the permanganate " " "

These figures prove that the degree of alkalinity of the solution has a very marked effect on the rate of the oxidation; all subsequent reactions were carried out in solutions containing sodium bicarbonate in such large quantity that the potash and carbon dioxide generated during the experiment could not materially alter the alkalinity of the solution.

Method of Determining the Permanganate

As the solutions in which the permanganate was to be determined contained (or might contain) phthalonic acid, and as this substance is quickly oxidized by permanganic acid, it seemed necessary to carry out the analysis in such a manner that no acid was added until the permanganate was destroyed.

A number of blank experiments showed that satisfactory results could be obtained by adding potassium iodide to the alkaline (bicarbonate) solution, which liberates iodine and precipitates manganese dioxide; and then acidifying, and determining the iodine with fiftieth-normal thiosulphate.

This method of working gives satisfactory results in the presence of homophthalic and phthalid-carbonic acids; but if phthalonic acid be present, an error of about 1 percent is introduced. If the acid and iodide be added simultaneously, however, in the form of a solution containing 0.4 gram potassium iodide 2 grams sulphuric acid and 110 cc water, the results are accurate; and as this second way of working gives good results in the presence of other acids as well, it was adopted in all cases.

I. RATE OF OXIDATION OF NAPHTHALENE

Method of Working

Five grams of naphthalene finely powdered, 25 cc decinormal permanganate, and 25 cc of a decinormal solution of sodium bicarbonate, were brought to the temperature of 40° C, mixed in each of eight wide-mouthed glass-stoppered 100 cc bottles, and shaken in a thermostat for periods varying from 30 minutes to four hours and a half.

As each was removed from the bath, its contents were poured into a quarter liter measuring flask containing about 60 cc of ice water, which was then filled to the mark with water of the temperature of the room. This stopped the reaction. The dilute solution was filtered through ordinary analytical filter paper, rejecting the first 30 or 40 cc of the filtrate to avoid error due to the action of the permanganate on the paper. (Hardened filters have less action on the permanganate, but the filtration lasts longer, and blank experiments showed that the method as described is satisfactory).

In fifty cubic centimeters of the filtrate, the permanganate was determined as described above; and in a second portion of 50 cc, the phthalonic acid.

Determination of Phthalonic Acid

To the fifty cubic centimeters of the filtrate, was added about 50 cc 2 percent sulphuric acid, and a few drops of F/10 manganous sulphate.[1] After standing for two minutes, during which the whole of the phthalonic acid is oxidized to phthalic acid and a brown precipitate is formed, the mixture of potassium iodide, sulphuric acid and water given on page 96 is added, and the iodine determined by fiftieth-normal thiosulphate. This method of analysis, for which I am indebted to Mr. Boswell, gives accurate results in the presence of homophthalic and phthalid-carbonic acids; if the mixture is let stand for longer than two minutes before adding the hydriodic acid, however, a correction has to be made for oxidation of phthalid-carbonic acid.

Method of Recording the Results of the Analyses

Let x represent the number of cubic centimeters of decinormal[2] permanganate reduced in alkaline solution during the experiment; and y the additional number reduced in acid solution by the phthalonic acid during the analysis. A is the permanganate initially present, in the same units.

Then the number of cubic centimeters of fiftieth-normal thiosulphate used in the permanganate determination (page 96), divided by five, and multiplied by the ratio between the whole volume of the solution and the part taken for analysis, given $A-x$; whence, if A be known, x can be obtained.

The number of cubic centimeters of fiftieth-normal thiosulphate used in the phthalonic acid determination (page 97), divided by five, and multiplied by the volume ratio, gives $A-x-y$.

These relations hold only if the manganese dioxide be removed before the analyses, as prescribed on page 96. In certain cases this is not possible, and the oxidizing value of the dioxide in acid solutions has to be reckoned with. The "permanganate determination" then gives $A-0.6x$, and

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[1] One-tenth formula-weight per liter.

[2] One-fiftieth formula-weight $KMnO_4$ per liter.

the "phthalonic determination" gives $A—0.6x—y$. In both cases the difference between the two determinations gives y.

Results of the Measurements of the Rate of Oxidation of Naphthalene

The results of the measurements are arranged in tables, at the head of which are given the amounts of the various reagents taken, under t is given the duration of the oxidation in hours; under $A—x$ the residual permanganate (calculated for the whole bottle full) and under x the permanganate reduced, in cubic centimeters of decinormal solution. In all cases the temperature was 40° C; the permanganate solution "Pm," and the sodium bicarbonate,[1] "Bicarb" were decinormal. The titre of the permanganate changed somewhat; the accurate value is given after "A."

TABLE I

Naph., 5 gram ; Bicarb., 25 cc ; Pm., 25 cc; $A = 24.9$

t	$A-x$	x	x/t
0.5	23.1	1.8	3.6
1.0	21.3	3.6	3.6
1.75	17.4	7.5	4.3
2.33	14.1	10.8	4.6
3.33	10.4	14.5	4.4
4.5	6.3	18.6	4.1

As will be seen from the table, the rate at which the naphthalene is oxidized is as great when the permanganate is three-quarters reduced as it is at the beginning of the experiment. This suggested that, perhaps, the manganese dioxide which is precipitated at the end of the first hour might affect the rate; and a second series of experiments was undertaken, in which manganese dioxide was added at the beginning.

The "manganese mud" used was prepared by mixing 320 cc of decinormal permanganate, with 96 cc of a solution of manganous sulphate containing one formula-weight $MnSO_4$ in ten liters, and 400 cc fifth-normal sodium bicarbonate

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[1] 8.4 grams per liter.

Twenty-five cubic centimeters of this mixture contain as much manganese dioxide as would be formed by the reduction of 25 cc of the permanganate by naphthalene, and 0.75 times as much sodium bicarbonate as in 25 cc of the $n/10$ "bicarb" solution. Special experiments showed that, in the absence of permanganate, this "mud" is without action on naphthalene.

TABLE II

Naph., 5 gram; Mangan. mud, 25 cc; Pm., 25 cc; $A = 23.1$

t	$A-x$	x	x/t	$A-x-y$	y	$40y/3$
1	18.57	4.54	4.5	18.6	0.35	4.66
2	13.84	9.27	4.6	13.5	0.62	8.3
3	9.62	13.48	4.5	8.95	0.85	11.3
4.75	4.26	18.84	4.0	3.2	1.15	15.3

In these experiments the rate, x/t, is much more constant than in those of Table I; in particular, the increase after the first hour has disappeared.[1] The addition of the mud has therefore simplified matters, and it has been added in all subsequent experiments.

The Product of the Oxidation of the Naphthalene in the Experiments of Table II

Under $A-x-y$, in column 5 of Table II, is entered the amount of permanganate left after acidifying the filtrate and standing for two minutes, as described under "determination of phthalonic acid" on page 97. The difference between the second and fifth columns therefore gives the amount of permanganate reduced in the acid solution, presumably by phthalonic acid.

If the reaction between naphthalene and permanganate in alkaline solution takes place according to the equation given on page 94, then for every mol of naphthalene oxidized,

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[1] A number of experiments were made to study the effect of the concentration of the permanganate on the rate of oxidation of naphthalene. As this matter is apart from the main purpose of the present paper the results are not given here.

one mol of phthalonic acid will be formed, and 16/3 mol permanganate or 80/3 liters of normal solution will be required.

The oxidation of phthalonic acid to phthalic acid, however, as carried out in the analyses, takes place in acid solution, according to the equation:

$$C_9H_6O_6 + 2/5\ KMnO_4 + 3/5\ H_2SO_4 = 1/5\ K_2SO_4 + 2/5\ MnSO_4 + 3/5\ H_2O + C_8H_6O_4$$

Thus every mol of phthalonic acid oxidized by the acid permanganate reduces 2/5 mol of the latter, or two liters of normal solution. From these calculations it appears, that if the naphthalene be oxidized to phthalonic acid in the alkaline solution, and if the subsequent reduction of the permanganate in acid solution is due exclusively to the phthalonic acid so formed, then for every cubic centimeter reduced in acid solution 40/3 cc must have disappeared in the alkaline solution. The last column of Table II gives the values of $40y/3$, and it will be seen that they agree very closely in value with those of x, the permanganate reduced in the alkaline solution. In each case the phthalonic acid formed in a little less than that corresponding to the naphthalene oxidized; but this is only what might be expected, as even in alkaline solution the phthalonic acid is slowly acted on by permanganate.

The agreement between the numbers in the third and seventh columns of the table thus shows that the main product of the oxidation in alkaline solution, under the conditions of my experiments, is phthalonic acid.

II. RATE OF OXIDATION OF HOMOPHTHALIC ACID

The experiments were carried out in the same manner as those with naphthalene; homophthalic acid solution was made up by neutralizing 1 gram of the acid with sodium bicarbonate, and making up the volume to 100 cc with water.

TABLE III

Homoph. soln., 5 cc; Mud, 20 cc; Pm., 25 cc; $A = 23.2$

t	$A-x$	x	$A-x-y$	y	$10y/3$
1	22.5	0.7	22.4	0.1	0.33
2	22.1	1.1	21.98	0.12	0.4
3	21.65	1.65	21.5	0.15	0.5

The homophthalic acid present was enough to reduce about 19 cc of the permanganate in alkaline solution, if it itself were oxidized to phthalonic acid.

Two points are to be noticed in the results of these determinations. In the first place, the yield of phthalonic acid is only half or one-third of that corresponding to the permanganate reduced by the homophthalic acid, as may be seen by comparing the numbers under x with those under $10y/3$. This discrepancy may possibly be due in part to the difficulty of determining such small quantities with accuracy, but is nevertheless worth noting.

The second point is the extreme slowness with which the homophthalic acid is acted on by the permanganate. As it seemed possible that this oxidation might be accelerated by the simultaneous oxidation of naphthalene, after the manner of the "induced reactions," a parallel series of experiments was carried out in which both naphthalene and homophthalic acid were oxidized together, and the amount of homophthalic acid acted on was arrived at by subtracting the permanganate reduced by the naphthalene as determined in Table II. The results of these experiments and calculations, which are naturally strongly affected by the unavoidable errors of manipulation and method, were in full accord with those of Table III, and showed clearly that the simultaneous oxidation of naphthalene causes no acceleration in the oxidation of homophthalic acid.

According to the experiments of Table II, 13.48 cc of permanganate are reduced in three hours by naphthalene, which itself is converted almost quantitatively into phthalonic acid. If homophthalic acid were one of the intermediate products, enough must have been formed to reduce one-quarter of 13.48, or 3.37 cc of permanganate on its subsequent oxidation to phthalonic acid. The experiments of Table III show, however, that even with a relatively high concentration of homophthalic acid, less than half that amount is oxidized in the three hours. They thus definitely exclude the possibility that homophthalic acid is one of the intermediate compounds produced during the oxidation of naphthalene to phthalonic acid by potassium permanganate.

III. RATE OF OXIDATION OF *o*-CARBOXY-MANDELIC ACID

A solution of the sodium salt of this acid was prepared by neutralizing 1 gram of phthalid-carbonic acid with sodium bicarbonate, and making up to 100 cc with water. Five cubic centimeters of this solution would require 9.95 cc of my permanganate to oxidize it in alkaline solution to phthalonic acid.

TABLE IV

Carbox. soln., 5 cc; Mud, 20 cc; Pm., 25 cc; $A = 23.1$

t	$A-x$	x	$A-x-y$	y	$5y/3$	K
0.5	22.2	0.9	21.8	0.4	0.66	0.082
1.0	21.2	1.9	20.35	0.85	1.4	0.092
1.75	20.6	2.5	18.25	2.35	2.25	0.072
2.5	20.1	3.0	18.3	1.8	3.0	0.062
3.5	19.15	3.95	17.0	2.15	3.6	0.062
4.5	18.45	4.65	15.9	2.55	4.25	0.062

TABLE V

Carbox. soln., 10 cc; Mud, 15 cc; Pm., 25 cc; $A = 23.63$

t	$A-x$	x	$A-x-y$	y	$5y/3$	K
0.5	21.23	2.4	19.5	1.65*	2.75	0.12
1.25	19.24	4.39	16.62	2.62	4.36	0.086
2.25	17.2	6.43	13.0	4.2*	7.0	0.075
3.37	15.38	8.25	10.42	4.96	8.25	0.064

The values of K in the last columns of Tables IV and V have been calculated from x and t by the formula

$$K = \log_{10} \frac{B}{B-x}$$

in which B is the amount of permanganate equivalent to the carboxy-mandelic acid initially present; that is, 9.95 in Table IV, and 19.9 in Table V.

The agreement between $5y/3$ and x, shows that the product of oxidation of the carboxy-mandelic acid is phthalonic acid; and the agreement between the values of K in the two tables shows that the rate of oxidation is proportional to the concentration of the carboxy-mandelic acid. The decrease of K as the reaction proceeds is due, no doubt, to the fall in concentration of the permanganate, while the irregular values of y in Table V, which are marked by an asterisk, are due to two faulty analyses in which the acidified solution was let stand longer than two minutes before adding the hydriodic acid (see page 97).

As in the case of the homophthalic acid, a series of measurements was carried out to see whether the simultaneous oxidation of naphthalene accelerated the action of permanganate on the carboxy-mandelic acid. This was found not to be the case.

These results in connection with those of Table I, are sufficient to show that carboxy-mandelic acid can not be one of the intermediate substances formed during the oxidation of naphthalene to phthalonic acid.

In three hours naphthalene reduced 13.48 cc of permanganate; if carboxy-mandelic acid were formed, one-eighth of the 13.48 cc, or 1.69 cc of the permanganate must have been employed to oxidize the latter to phthalonic acid. In the experiments of Table IV, about 3.5 cc of permanganate were reduced in the same time, and in Table V, about 7.0 cc. At first sight, therefore, the intermediate formation of carboxy-mandelic acid seems possible; closer inspection, however, shows that this is not the case. In the naphthalene experiments (Table II), 4.5 cc of permanganate were reduced per hour, which, on the hypothesis under consideration, means that 0.56 cc of permanganate per hour are reduced by carboxy-mandelic acid. As the rate of oxidation of the latter is proportional to its concentration in the solution, it follows (from Table V) that the amount constantly present in the 50 cc, must be equivalent to $0.56/1.9 \times 9.3 = 2.7$ cc permanganate. To form this much of the carboxy acid from naphthalene would require 18.9 cc permanganate; and until this amount of permanganate had been reduced, the formation of phthalonic acid could not take place at the rate observed. In point of fact, however, the rate 4.5 cc per hour is attained in the very first hour, when not one-quarter of 18.9 cc permanganate has been reduced, so that the hypothesis that carboxymandelic acid is one of the intermediate substances formed during the oxidation of the naphthalene must be definitely rejected.

IV. RATE OF OXIDATION OF *o*-CARBOXY-BENZOYL-ACETIC ACID

Having thus shown that the substances which stand in the closest relation to phthalonic acid can not be considered as intermediate stages in its formation from naphthalene, I took up the study of *o*-carboxy-benzoylacetic acid, and then made a few experiments with the two naphthoquinones, both of which I find are readily oxidized to phthalic acid by permanganate in acid solution, and one of which has been prepared from naphthalene by the action of chromic acid.

Table VI

Phthal.-acet. acid, 0.0100 gram; Bicarb., 0.15 normal, 25 cc; Pm., 25 cc; $A = 24$

t	$A-x$	x	$A-x-y$	y
0.25	19.90	4.9	18.85	1.05
0.50	19.30	5.5	18.20	1.10
1.00	19.40	5.4	18.35	1.05
2.00	19.48	5.3	18.45	1.03
3.00	18.80	6.0	17.75	1.05

The 0.0100 gram of phthalyl-acetic acid (inner anhydride of the *o*-carboxy acid) employed in the experiments, would require 5.3 cc decinormal permanganate to oxidize it to phthalonic acid in alkaline solution; and the phthalonic acid so formed would be further oxidized in acid solution to phthalic acid by 1.06 cc of the permanganate.

As Table VI shows, these amounts of permanganate were reduced in the first half hour; so far as these rate measurements go, then, *o*-carboxy-benzoylacetic acid may be regarded as one of the intermediate stages in the oxidation of naphthalene;

but neither homophthalic nor *o*-carboxy-mandelic acid can be formed during the oxidation of *o*-carboxy-benzoylacetic acid to phthalonic.

V. RATE OF OXIDATION OF β-NAPHTHOQUINONE

The β-quinone is slightly soluble in decinormal sodium bicarbonate, giving a dark red solution from which it cannot be extracted by ether; after acidifying, however, the naphthoquinone may be ethered out, unchanged.

The solution in bicarbonate is very dilute; and, in consequence, the amount of permanganate reduced was small. It was therefore decided to dispense with filtration in making the analyses, for fear that the error due to the action of permanganate on the paper might be large enough to affect the result.

TABLE VII

Quin. soln., 30 cc; filtrate from "mud," 10 cc; Pm., 10 cc; $A = 10$

t	$A - 0.6x$	$A - 0.6x - y$	x	$5y/3$
0.25	8.6	—	2.3	—
0.50	8.45	—	2.6	—
0.75	8.4	7.61	2.7	1.32
1.0	8.35	7.5	2.7	1.42

As will be seen from the table, the amount of oxygen needed to oxidize the quinone in alkaline solution, (x), is just double that required to oxidize the product of that oxidation to phthalic acid ($5y/3$). In other experiments, in which the quinone was shaken with sodium bicarbonate solution and permanganate, the values of $5y/3$ were about one-third those of x. These numbers cannot be reconciled with the hypothesis that phthalonic acid is the product of the oxidation of the quinone; they suggest rather the formation of the diketo-dibasic acid $C_6H_4(CO.COOH)_2$. No account of this substance can be found in the literature; and attempts to prepare it, by acting on phthalyl chloride with potassium or mercuric cyanides and saponifying the nitrile, have not as yet led to the desired result.

VI. RATE OF OXIDATION OF α-NAPHTHOQUINONE

To convert one mol of the quinone to phthalonic acid requires five atoms of oxygen, and a sixth is necessary to complete the oxidation to phthalic acid. For every cubic centimeter of permanganate reduced in acid solution, 25/3 should be reduced in alkaline.

Table VIII

Quinone, 0.0166 gram; Bicarb., 25 cc; Pm., 25 cc; $A = 24.80$

t	$A-x$	x	$A-x-y$	y	$25y/3$	y calc.	x calc.
0.25	11.75	13.05	9.70	2.05	17.1	2.10	17.5

As the quinone is insoluble in the bicarbonate solution, it is possible that part of it became coated with dioxide, and was thus protected from oxidation until acid was added, which would account for x being less than $25y/3$. This experiment, therefore, leaves it quite possible that α-naphthoquinone is a stage in the oxidation of naphthalene to phthalonic acid; while the rapidity of the oxidation precludes the possibility of either homophthalic or *o*-carboxy-mandelic acids being stages in the oxidation of the quinone.

CONCLUSION

The experiments described in this paper are of interest as laying the foundation of a method for studying the mechanism of complex organic reactions.

In the special case selected for study, they show conclusively that homophthalic acid and carboxy-mandelic acid are not intermediate stages in the formation of phthalonic acid by the action of alkaline solutions of potassium permanganate on naphthalene, on phthalyl acetic acid, or on the naphthoquinones; β-naphthoquinone is probably not an intermediate stage in the oxidation of naphthalene, while *o*-carboxy-benzoylacetic acid and α-naphthoquinone may be.

In conclusion, my thanks are due to Prof. W. Lash Miller at whose suggestion this research was undertaken, and under whose supervision it was carried out.

University of Toronto,
December, 1906.

MANOSTATS

BY RESTON STEVENSON

The purpose of the following paper is to review all the forms of pressure regulators which have been devised; to suggest new forms and modifications; and to classify them according to the methods of pressure regulation.

Scientific literature contains references to but few forms of manostats. Pressure is one of the variables which so often determine the velocity, direction and equilibrium of reactions; therefore, it is frequently necessary to control pressure—to keep it constant and to vary it at will. Some of the uses for which manostats are adapted are:

Determination of vapor-pressures and boiling-points.

Distillation under pressure.

Study of the velocity of reaction.

Constant temperature bath.

Desiccation in vacuo or under pressure.

Work involving the use of the Phase Rule (particularly where there is a vapor-phase).

Although pressure is a factor in so many reactions and equilibria, the effect of a change in pressure is usually relatively small. For example, to change the boiling-point of water from 100° to 99°, requires a change in the pressure of 33 mm Hg. Therefore a manostat, in order to be serviceable for general laboratory work, need not be so accurate or so sensitive but should possess a wide range of pressures.

Manostats may be classified thus·

I. Regulation by use of a continuous current of gas (or vapor).

II. Regulation by an intermittent or oscillatory supply of gas (or vapor).

III. Regulation by means of compensatory volume or temperature changes within the system.

Manostats of Class I

Principle: Continuous compression and continuous escape of a gas when the desired compression is exceeded, or continuous rarefaction and continuous entrance of air when the desired point of exhaustion is exceeded. The oldest form of pressure regulator and the simplest example of Class I is that devised by Lothar Meyer.[1] It is shown in Fig. 1.[2]

Fig. 1

Key to uniform lettering

P, point of connection to the source of pressure.
A, " " " " " atmosphere.
M, " " " " " manometer.
V, " " " " " system whose pressure is to be kept constant.

The height of the column of mercury is regulated by removal of mercury by means of the stop-cock. As represented, the apparatus is used for pressures less than atmospheric; P and A are interchanged if the apparatus is used for pressures greater than atmospheric. The mode of operation is obvious. The objections to this form are:

(1) Errors due to barometric fluctuations, to changes in the friction of the gas passing through the tubes, and to oscillations in the level of the mercury, caused by the rising bubbles of gas.

(2) The apparatus can be used through only a narrow range of pressures.

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[1] Liebig's Ann., 165, 303 (1873).

[2] The key to the uniform lettering of the figures is given just below Fig. 1.

(3) Expense and inconvenience of producing a constant stream of gas.

Staedel and Hahn[1] have modified Meyer's manostat so that the tube which contains the mercury can be rotated and the pressure speedily changed. This form is open to the same objections as the Meyer manostat. The author constructed and tested a Staedel and Hahn manostat and found it unwieldy and inapplicable to general laboratory use.

The author has modified the Meyer manostat so that the pressure effect is multiplied. This apparatus is of a convenient size and form, it is easily regulated, and the range of pressures obtainable is limited only by the bursting pressure of the tubes and the number of tubes used. It is shown in Fig. 2.

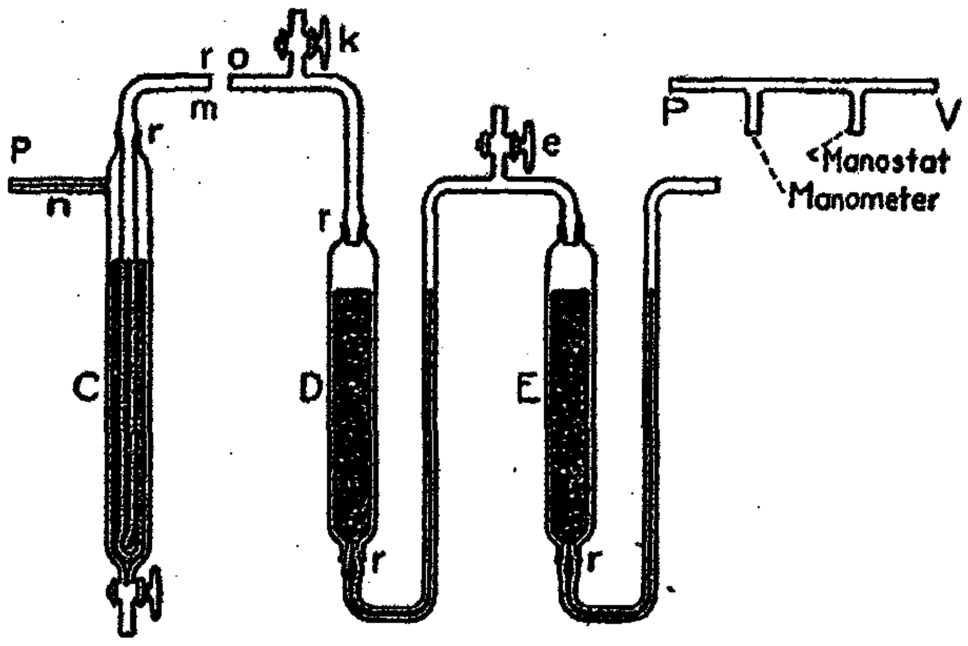

Fig. 2

The tube C is filled as shown with mercury or other liquid, by sucking at *n*, while *m* dips under the liquid. Tubes D, E, etc., are filled similarly. For pressures greater than atmospheric, the source of pressure is connected to a manometer, from the manometer to *m*, *n* is attached to *o*, *k* and *e* closed. The pressure is adjusted by opening *e* or *k* and the final adjustment is made by removing mercury from C by means of the stop-cock. For pressures less than atmospheric,

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[1] Liebig's Ann., 195, 218 (1879).

suction is attached to a manometer, thence to *n*, *m* and *o* are attached as shown in the figure, and *k* and *e* are closed. Adjustment is made, as before, by opening *k* or *e* and by removing mercury at C.

The capillary tube shown at *n* is necessary to secure easy bubbling of the gas through the mercury. Without this resistance the gas would alternately not bubble at all and bubble violently in a manner analogous to the bumping of a liquid during ebullition. The final adjustment tube C could be mounted separately and reversal sets of varying numbers of the tubes D and E could be made. Then, all of these sets could be used together in series or in multiple, or each set separately and the final adjustment made in each case by the tube C. The apparatus as made and tested consisted of the tube C mounted separately and the tubes D, E, etc., were fastened by wires on both sides of a vertical board ten inches high, set in a wooden base, so that the set of six tubes connected in series occupied about one cubic foot of space. This set, together with the tube C, afforded a range of pressures from 0–3$^1/_2$ atmospheres. This apparatus was tested by distilling water under varying pressures both greater and less than atmospheric. In no instance was a variation greater than 0.08° in the boiling-point noted. The errors involved in its operation are the same as for the Meyer manostat. The necessity for a source of constant compression or exhaustion is objectionable.

Resistance to the passage of a gas or vapor, such as offered by capillary tubing, can be used for the maintenance of pressure, instead of a mercury column. The relation between the pressure, current and resistance is given by the well-known equation

$$c = \frac{E}{R} \cdot K. \qquad (1)$$

c = rate of flow of gas or vapor.

E = difference in pressure at the two ends of the resistance.

R = resistance to passage of the gas or vapor.

K = a constant depending upon the units used.

In an industrial chemical laboratory in which the author once worked, it was attempted to regulate pressure by altering the size of the opening of a reducing valve. The method was unsatisfactory. Since the use of such a valve is the usual industrial practice, and because of theoretical considerations, the method will be given somewhat in detail. As shown in the diagram, Fig. 3, air from a source of high pressure was passed through a reducing valve over gasoline in a tank, through the gas pipes and Bunsen burners, to the air.

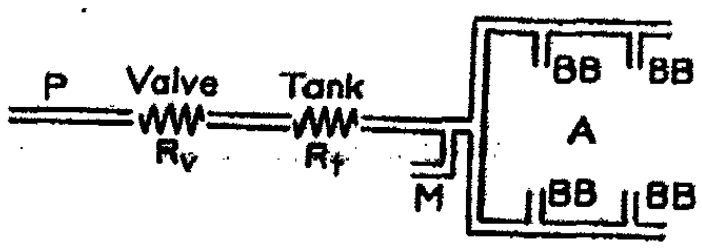

Fig. 3

$$c = \frac{E}{R} \cdot K$$

c = current flowing through the system.
$E = M - A$.
R_v = resistance of the reducing valve.
R_t = " " " tanks, etc.
$R_{B.B.}$ = " " one Bunsen burner.

$$c : c' = \frac{E}{R} K : \frac{E'}{R'} K$$

$\therefore$ if M = constant

$$c : c' = R' : R.$$

Here $R = R_{B.B.}$

$R' = \frac{R_{B.B.}}{n}$ where n = number of burners used.

$\therefore c' = nc$.

Therefore, if the pressure as shown by the manometer M were kept constant, each burner would have the same current passing through it, irrespective of the number of burners used. Actually, however, M did not remain constant and the current, therefore, did not vary with the number of burners used.

c = current when 1 B. B. was used.
c' = " " n " " "
$R = R_v + R_t + R_{B.B.}$.
$R' = R_v + R_t + \frac{R_{B.B.}}{n}$.

But

$$\frac{R_v + R_t + R_{B.B.}}{R_v + R_t + \frac{R_{B.B.}}{n}} \neq \frac{n}{1}. \qquad (2)$$

$$\therefore \frac{c}{c'} \neq \frac{1}{n}.$$

Since the current does not vary directly as the number of burners used, M does not remain constant. Actually, M varied and the burners burnt erratically. If the valve were removed, the pipe and tank resistances made small, and capillary tubing inserted before each burner, then $R_v + R_t$ would become negligibly small in comparison with $R_{B.B.}$ and equation (2) would become

$$\frac{R_{B.B.}}{\frac{R_{B.B.}}{n}} = \frac{n}{1}.$$

$\therefore c' = nc.$

Such a use of capillary tubing, however, would be impracticable and objectionable.

Fig. 4

Fig. 4 shows a manostat of but little practical value but important from theoretical considerations. If a source of constant pressure is attached to one end of a fine capillary tube the "drop in potential" or fall in pressure is equal to the difference between the original and the atmospheric pressure. If the system in which pressure is to be controlled is connected to one of the openings on the side (all of the other openings being closed), the pressure will increase as the side opening approaches P. In this way, one source of constant pressure can be used as a source of a series of constant pressures. The pressure at P may also be less than atmospheric.

For distillation under pressure greater than atmospheric, a distillation flask may be fitted with a capillary outlet. From equation (1), it is evident that if the current of vapor is kept constant, the pressure will remain constant. This constant current can not be obtained by use of constant heat because the radiation varies. Such a constant current can be obtained by connecting the distillation flask with a manometer which controls the supply of gas to the burner (see Fig. 8).

Class II

Principle: The system is connected alternately with a pressure greater or less than desired, as the pressure in the system becomes less or greater than desired.

F. D. Brown's[1] manostat (Fig. 5) is operated in the following manner: When the desired pressure is obtained, the tube O is lowered until the platinum wires are just above the surfaces of the mercury columns. From a battery, a wire runs to the shaft of the electromagnetic clutch which is elec-

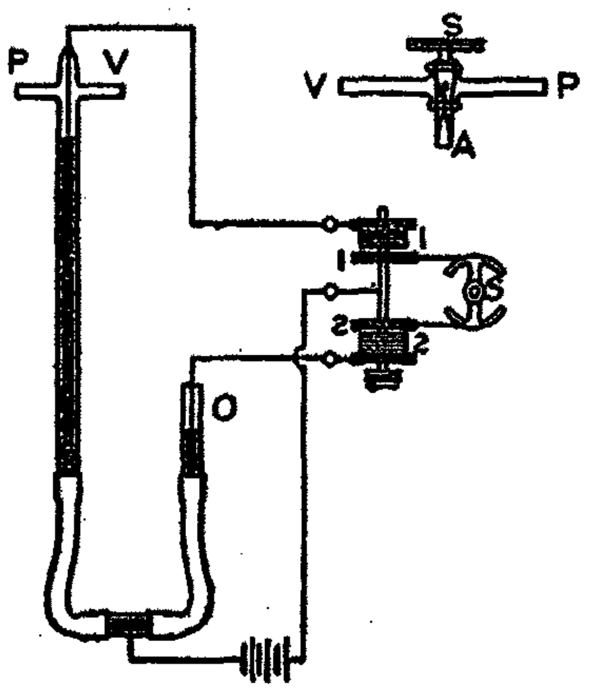

Fig. 5

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[1] Phil Mag. [5] 7, 411 (1879).

trically connected to the electromagnets 1 and 2. The other wire from the battery runs to the middle of the column of mercury. The shaft of the clutch with the electromagnets is rotated continuously in the direction shown by the arrow; pulleys 1 and 2 fit loosely and do not rotate. When the pressure becomes greater than desired, the electric circuit is completed through the platinum wire in the arm O, electromagnet 2 becomes magnetized and clutches pulley 2 which revolves and turns the three-way stop-cock (shown in detail at S) so that connection is made between the vessel and the suction. Similarly, when the pressure becomes less than desired, the electric circuit is completed through electromagnet 1 and the pulley 1 is clutched, so that it revolves and turns the stop-cock, connecting the vessel with the atmosphere.

The objections to this type of manostat are: (1) errors due to barometric fluctuations and to the lag of regulation behind pressure variation; (2) the necessity for a source of power to turn the shaft; (3) only a narrow range of pressures obtainable; and (4) the expense and difficulties of construction.

A. Smits[1] has designed a manostat (Fig. 6) which also

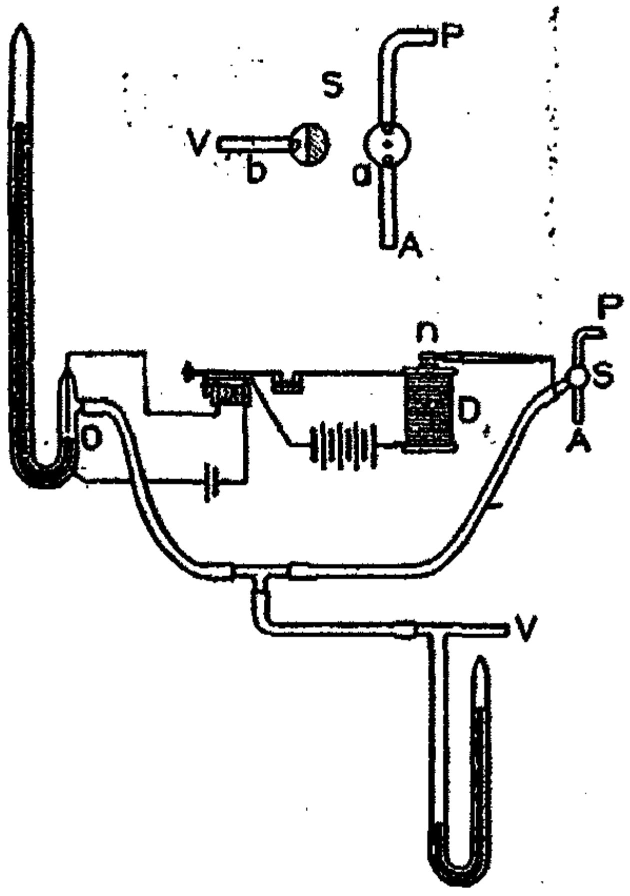

Fig. 6

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[1] Zeit. phys. Chem. 33, 39 (1900).

uses the mercury column in a manometer to make and break an electric circuit. A relay of electromagnets is used to furnish the power to turn the three-way stop-cock. When the circuit is broken at the platinum wire in the tube O, the current flows through electromagnet D, the lever of the stop-cock is attracted and the vessel is connected with the atmosphere. When the circuit is completed in O, the lever is released and falls, connecting the vessel with the source of pressure. The stop-cock is shown in detail at S. The objections to this form are: (1) the error due to the lag of regulation behind variation of pressure; and (2) the difficulty of construction and operation.

Fig. 7 represents a strong and simple apparatus which if properly constructed, would give good results. A smooth and well lubricated metallic piston works inside of a smooth metallic barrel. To operate this device for pressures greater than atmospheric, place weights at W until they represent the desired pressure, connect P with a source of pressure higher than that desired and then leave the apparatus alone. As represented, the pressure in V is exactly as desired and the openings P and A are closed. If the pressure in V increased, the piston would move up and gas would escape at A. If the pressure becomes too small the piston falls and gas rushes in at P. By use of a pulley and cord, as shown, the apparatus can be used for pressures less than atmospheric. P would then be connected with the atmosphere and A with a source of pressure less than that desired. The only error involved in the use of this form is due to the lag of regulation behind variation of pressure.

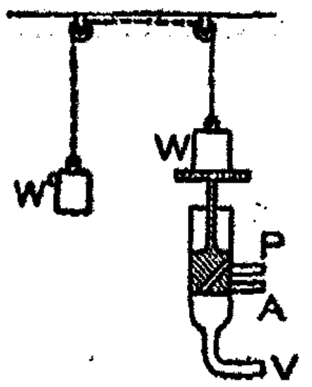

Fig. 7

Class III

Principle: The variation of the pressure of a system can be corrected by change of the volume or temperature of the system.

If the piston in Fig. 7 fits almost hermetically, and the barrel is very long, and the variation at V small, then such an apparatus can be used without the P and A connections. The piston would move up and down the cylinder, always with the same pressure in the system—the pressure determined by the weights at W.

In Fig. 8 is shown a manostat adapted particularly for use in distillation but easily used for other purposes. After the proper pressure is obtained in the flask, as shown by the height of the mercury column in O, stop-cock S is closed. Then, if the pressure in flask V becomes too great, the mercury column in the gas regulator R rises and the flow of gas to the burner under the distilling flask is diminished. Conversely, if the pressure in V becomes too small, the mercury column in R falls and more gas goes to the burner under the flask. This apparatus is made more sensitive by making the tube O of relatively larger bore. A test of this apparatus was made by boiling water in a flask fitted with a reflux condenser. The following readings of the thermometer with its bulb in the water in the flask, were observed:

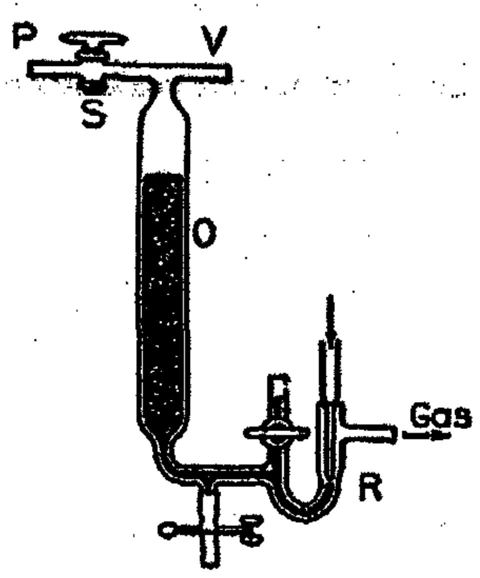

Fig. 8

Time	Temperature
7:55	59.45°
8:00	59.45
8:05	59.35
8:10	59.45
8:15	59.45
8:20	59.30
8:25	59.40
8:30	59.35
8:35	59.40
8:40	59.42
8:45	59.35
8:50	59.40
8:55	59.30
9:55	59.33

From these results, there is shown a maximum deviation in the boiling-point of ±0.075°, equivalent at this temperature to 0.0525 mm mercury. The chief objection to this manostat is the necessity for having the system absolutely air-tight. As described, the manostat is used for pressures less than atmospheric; it is also adaptable for pressures greater than atmospheric.

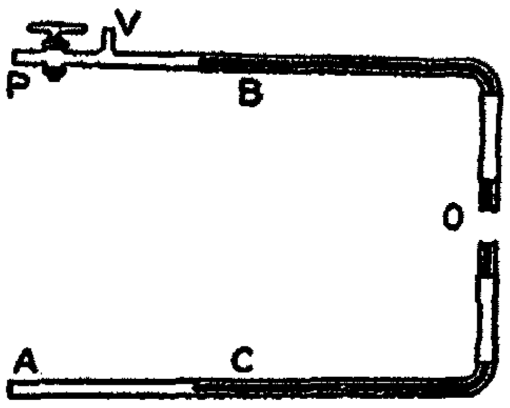

Fig. 9

In Fig. 9 is shown another form of manostat which does not require a current of gas for its operation. The vertical tube O has a height slightly greater than the difference between the pressure desired and the atmospheric pressure, and final adjustment of the pressure is made by inclining O at an angle with the vertical. Suction is applied at P until the ends of the mercury columns stand in the middle of the horizontal tubes B and C. If the temperature or amount of the gas in the system changes, the horizontal columns of mercury move and change the volume of the system, but the pressure remains constant because the vertical height of mercury remains constant. Therefore, this manostat, theoretically, maintains the pressure as constant as the barometer, but in actual operation, the inertia due to the friction of the mercury against the glass tubes, decreases the sensitiveness to pressure changes. A modification of this apparatus, particularly useful in distillation, would consist in attaching to the tube *c* a gas regulator such as shown in Fig. 8, so that the horizontal tubes would correct the small changes in pressure, and the gas regulator the larger changes. This manostat was tested by boiling water in a flask provided with a reflux condenser. The following readings of the thermometer with its bulb in the liquid, were observed.

Time	Temperature
9:10	40.80°
9:15	40.82
9:20	40.85
9:25	40.75
9:30	40.80
9:45	40.82
9:55	40.75
10:00	40.75
10:10	40.80
10:15	40.80

The maximum deviation here is +0.050°; equivalent to 0.15 mm mercury. This form is open to the same objections as that shown in Fig. 8.

It is hoped that the foregoing pages have shown what difficulties are encountered in pressure regulation, what principles may be used, and what forms of apparatus have been suggested. The apparatus which should be used depends upon the nature of the use to which it is to be put—whether the range of pressures desired is large or small and whether change in pressure has a relatively large or small effect. In conclusion, the author desires to thank Dr. H. R. Carveth and Professor Bancroft, of Cornell, for assistance and encouragement.

Cornell University.

(On the Mechanism of the Oxidation of Naphthalene. II.)

THE COURSE OF THE OXIDATION OF β-NAPHTHOQUINONE TO PHTHALIC ACID

BY MAITLAND C. BOSWELL

In many of the reactions of organic chemistry, where the ultimate product is only distantly related to the substances initially present, it is of great interest to trace the intermediate steps of the reaction; either, for example, to elucidate some theory—as that of ring opening in the oxidation of cyclic compound—or in the hope of discovering constitutional formulas for, and ultimately achieving the synthesis of, the substances experimented on.

Up to the present, information as to the course of such reactions has been sought by examining the reaction products for the intermediate compound suspected; and by varying the conditions of the reaction, such as temperature and concentrations, by exchanging one oxidation or reduction agent for another, by adding alkali or acid, etc., to discover, if possible, conditions under which they would be formed in isolable quantities. Much has been accomplished in this manner.

There is, however, a second method of procedure which is illustrated by the experiments of the present paper; and which, so far as I am aware, has not hitherto been put in practice. This consists in studying the behavior of the suspected intermediate products with the reagents used in the reaction in question, in order to see whether, if formed, they would accumulate in the reaction mixture, or would be converted at once into the final product.

This second method is, in a sense, a complement of the first; each furnishes information that the other cannot give. Failure to isolate any particular substance cannot be regarded as proof that it did not exist temporarily at some stage of the reaction; and on the other hand, proof that the substance in question could not remain unaltered in the presence of the reagents, is proof merely that it might have been—not that it actually was—formed as an intermediate stage of the reaction.

The first method, then, may lead to positive evidence that a given substance is one of the intermediate products of the reaction; the second, to positive evidence that it is not. Neither method can furnish evidence of the kind peculiar to the other.

A few simple experiments carried out by either of the two methods may often give valuable information; but to obtain really conclusive evidence by either of them, all the precautions suggested by the study of chemical kinetics must be observed. In applying the first method, in particular, it has too often been forgotten that change of conditions often entails a radical change in the mechanism of the reaction. An example of such a change is afforded by my experiments on the oxidation of β-naphthoquinone, discussed on page 127.

In a paper which has just been published, Mr. Daly[1] has made a careful study of some of the likely intermediate stages in the formation of phthalonic acid by the action of potassium permanganate on naphthalene. The present experiments with β-naphthoquinone and some of its possible oxidation products show how, under favorable circumstances, a few simple measurements may lead to equally definite results.

In the oxidation of β-naphthoquinone to phthalic acid,[2] the ring may be broken at the double bond, between the two keto groups, or between the CO and CH groups; of these, the last named seems the least likely, from chemical analogies, while simultaneous dissolution of two or more bonds is least likely of all.

The first alternative would result in the formation of carboxy-phenylglyoxyl-formic acid, which on further oxidation might be converted into phthalonic acid and then into phthalic acid (Series *A*). The experiments of Zincke[3] and of

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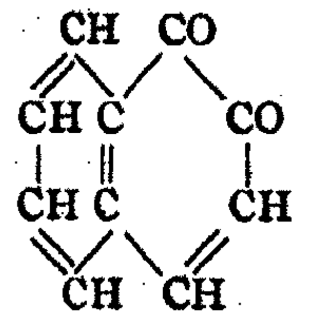
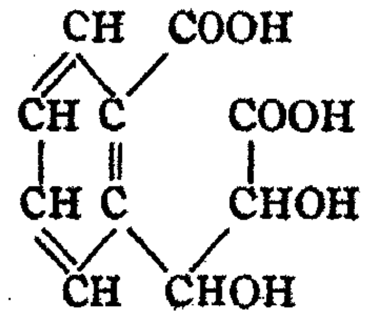
[1] Jour. Phys. Chem., 11, 93 (1907).

[2] Liebig's Ann., 189, 155 (1877).

[3] Ber. chem. Ges., Berlin, 25, 400 (1892).

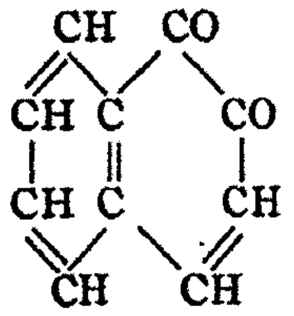
Bamberger and Kitschelt,[1] who prepared ortho-carboxy-phenylglyceric acid by the action of chloride of lime on β-naphthoquinone, lend probability to the second supposition (Series *B*); and I have accordingly undertaken experiments to ascertain whether the oxidation by chromic acid follows the same course.

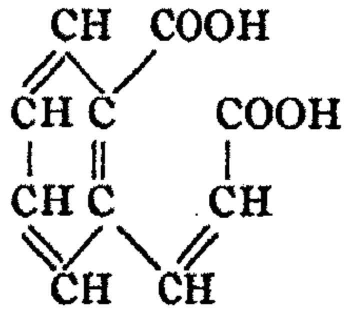

β-Naphthoquinone

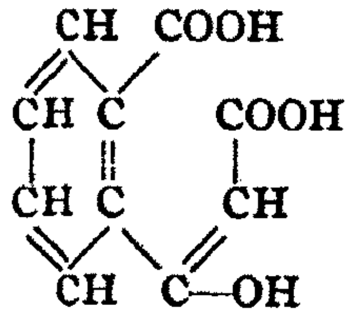

Ortho-carboxy-phenyl-glyceric acid

The first product of the oxidation, if the bond between the two keto groups be broken, would be *o*-carboxy-cinnamic acid. I do not find in the literature any account of this substance having been oxidized without loss of carbon, but cinnamic acid itself gives phenylglyceric acid;[2] *o*-carboxy-phenylglyceric acid may therefore be assumed, with perhaps *o*-carboxy-benzoylacetic acid (the hydrate of phthalyl-acetic acid) intermediate. Homophthalic acid, and carboxy-mandelic acid (the hydrate of phthalid-carbonic acid), both of which may be obtained from phthalonic acid by reduction, may also reasonably be regarded as possible stages in the oxidation, since my own experiments show that phthalonic acid is actually formed from each of them.

The steps by which β-naphthoquinone is oxidized to phthalic acid, on the assumption that the bond between the two CO groups is the first to break, may thus with some probability be assumed to be:


β-Naphthoquinone


o-Carboxy-cinnamic acid


o-Carboxy-benzoyl-acetic acid

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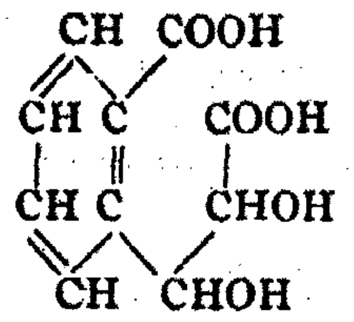
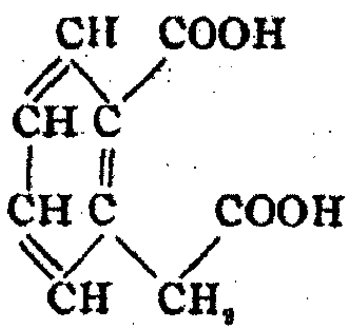
[1] Ber. chem. Ges., 25, 888 (1892).

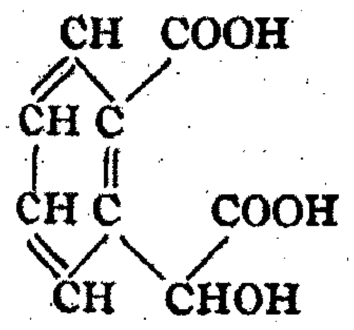
[2] Fittig: Liebig's Ann., 268, 27 (1892).



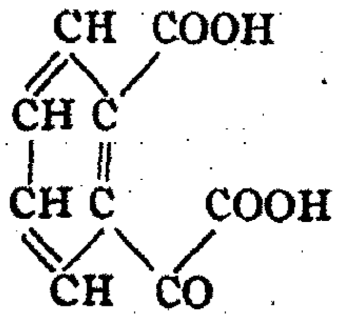
o-Carboxy-phenyl-glyceric acid



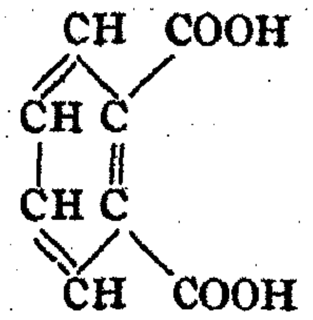
Homophthalic acid



o-Carboxy-mandelic acid



Phthalonic acid



Phthalic acid

Substances Used in the Experiments

β-Naphthoquinone, prepared by the method of Lagodzinski and Hardine[1] and purified by the method described in my paper on "Analytical Methods."[2]

The lactone of ortho-carboxy-phenylglyceric acid, by the method of Zincke;[3] melting-point 202°.

Ortho-carboxy-cinnamic acid, by the method of Ehrlich and Benedikt.[4]

Phthalyl-acetic acid, by the method of Gabriel and Neumann.[5]

Homophthalic acid, by the method of Graebe and Trümpy,[6] melting-point 174°–175°.

The lactone of phthalid-carbonic acid, by the method of Graebe and Trümpy,[7] melting-point 150°–152°.

Phthalonic acid, by the method of Graebe and Trümpy.[8] As I found that air-dried phthalonic acid does not contain a

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[1] Ber. chem. Ges., Berlin, 27, 3075 (1894).

[2] Jour. Am. Chem. Soc., 29, 230 (1907).

[3] Ber. chem. Ges., Berlin, 25, 405 (1892).

[4] Monatsheft, 9, 528 (1888).

[5] Ber. chem. Ges., Berlin, 26, 952 (1893).

[6] Ibid., 31, 375 (1898).

[7] Ibid., 31, 373 (1898).

[8] Ibid., 31, 369 (1898).

definite amount of water of crystallization,[1] I used anhydrous acid which I prepared by heating the air-dried acid at 115° to constant weight.

α-Naphthoquinone, by the method of Japp and Miller,[2] and purified by repeated crystallization from petroleum ether; melting-point 124°–126°.

The α-naphthol and the naphthalene were "chemically pure" preparations of Kahlbaum.

Method of Working

The rates of oxidation were measured as follows: In a 150 cc glass stoppered bottle was placed 0.1000 gram naphthoquinone (or an amount of one of the other substances proportional to its formula weight); and a mixture of 70 cc of potassium bichromate solution (7.648 grams $K_2Cr_2O_7$ per liter) with 5 cc of dilute sulphuric acid (150 grams H_2SO_4 per liter) was added. The bottle was completely immersed in a bath of boiling water; at the expiration of a measured interval it was removed, emptied into a beaker containing 75 cc ice water and titrated with approximately fortieth-normal ferrous sulphate, using potassium ferricyanide as external indicator in the usual way. The results of the measurements are contained in Table I.

In the first column are the names of the substances; in the second the formulas; in the third the weights taken; in the fourth, after the duration of the oxidation in minutes, and after *Bi* the amount of bichromate reduced expressed in cc of a *solution* containing 7.648 grams $K_2Cr_2O_7$ per liter. In the fifth column, under *P*, are entered the number of cc of bichromate (calculated from the formulas) necessary to oxidize the substance to phthalonic acid, and under *T* the number of minutes (obtained graphically from the data of the table) in which these quantities of bichromate are reduced.

Of course, it cannot be assumed that at the moment *T* nothing but phthalonic acid is present in the solution, for that

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[1] Jour. Am. Chem. Soc., 29, 230 (1907).

[2] Jour. Chem. Soc., 39, 220 (1881).

TABLE I

Substance	Formula	Weight taken Gram	Results of the Measurements								P	T
β-Naphtho-quinone	$C_{10}H_6O_2$	0.1000	t — 2.5	5	10	20	40	80	150	210		
			Bi — 4.4	14.4	21.6	27.3	31.6	37.7	41.5	45.7	40.5	128
Ortho-carboxy-cinnamic acid	$C_{10}H_8O_4$	0.1215	t — 30		60	90		120	150	180		
			Bi — 9.1		12.7	18.8		19.3	21.5	21.2	32.4	250
Ortho-carboxy-phenylglyceric acid	$C_{10}H_8O_5$ (Lactone)	0.1317	t — 30		60	90		120	150	180		
			Bi — 1.2		5.0	9.5		12.8	17.8	21.9	24.3	200
Phthalyl-acetic acid	$C_{10}H_6O_4$	0.1203	t — 30		60	90		120	150	200		
			Bi — 8.5		12.7	15.1		17.2	20.6	24.6	24.3	200
Homophthalic acid	$C_9H_8O_4$	0.1140	t — 30		90	120						
			Bi — 0.5		1.2	1.9					16.2	over 1000
Phthalid-carbonic acid	$C_9H_6O_4$ (Lactone)	0.1130	t — 30		60	90		120				
			Bi — 1.5		3.6	5.1		6.9			8.1	160
Phthalonic acid (anhydrous)	$C_9H_6O_5$	0.1230	t — 40		80	140						
			Bi — 8.2		10.2	16.9					0	0
Phthalic acid	$C_8H_6O_4$	0.1050	t — 30		60	90						
			Bi — 1.0		3.0	6.0					—	—

substance itself is oxidized by chromic acid. This reaction, however, takes place slowly in the relatively dilute solution of chromic acid left by the previous oxidation, as is shown by the measurements of Table II.

TABLE II

Phthalonic acid Gram	Bichromate cc.	Sulphuric acid cc.	t. minutes	Bi. cc.
0.1230	70	5	40	8.2
0.1230	70	5	80	10.2
0.0615	70	5	40	2.7
0.0615	70	5	80	4.4
0.1230	35	5	40	6.0
0.1230	35	5	80	8.0
0.1230	70	2.5	40	6.3
0.1230	70	2.5	80	7.0

The weights of anhydrous phthalonic acid taken are entered under *Phthalonic acid*, the volumes of the bichromate solution and of the acid (page 123) under *Bichromate* and *Sulphuric acid* respectively, the duration of the oxidation under *t*, and the bichromate reduced under *Bi*. The great effect of the concentrations of the reagents on the rate is sufficiently obvious. From a graph of the results it appears that the rate is proportional to the concentrations of the sulphuric acid and of the bichromate respectively, and to the square of that of the phthalonic acid; but for the purposes of this paper it was not necessary to undertake special measurement to establish this relation rigorously.

Far the greater part of the phthalonic acid formed in my experiments would thus escape further oxidation: and, in fact, the presence of that substance in each of the solutions at the expiration of *t* minutes was established by the test with potassium permanganate described in my paper on "Analytical Methods."[1] This test was carried out as follows. First, the chromic acid remaining was reduced with ferrous sulphate. The phthalonic acid

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[1] loc. cit.

was then isolated by neutralizing with sodium carbonate, acidifying with hydrochloric acid, evaporating to dryness on the water-bath, extracting with absolute alcohol and evaporating the alcoholic extract to dryness; the residue was then dissolved in a little water and filtered. The solution so obtained was acidified with dilute sulphuric acid, and decinormal permanganate was added; in every case the color was discharged, a reaction characteristic of phthalonic acid and serving to distinguish it from phthalic, homophthalic and phthalid-carbonic acids.

Phthalonic acid is thus an isolable product of the oxidation of all six substances studied; similar experiments showed that it is formed by the oxidation of α-naphthoquinone; hitherto it has been known as a product of oxidation of naphthalene[1] and of α-naphthol[2] only.

I

β-Naphthoquinone

A glance at Table I shows that the number entered under *T* opposite β-naphthoquinone is the smallest in the column. In other words, 0.1000 gram of the quinone is oxidized to phthalonic acid in less time than it would take to oxidize any of the hypothetical intermediate oxidation products of Series B (page 121), even if they had been present in full concentration and had the chromic acid all to themselves.

This shows conclusively that neither orthocarboxycinnamic, ortho-carboxy-phenylglyceric, phthalyl-acetic, homophthalic, nor phthalid-carbonic acid can be formed in the course of the oxidation of β-naphthoquinone to phthalic acid; and, as has been pointed out in the introduction, positive evidence of this nature can be obtained in no other way. That phthalonic acid is an intermediate product is shown by the permanganate test described above.

The measurements with *o*-carboxy-phenylglyceric acid

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[1] Tscherniac: Ber. chem. Ges., Berlin, 31, 139 (1898); Graebe and Trümpy: Ibid., 31, 369 (1898).

[2] Henriques: Ibid., 21, 1607 (1888).

are particularly interesting, because the very preparation of this substance used in my measurements was itself made from β-naphthoquinone by the action of chloride of lime. There was therefore, *a priori*, a high degree of probability that it would prove to be one of the products of oxidation with chromic acid. Changing the oxidizing agent, however, has changed the whole course of the oxidation.

The experimental study of Series *A* was prevented by the circumstance that carboxy-phenylglyoxyl-formic acid has not yet been described in the literature, and that as yet I have had no leisure to attempt its preparation. In the present almost total absence of data of the kinetics of organic reactions, it is impossible to draw from its formula any sure conclusions as to its behavior on oxidation. The analogous phenylglyoxyl-formic acid, or rather an amino derivative of it, has been prepared by Baeyer and Homolka,[1] but nothing is said as to its behavior with oxidizing agents; similarly, nothing could be found as to the oxidation of dioxytartaric acid, or diphenyltriketone, both of which likewise contain the group CO.CO.CO. The result of my measurements, then, while conclusively disproving the possibility of the mechanism represented by the formulas of Series *B* leaves the question open as to Series *A*.

II

Genetic Relations between the Six Acids

From the data of Table I, collected in order to study the oxidation of β-naphthoquinone, some information as to the relations of the acids involved may be drawn. It is immediately obvious for instance, that homophthalic acid cannot be an intermediate product of the oxidation of either orthocarboxy-cinnamic, orthocarboxy-phenylglyceric, or phthalyl-acetic acids to phthalonic acid. Without further study of the relations between rates and concentrations, which (as aside from the main purpose of the research) was

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[1] Ber. chem. Ges. Berlin, 16, 2219 (1883).

not undertaken, nothing further definite can be said; but if the plausible assumption be allowed, that in each case the rate is proportional to at least the first power of the concentration of the acids oxidized, then none of the acids studied can be considered as intermediate stages in the oxidation to phthalonic acid of those higher in the Table.

III

α-Naphthoquinone

In this connection, a few experiments were conducted with α-naphthoquinone, the results of which are given in Table III.

TABLE III

α-Quinone taken Gram	Results of the Measurements						P	T
0.1000	*t*—30	60	90	120	150	180		
	Bi—5.1	11.6	20.8	26.2	31.6	35.6	40.5	220

Taken with the data of Table I these measurements show that orthocarboxy-cinnamic and homophthalic acids cannot be intermediate products in the oxidation of α-naphthoquinone to phthalonic acid under the circumstances of my experiments. Without further measurements to ascertain the effect of concentrations on the rates the same cannot be said of ortho-carboxy-phenylglyceric and phthalid-carbonic acids. Consideration of the structural formulas, however, makes it very unlikely. It is possible, however, to show from the data of Tables I and III that phthalyl-acetic acid cannot be an intermediate product.

40.5 cc bichromate are necessary to transform 0.1 gram of α-quinone into phthalonic acid and need 220 minutes to do it. 16.2 cc bichromate would be necessary to oxidize the quinone to phthalyl, acetic acid, and the table shows that this amount of bichromate is reduced in 77 minutes. Experiments on the rate of oxidation of phthalyl-acetic acid show (by interpolation) that in the last 22—077 = 143 minutes at most 0.51 equivalent[1]

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[1] By one "equivalent" is to be understood the weight of substance entered in column 3 of Table I.

of that substance could be oxidized, leaving at least 0.49 equivalent that must have been oxidized in the first 77 minutes. This oxidation would require 0.49 × 24.3 = 11.9 cc of bichromate out of the 16.2 actually reduced, leaving only 4.3 reduced by the quinone. The phthalyl-acetic acid formed by the reduction of this amount of bichromate, however, amounts to only 4.3/16.2 = 0.26 equivalent instead of the minimum of 0.49 required by the assumptions.

The assumption that phthalyl-acetic acid is an intermediate product of the oxidation of α-naphthoquinone to phthalonic acid is therefore disproved by the rate measurements.

The same process of reasoning makes it most improbable that phthalid-carbonic acid can be intermediate in the oxidation of orthocarboxy-cinnamic acid to phthalonic acid.

IV

α-Naphthol

The results of a series of experiments with α-naphthol given in Table IV show that homophthalic acid cannot be formed "on the way" to phthalonic acid; so far as my experiments go, however, any of the other six compounds studied may be intermediate compounds.

TABLE IV

α-Naphthol taken Gram	Results of the Measurements					P	T
0.091	*t*—30	60	90	150	180		
	Bi—18.6	20.1	25.1	26.7	29.2	56.7	580

V

The Action of Nitric Acid on Naphthalene

Laurent[1] and Beilstein[2] have shown that phthalic acid can be prepared by the action of nitric acid (sp. gr. 1.15) on naphthalene, and the latter even stated that "apart from the trouble of working in sealed tubes this is the cheapest way of

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[1] Liebig's Ann., 19, 38 (1836).

[2] Ibid., 202, 215 (1880).

preparing this substance." I undertook a long series of measurements in the hope of ascertaining the mechanism of this reaction but without success, as in all my experiments—whether carried out in tubes or in open vessels—large quantities of nitro compounds were formed, and conditions could not be found under which oxidation took place anything like quantitatively.

The following table gives the results of a series of determinations of the phthalic acid produced by the action of 40 cc of nitric acid (sp. gr. 1.15) in six hours at 100° on naphthalene, α- and β-naphthoquinones, homophthalic, and phthalid-carbonic acids.

TABLE V

Substance	Weight taken	Phthalic acid formed
Naphthalene....................	2.0000	0.076
"	2.0000	0.074
α-naphthoquinone..............	0.0712	0.057
"	0.0712	0.045
β-naphthoquinone..............	0.0712	0.043
"	0.0712	0.038
Homophthalic acid..............	0.0814	0.036
"	0.0814	0.047
Phthalid-carbonic acid...........	0.0804	0.041
"	0.0804	0.041

SUMMARY

The method of determining the course of an organic reaction discussed in this paper is complementary to the method of isolation of intermediate compounds heretofore exclusively employed. It is shown that under favorable circumstances simple measurements may quickly lead to definite conclusions.

In the case of the oxidation of β-naphthoquinone to phthalic acid, phthalonic acid is an intermediate product, while *o*-carboxy-cinnamic, *o*-carboxy-phenylglyceric, phthalyl-acetic, homophthalic, and phthalid-carbonic acids are not.

Homophthalic acid is not an intermediate product in the oxidation of any of the other acids named, of α-naphthoquinone, or of α-naphthol.

o-Carboxy-cinnamic and phthalyl-acetic acids are not intermediate products in the oxidation of *α*-naphthoquinone.

These conclusions hold only for chromic acid as oxidizing agent; changing the oxidizing agent may change the whole course of the reaction.

My thanks are due to Prof. Lash Miller, at whose suggestion this research was undertaken.

The University of Toronto,
December, 1906

MOLECULAR ATTRACTION. VI. ON THE MUTUAL NEUTRALIZATION OF THE ATTRACTION BY THE ATTRACTED PARTICLES AND ON THE NATURE OF ATTRACTIVE FORCES

BY J. E. MILLS

Introduction

We have in several previous papers[1] discussed an equation of the form, $\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, (L is heat of vaporization of a liquid, E_1 is the energy spent in overcoming external pressure, *d* and D are the densities of liquid and vapor respectively). This equation was derived theoretically on the assumption that the attraction between the molecules of a liquid varied inversely as the square of their distance apart and did not vary with the temperature. The equation has now been tested for thirty-three substances over wide ranges of temperature (usually from near the freezing-point of the liquid to the critical temperature), and the evidence in favor of the truth of the equation is exceedingly strong. This evidence will be briefly reviewed later. But admitting the truth of the equation, does it necessarily follow that the assumed law of attraction was the true one? Could it be possible that some other law of attraction, operating either by itself, or in connection with other energy changes, would give a similar equation? It is with this phase of the question that the present paper is concerned and we will endeavor to show that the assumptions upon which the equation is based are correct and that the equation is correctly deduced. Having given the evidence upon this point, we show further that the conclusion may be drawn with considerable certainty that the molecular attraction is mutually neutralized by the attracted particles. Finally, our knowledge of the laws of molecular

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[1] Jour. Phys. Chem., 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905); 10, 1 (1906).

attraction enables us to institute a comparison with other attractive forces and obtain some very suggestive results.

The conclusions to be drawn so closely concern our fundamental ideas of matter that we may be pardoned for briefly calling attention to laws and ideas, more or less generally admitted, upon which the present work is based.

The Fundamental Ideas Serving as a Basis for the Present Work

Our Idea of Matter.—Since scientists are somewhat divided in their belief as to the ultimate nature of matter, we would, even though it involves repetition from a previous paper, make clear our own position in this regard, for the question with which we are dealing leads back to a consideration of the nature of mass as we measure it, if not to a consideration of the nature of matter. Because we use the terms "molecule," "molecular attraction," and "distance between the molecules," we do not wish to be understood as possessing the idea that a molecule is *necessarily* a little hard sphere or some other particular shape of a piece of "something" extended in space. In the latter part of this paper we have something to say (by way of speculation suggested by the facts to be considered), regarding the possible ultimate nature of mass. But in the present part of this paper we do not care to consider the nature of matter. We do not care whether it consists wholly of a "something" that possesses the property of extension, or wholly of energy, or is a mixture of the two. The law of gravitation has been shown to hold between certain large masses of a thing commonly called "matter." If later it happens to be proved that matter (in the sense of an "extended something") is not reality and that only energy exists, we do not suppose the proof will greatly affect the calculations of the astronomers, or the position of the heavenly bodies, or their movement in accordance with the law of gravitation. The object of this series of papers is to throw light upon the law of attraction which exists between smaller masses of the same material of which these larger bodies are more conspicuous representatives. Following considerable precedent, we have called these "smaller masses" molecules, a term which conveys to every scientist a group of properties sufficiently clearly defined for the purpose in view. By the expression "distance between the molecules," we mean the distance between their centers of mass—an expression exactly analogous to the distance between two heavenly bodies. The "center of mass" is therefore a mathematical point, determined by the same principles that would be used for large masses. The term "molecular attraction" indicates a force which can be regarded as having its origin at the mathematical point thus determined. We are accordingly entirely free from any assumption as to the size of the particles (molecules), their nature or the ultimate cause of the force. What we really assume is, that in nature certain forces *act as though they proceeded from mathematical points*, and we clothe these mathematical points with the name "molecule."

The Kinetic Theory of Gases.—It is by no means necessary for us to point out how the laws of gases discovered by Boyle and Gay-Lussac, and the simple relations connecting the densities of gases, discovered by Gay-Lussac, but stated most clearly in terms of Avogadro's hypothesis, that 'equal volumes of all gases contain the same number of molecules, are explained by the kinetic theory of gases. Nor how this theory similarly explains Dalton's law for the pressure of mixed gases and Henry's law governing the solution of a gas in a liquid. Nor how the theory led Clerk Maxwell to the discovery of the law governing the viscosity of gases, and Waterston to the simple relation existing between the two specific heats of a gas. The Van der Waals theory also is a fruit of the kinetic theory and indeed the kinetic theory has been the stimulus and the guide to much of the work upon both liquids and gases. We do not believe that there are many chemists who will object to the acceptance of the kinetic theory of gases as a basis for further work.

According to the kinetic theory of gases we may regard the total energy of a gaseous molecule as being the sum of certain amounts of energy which may be quite clearly differentiated from each other. We would distinguish these energies as follows:

(1) *The Cheimcal Energy, or Energy of Combination of the Atoms Constituting the Molecule.*—It can be shown, independently of theory, that the molecule must possess this energy at the absolute zero of temperature, —273° C. (We do not suppose that all motion ceases at this temperature. Just what part of the motion ceases is perhaps even yet a matter of doubt.) To prove this proposition we will consider the reaction:

2.016 grams hydrogen (gas) + 16.00 grams oxygen (gas) = 18.016 grams water (liquid).

The amount of heat evolved by this reaction, when taking place at 18° C, has been measured by Thomsen and found to be 68420 calories. Now the total amount of heat necessary to raise the hydrogen and oxygen from the absolute zero to 18° C can be ascertained from the following data.

	Hydrogen	Observer	Oxygen	Observer
Melting-point........	14.1°	Travers	Below 50°	Travers
Boiling-point.........	20.41	Travers	90.20	Travers
Specific heat of solid.	2.3 cals.	Kopp	0.25 cals.	Kopp
Specific heat of liquid	6.00 "	Estimated Dewar	0.347 "	Alt
Specific heat of gas..	3.410 "	Wiedemann	0.2175 "	Regnault
Heat of fusion.......	16.0 "	Estimated Dewar	4.9 "	Estimated
Heat of vaporization.	125.0 "	Dewar	50.92 "	Alt

The specific heat of ice is given as 0.4627 by Regnault and the heat of fusion of ice as 79.90 calories by Smith.

If to the energy added to the substance as specific heat of the solid, liquid and gas respectively, there be added the heat of fusion and the heat of vaporization, we will obtain the total heat required to raise the body from the absolute zero of temperature to the chosen temperature, in this case to 18° C. We have therefore for the total energy necessary to raise the temperature from 0° absolute to 18° C for,

2.016 grams of hydrogen	= 2286	calories
16.00 grams of oxygen	= 2015	"
18.016 grams of water	= 3865	"

The values given are probably maximum values and not very far from the truth except in the case of water, where we think the value would probably be considerably too large, due to the use of the specific heat for ice as found by Regnault between —78° and 0° C as representative of the average specific heat of ice, —273° to 0°. The value of the specific heat, judging from analogy, probably decreases as the temperature is decreased.

It appears therefore that in raising the 2.016 grams of hydrogen and the 16.00 grams of oxygen from the absolute zero to 18° C only 4301 calories of energy were required, while at this temperature 68420 calories were given out when they combined. Since the water formed possesses about 3865 calories of energy, it follows that the hydrogen and oxygen possessed at least 67,984 calories of chemical energy at the absolute zero. Further, since only the difference between the chemical energy of the H_2 and O_2 on the one hand and of the H_2O on the other, is ascertained, we cannot make any statement as to the actual amount of chemical energy possessed by the H_2 and O_2 at the absolute zero. We can only say that it is certainly *not less than* 67,984 calories. It may be many times more.

It follows from the above that the chemical energy has been either entirely unaffected by the change in temperature of 291°, or has been affected only in a very minor degree. For a stable chemical body, where the change in temperature is not large, we have little hesitation in saying that the chemical energy, E_C, of the body is a constant.

$$E_C = \text{constant}. \tag{1}$$

We will return later to a further discussion of the chemical energy.

(2) *The Translational or Kinetic Energy of the Molecule.*—This energy for any particular molecule is equal to one-half the mass of the molecule multiplied by the square of its velocity. It follows from the well-known investigation of Clerk Maxwell that the velocities of the different molecules of a gas vary somewhat, but the variation is confined within rather narrow limits and only very few of the molecules have a velocity greatly above or greatly below the average molecular velocity. This theorem of Maxwell regarding the distribution of velocity among the molecules of a gas has been proved with strictness for the supposition that the molecules act on each other only at the moment of collision. For such a condition, using the constants adopted in former papers, the sum of the translational energy, E_K, of all of the molecules can be represented by

$$E_K = {}^3/_2\,RT = 2.9817\,\frac{T}{m}\ \text{calories}, \tag{2}$$

where T is the absolute temperature, and *m* is the molecular weight referred to oxygen = 16.00 as standard.

It has never been shown that the translational energy of a molecule, when the molecule is subject to attractive force, can be calculated by this formula and the formula is therefore proven (with assumption of the kinetic theory) only for so-called "perfect" gases.

(3) *The Internal Energy of a Molecule.*—Experiments have shown that the specific heat of a gas at constant pressure is nearly a constant over considerable ranges of temperature. The variation from absolute constancy appears to be due to variations from the gas laws, when the gases examined are far removed from the condition designated as "perfect" gases, and also to certain progressive changes taking place within the molecule as the temperature is raised—the progressive changes finally ending in the decomposition of the molecule. The measurements therefore make it very prob-

able that for a perfect gas, and one that is chemically stable (that is, one in which the chemical energy does not change with the temperature), the specific heat at constant pressure would be a constant.

But for such gases the law, $PV = RT$, holds true, and consequently, $PdV = RdT$, which for a change of one degree gives, $PdV = R$. If σ_p and σ_v denote the specific heat at constant pressure and constant volume respectively, we have,

$$\sigma_p - \sigma_v = PdV = R. \tag{3}$$

If the increase in the translational energy of the molecules of any gas be subtracted from the specific heat at constant volume of the gas, a certain residue remains (equal to zero for monatomic gases), which we shall consider as being due to a change in the internal energy, E_I, of a molecule. We will have, therefore,

$$\sigma_v = \frac{dE_K}{dT} + \frac{dE_I}{dT} = \text{constant}. \tag{4}$$

True strictly only for a "perfect" gas.

Now from the theory by Waterston,

$$\gamma = \frac{\sigma_p}{\sigma_v} = \frac{dE_K + dE_I + R}{dE_K + dE_I}, \ dT \text{ being equal to } 1° \text{ C}. \tag{5}$$

Wherefore, substituting for R its value, $2/3dE_K$, and solving,

$$E_I = \frac{{}^5/_3 - \gamma}{\gamma - 1} E_K = 2.9817 \left(\frac{{}^5/_3 - \gamma}{\gamma - 1}\right) \frac{T}{m} \text{ calories}. \tag{6}$$

The internal energy in a perfect gas is therefore proportional to the translational energy.

The exact function of the internal energy required by a molecule has never been satisfactorily explained, but the fact that it is proportional to the translational energy leads to the belief that the internal energy is a direct consequence of the translational energy. It should be understood, however, *that equation 6 embodies no assumption whatever regarding the internal energy.* That it is proportional to the translational energy follows necessarily, if the specific heat at constant volume is a constant, and if the gas law, PV = RT, holds. Nor will the possibility that this internal energy is merely the rate of change of (the differential of) the chemical energy with the temperature, in any way affect our conclusion.

The data upon the specific heat of gases cannot be discussed briefly. Much of the data is given and discussed in Meyer's Kinetic Theory of Gases and in Nernst's Theoretische Chemie. Reference must be made to these or similar works for the actual data showing the constancy of the specific heat under the conditions set forth above.

(4) *The Energy of Position Due to the Attraction between the Molecules.*—It is the purpose of this series of papers to show that this potential energy is due to an attractive force emanating from each molecule—that this force varies inversely as the square of the distance apart of the molecules—is mutually neutralized by the attracting particles—and is unaffected by temperature changes. We will later deduce the law governing this energy.

(5) *The Energy of Volume Due to the External Pressure.*—This energy, it is evident, is measured simply by the pressure times the volume. Denoting the energy by E_E we have,

(7) $$E_E = 0.0_4 31833 \text{ PV calories,}$$

where P is expressed in millimeters of mercury. The constants used have been given in previous papers.

We can regard a perfect gas as a gas in which there is no energy due to attraction and therefore the energy of such a gas could be represented thus:

(8) $$\Sigma E = E_{\text{Chemical}} + E_{\text{Kinetic}} + E_{\text{Internal}} + E_{\text{External}}.$$

We can also regard a perfect gas as one in which the molecules are so far removed from each other that their mutual attraction has no appreciable effect in modifying the motions of the particles. Such a gas would still possess potential energy due to the attraction and we would therefore have,

(9) $$\Sigma E = E_{\text{Chemical}} + E_{\text{Kinetic}} + E_{\text{Internal}} + E_{\text{Attraction}} + E_{\text{External}}.$$

We could differentiate between the chemical energy as being a function of the atoms, the kinetic, internal, and attractive energies, as being a function of the molecule, and the external energy as being a function of the mass. The internal energy may be only the differential of the chemical energy with respect to the temperature, and consequently, be more directly a function of the atoms.

Equations 8 and 9 represent the condition of things in a perfect gas. If we now consider a saturated vapor, or a liquid, where the molecules are so close together that the gas laws are not obeyed, it is evident from what has been already stated that E_C, is, if the body be chemically stable, the same as for that substance when existing as a perfect gas. The value for the external energy, E_E, can be readily calculated independently of assumptions save the first law of thermodynamics. The internal energy, E_I is, we have seen, proportional to the translational energy, E_K, and it is highly improbable that this proportionality would be destroyed by the nearness of the molecules and their increased mutual attraction. The kinetic energy of the molecules might itself be altered, equation 2 having been proved to hold only for a perfect gas. But where mathematical proof is lacking, experimental evidence has taken its place. Since van't Hoff showed that for undissociated dissolved substances the osmotic pressure given by a dissolved substance was equal to the pressure that the dissolved substance would exert were it a gas at that volume and temperature, it has been very probable that the osmotic pressure was due to the same cause as the gas pressure, *viz.*, the motion of the dissolved particles, and therefore, the kinetic energy of the dissolved substance is the same that it would be for a gas under the same conditions of temperature and volume.

The molecules of the dissolved substance could not have an average kinetic energy different from the average kinetic energy of the molecules of the solvent, a fact long ago pointed out by Ostwald.[1] Therefore it seems probable that equation 2 holds also for liquids.

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[1] Solutions, pp. 147, 148.

(The work of Morse and Frazer[1] shows that the theory of van't Hoff needs some modification, and the work of Kahlenberg[2] is in evidence against the theory. We would, as regards the work of Kahlenberg, point out that his experiments, Nos. 53 and 59 and 60, show that the dissolved substance was obeying Boyle's law for gases (as concerns concentrations), and experiment No. 53 was *performed without stirring.* Also the manometer tube attached to Kahlenberg's osmotic cell, as given by him, was only of 0.5 mm bore, and consequently, to produce a rise of 50 cm in his manometer tube only 1/10 of a cubic centimeter of liquid needed to enter the cell. The amount of LiCl leaving the cell was 0.0130 and 0.0267 and of cane sugar 0.1149 and 0.2205 of a gram and *the osmotic pressure is determined by the relative rate of inflow and outflow.* It seems to us possible, also, that thermometer effects of the cell were not wholly eliminated from influencing the results. We would not therefore, as yet, abandon van't Hoff's theory and its results as a reason for believing that Equation 2 holds also for liquids and that the average kinetic energy of the molecules of a liquid is equal to the average kinetic energy of the molecules of its vapor at the same temperature.)

Further, Traube finds that his "co-volume" for liquids varies as the absolute temperature.[3]

We will give additional evidence on this subject in a subsequent paper.

If it be granted, then, that equation 2 holds also for liquids and for saturated vapors the energy of a molecule of a vapor differs from the energy of a molecule of a liquid only because of changes in E_A and E_E. The latter change is easily calculated and we can therefore obtain a measure of the former—the energy change due to the attraction.

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[1] Am. Chem. Jour., 34, 1 (1905).

[2] Jour. Phys. Chem., 10, 3, 141 (1906).

[3] Numerous papers. Among others, J. Traube: Grundriss d. phys. Chemie. Boltzmann: Festschrift (1904); Zeit. anorg. Chem., 40, 380 (1904). Sammlung: Chemischer und chemisch-technischer Vortrage, 4, 255.

Expressing the above belief in a different form, we may say that the energy necessary to change a liquid into a gas must, then, be spent solely in overcoming the external pressure and in altering the distance apart of the molecules. (Unless the molecule breaks apart also or nears the point of disruption.)

Denoting the heat of vaporization by L and the energy necessary to overcome the external pressure during the change from liquid to gas by E_E, $L - E_E$ must equal the energy spent in overcoming the molecular attraction.

Derivation of the Equation.—The derivation of this equation as given in the first paper of this series was not carried out with strictness and we therefore give below a proof which we believe to be mathematically rigorous.

Let v and V represent the volume of the liquid and vapor before and after expansion, and d and D represent the corresponding densities. Let n equal the number of molecules and m the mass of each molecule. Suppose the molecules evenly distributed throughout the space occupied by them. Then $\sqrt[3]{v/n}$ and the $\sqrt[3]{V/n}$ represent the relative distance apart of the molecuiles of liquid and vapor respectively.

It is highly improbable that the molecules of a liquid are evenly distributed throughout the space occupied by them. But if they are shifted from their ideal position by reason of the attractive force, the particles would gain in kinetic energy exactly so much as they would lose in potential energy. We may therefore, without error, consider them to be shifted back into this ideal position of even distribution, and the fundamental supposition upon which the mathematical work given below is based, is, that the molecules of a liquid and the molecules of its vapor have *per se* (exclusive of E_A and E_E), the same energy *when they are in this ideal position of even distribution throughout the space occupied by them.*

If this supposition represents truly the condition of the molecular energy, then it is possible to find the law governing the forces which act between the molecules. For we have only to assume the law and deduce the corresponding equation. If the deduced equation fails to agree with the experimental facts then another law could be assumed and the process repeated until the correct supposition had been made.

We will assume that the molecular attraction varies inversely as the square of the distance apart of the molecules and is a mutual property of each pair of molecules. Hence the force $= \frac{\mu^2 m^2}{r^2}$, where μ is the attraction at unit distance on unit mass and r is the distance apart of the molecules whose mass is represented by m.

If, now, we consider two molecules whose distance apart is $x\sqrt[3]{v/n}$ before expansion (vaporization), after expansion their distance apart will be $x\sqrt[3]{V/n}$ and the work done in pulling them apart will be

$$(10)\qquad \int_{x\sqrt[3]{V/n}}^{x\sqrt[3]{v/n}} m^2\mu^2\frac{dr}{r^2} = \frac{m^2\mu^2}{x}\left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}}\right),$$

where x is an unknown constant. If we in turn consider the work, W_1, done in pulling all of the molecules away from one molecule, and sum up, we will have, similarly,

$$(11)\quad W_1 = m^2\mu^2\left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}}\right)\left(\frac{1}{x} + \frac{1}{x_1} + \frac{1}{x_2} + \quad + \frac{1}{x_{n-2}}\right).$$

If now we take any other molecule and similarly sum up the energy, W_2, required to pull all of the molecules away from it, we have for the work so done,

$$(12)\quad W_2 = m^2\mu^2\left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}}\right)\left(\frac{1}{x'} + \frac{1}{x_1'} + \frac{1}{x_2'} + \quad + \frac{1}{x'_{n-2}}\right).$$

By similarly extending the process to other molecules, each considered in turn as a center, we will obtain a series of similar expressions, n in number. The last factor of each member of the series depends only upon the number of the molecules n, and is entirely independent of the nature of the molecules or of the forces. We may, therefore, denote this last factor in the different series by $c_1, c_2, c_3, \ldots\ldots\ldots\ldots c_n$.

Summing up the entire n series of equations we will have

$$(13) \quad W_1 + W_2 + W_3 + \quad + W_n = m^2\mu^2\left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}}\right)(c_1 + c_2 + c_3 + \quad + c_n).$$

The last factor of this equation is a constant if the number of molecules remains the same. Let C represent this constant. We have then for the total work of expansion, W,

$$(14) \qquad W = m^2\mu^2\left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}}\right)C.$$

Equation 14 gives the entire energy required to pull all of the molecules from each other as vaporization proceeds. It must therefore equal the internal heat of vaporization and we have for mass M,

$$(15) \qquad M(L - E_E) = m^2\mu^2 C\left(\frac{1}{\sqrt[3]{v/n}} - \frac{1}{\sqrt[3]{V/n}}\right).$$

Letting $d = \frac{nm}{v}$, $D = \frac{nm}{V}$, $M = nm$, we have

$$(16) \qquad \frac{M(L - E_E)}{\sqrt[3]{d} - \sqrt[3]{D}} = \frac{M^2\mu^2 C}{n^2\sqrt[3]{m}},$$

or for a constant mass,

$$(17) \qquad \frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}.$$

The constant of equation 17, we shall call μ'.

(In the previous derivation of this equation, 17, we assumed, $c_1 = c_2 = c_3 = \ldots\ldots = c_n$, a fact which is experimentally true, but which is contradictory to the law of attraction assumed, if the latter is unmodified. Also we regarded the entire attraction in each case as proceeding from one molecule and being measured by $\frac{\mu m}{r^2}$, instead of being a mutual property of the two molecules and being measured by $\frac{\mu^2 m^2}{r^2}$. See further below.)

Evidence Proving the Equation.—The evidence proving that $\frac{L - E_R}{\sqrt[3]{d} - \sqrt[3]{D}}$ is equal to a constant, has been given in the second, third and fifth papers of this series. We would only summarize here by saying that thirty-five substances have now been examined, at intervals of 10° C, over wide ranges of temperature, extending usually from near the boiling-point of the substance to the critical temperature. Within 10° of the critical temperature there is an apparent divergence due to causes shown. Omitting these observations out of 435 remaining observations on 26 different substances only thirty differed from the mean value of the constant for that substance by more than 2 percent and only four of these thirty by more than 5 percent. The reason for most of these divergences is suspected and investigation will be made of them later. Of the remaining substances, CO_2, N_2O, and SO_2 gave probably as good agreement as the data permitted. Five other substances were associated and showed, as was to be expected, a divergence from a constant value for the constant, and $SnCl_4$ likewise showed a divergence. The evidence in favor of the truth of the equation is therefore most convincing. That the equation itself is true can hardly be doubted when the evidence is examined. But does it follow that the assumed law of attraction is the true one?

The Neutralization of the Attraction by the Attracted Particles

The answer to this question is of great interest. For if the attraction between the molecules varies inversely as the square of their distance apart, then the resultant attraction caused by the large number of molecules must apparently increase as we proceed outward from an interior centrally chosen particle. This follows because the number of molecules increases as the cube of the distance from the centrally chosen molecule, whereas the attraction varies only inversely as the square of that distance. Hence the resultant attraction of any mass upon a particle exterior to the mass, when regarded as proceeding from the center of that mass, must vary as the mass.

The molecular sphere of action could not, therefore, be small but would embrace the entire mass taken. Now we regard the evidence that the molecular sphere of action is small, as being beyond dispute, and will not attempt here to give the evidence for this idea. But we will point out that the derived equation 16, itself bears evidence that we have in previous papers been considering only one phase of the question. The equation was given in the form, $\frac{M(L-E_E)}{\sqrt[3]{d}-\sqrt[3]{D}}=\frac{M^2\mu^2C}{n^2\sqrt[3]{m}}$, where M represents the mass of liquid taken for the vaporization. Now in the test of the equation, the number of molecules was assumed constant, and this was justifiable, since it would be experimentally possible to have them constant. But should they vary, we know experimentally that the left-hand side of the equation varies simply with the mass taken. While the right-hand side of the equation varies, not alone because of the variation thus caused in M, but also because of the variation caused at the same time in C and in n. Since C is a function of n it might be supposed, as one occurs in the numerator and the other in the denominator, that the variation would cancel. We have not succeeded in summing up the $n(n-1)$ terms represented by the C of equation 16, but the relation of C to n can be obtained by attacking the problem somewhat differently.

Helmholtz in 1854 investigated the amount of energy that would be given out by the contraction of the sun in order to determine if the energy continually radiated from that body could be thus obtained. In this investigation he assumed that the particles of which the sun was composed were at the same temperature before as after the contraction, the excess of energy having been radiated off into space. He also assumed that the force acting between the particles of the sun's mass obeyed the Newtonian law of gravitation. Hence the investigation was essentially the same as the one above carried out. But Helmholtz made possible a better mathematical treatment by the assumption that the sun was homogeneous in density. We take the liberty of giving below the investigation as given by Helmholtz.[1]

Consider a homogeneous gaseous sphere whose radius is R_0 and density σ. Let M_0 represent its mass. Let dM represent an element of mass taken anywhere in the interior or at the surface of the sphere. Let R be the distance of dM from the center of the sphere, and let M represent the mass of the sphere whose radius is R. The element of mass in polar coordinates is

$$dM = \sigma R^2 \cos\phi \, d\phi \, d\theta \, dR. \tag{18}$$

The element is subject to the attraction of the whole sphere within it. As can be shown, the attraction of the spherical shell outside of it balances in opposite directions so that it need not be considered in discussing the forces acting upon dM. Every element in the infinitesimal shell whose radius is R is attracted towards the center by a force equal to that acting on dM; therefore, the whole shell may be treated at once. Let dM_s represent the mass of the elementary shell whose radius is R. It is found by integrating 18 with respect to θ and ϕ. Thus,

$$dM_s = \sigma R^2 dR \int_0^{2\pi} \left\{ \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos\phi d\phi \right\} d\theta = 4\pi\sigma R^2 dR. \tag{19}$$

The force to which dM_s is subject is $-\frac{K^2 M dM_s}{R^2}$. The element of work done in moving dM_s through the element of distance dR is

$$dW_s = -dM_s \frac{K^2 M}{R^2} dR.$$

The work done in moving the shell from the distance CR to

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[1] Celestial Mechanics. Moulton, p. 58.

R is the integral of this expression between the limits CR and R, or

$$W_s = -dM_sK^2M\int_{CR}^{R}\frac{dR}{R^2} = \frac{dM_sK^2M}{R}\left(\frac{C-1}{C}\right).$$

But $M = {}^4/_3\pi\sigma R^3$; hence, substituting the value of dM_s from equation 19 and representing the work done on the elementary shell by $W_s = dW$, it follows that

$$dW = {}^{16}/_3\,\pi^2\sigma^2K^2\left(\frac{C-1}{C}\right)R^4dR.$$

The integral of this expression from 0 to R_o gives the total amount of work done in the contraction of the homogeneous sphere from radius CR_o to R_o. That is,

$$(20)\quad W = {}^{16}/_3\,\pi^2\sigma^2K^2\left(\frac{C-1}{C}\right)\int_0^{R_o}R^4dR = {}^{16}/_{15}\,\pi^2\sigma^2K^2\left(\frac{C-1}{C}\right)R_o^5,$$

which may be written

$$(21)\qquad W = {}^3/_5K^2\left(\frac{1}{R_o}-\frac{1}{CR_o}\right)M_o^2.$$

Now if the contraction takes place between the limits $\sqrt[3]{\frac{3v}{4\pi}}$ and $\sqrt[3]{\frac{3V}{4\pi}}$ we have for the work done,

$$(22)\quad W = {}^3/_5K^2M_o^2\left(\frac{1}{\sqrt[3]{\frac{3v}{4\pi}}}-\frac{1}{\sqrt[3]{\frac{3V}{4\pi}}}\right) = 0.9682\,K^2M^{5/3}\left(\sqrt[3]{d}-\sqrt[3]{D}\right).$$

Comparing this expression with equation 14 we have only to replace the attraction at unit distance between the elements of mass, K, by the molecular attraction at unit distance μ, and observe that $C = 0.9682n^{5/3}$, if the mass were of uniform density throughout. We cannot see how the transformation from a sphere of uniform density to one of uniformly distributed particles could effect any change in the energy relations involved. We would therefore write:

$$(23)\qquad \frac{M(L-E_E)}{\sqrt[3]{d}-\sqrt[3]{D}} = 0.9682\mu^2M^{5/3}.$$

So long as a constant mass is taken, the equation will reduce to the form, $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$. If, however, the mass be varied, the equation informs us that the work done should vary as the five-thirds power of the mass. It should require three and two-tenths times as much heat to vaporize 2 grams of a liquid as to vaporize 1 gram. As a matter of fact, we know that it only requires twice as much heat to vaporize 2 grams as to vaporize 1 gram. How is this discrepancy to be explained?

In attacking this problem we would call attention to the fact that the equation, $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant}$, does correctly represent the variation of the energy change caused by the attraction with the distance, as is shown by the evidence accumulated in previous papers and as indicated in the brief summary above. It seems reasonable therefore to suspect the cause of the variation to be due to the numerator of the function representing the law of the force, $f = \frac{\mu^2 m^2}{d^2}$, and not to the denominator.

If now, we study the action of other attractive forces, such as magnetic forces, we find an explanation of the apparent contradiction at once suggested. The magnetic force varies directly as the product of the strengths of the poles and inversely as the square of their distance apart. But the interposition of a piece of sheet iron into the magnetic field between the magnet and the attracted particles serves to cut off the attraction, more or less completely, from the formerly attracted particles. Whether we look upon the interposed sheet of iron as actually absorbing the force, or as merely changing the direction of the lines of force, is not essential, the result at least is clear—particles beyond the interposed sheet of iron are subject to less attraction because of the interposition. So if we were to imagine a magnetized particle of iron surrounded by other particles of iron, evenly distributed, and similarly magnetized, the attraction would vary inversely as the square of the distance apart of the particles and yet the sphere of action of any particular particle would be small, due to the shielding action of the particles. And it seems to us that we may have here an exact representation of molecular attraction.

There is much indirect evidence to support such a conclusion. The attraction designated as chemical affinity is mutually absorbed by the combining bodies. At least the force is canceled by the combination so far as its effect on other particles is concerned. The combination of one sodium atom with one chlorine atom certainly serves to shield other bodies from the attractions of both the sodium and the chlorine, rendering them in large measure chemically inert. And this action is commonly represented by saying that the "bond" of the sodium is neutralized or saturated by the "bond" of the chlorine. As we have just mentioned, a similar effect happens with magnetic forces. If electrical forces be considered we find again the same to be true. And if we undertake to consider yet more closely the nature of attractions in general, is it not apparent, that, whatever the ultimate nature of the attractive force may be, yet it cannot be infinitely multiplied? That just so much force must emanate from each particle, and if this force is exerted on one particle there will be somewhat less of the force remaining for the remaining particles? *Is it not unreasonable to suppose that a particle could exert its attractive pull upon one thousand, or one million, or one hundred million, particles and yet always have just as much of its force remaining to exert on other particles brought within the same distance*? We are not confusing force and energy. Can a man by means of a rope exert the same pull on each of twenty other men that he could exert on one man? Does not each stress exerted lessen by just so much the power of the man to exert a similar pull upon other things? Can we multiply, *ad infinitum*, any force about whose real nature we know anything at all, merely by the introduction of further objects upon which the force can be exerted? Is there any form of wave motion, vibration, or emanation, known, whose effect can be thus infinitely increased?

Look at the question from the other side. Is it reasonable, that the introduction of particles of matter into the space surrounding a molecule should be absolutely without influence on the emanation which proceeds from the molecule and gives rise to the phenomena of attraction? And that this filling in of the space surrounding a molecule with other particles of matter (or centers of energy, if you choose), should be able to continue, *ad infinitum*, without disturbing the attractive radiation proceeding from the body?

Moreover, the mere fact that all of the attractive forces, whose law of variation with the distance we know, do vary inversely as the square of the distance from the attracting body, *is evidence that the attractive force is in each case some sort of wave motion or emanation whose intensity decreases directly in proportion to the increase in the surface of the wave or emanation front,* since and because this surface varies as the square of its distance from the origin. Can we, on the one hand, believe that the intensity of these forces thus decreases, and on the other, consider them unmodified by the presence of matter and capable of infinite multiplication by the introduction of additional matter into an infinite range of action?

In place of such a conception we would introduce the idea *that the attractive forces, whatever their nature, whether chemical, molecular, magnetic, electrical, or gravitational, which proceed from a particle, are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount.*

We are of course aware that no such diminution of the attraction is supposed, or is supposed possible, for gravitational forces. That certain facts have led to the belief, difficult of conception as it may be, that this force attracts every particle of matter in the universe exactly as if no other particle of matter were present. And that these facts would at once be urged as contradicting the above statement as to the attractive forces. We would answer by calling attention in detail to the evidence in favor of the above idea.

Further Evidence Regarding the Molecular Attraction

As regards the molecular attraction the conclusions cited above have been based on evidence which, for purposes of examination, may conveniently be divided into five steps as follows:

1. The equality of the energy *per se* of the molecules of a liquid and of the molecules of its vapor at the same temperature. That is, $E_C + E_K + E_I$ for a molecule of a liquid equals $E_C + E_K + E_I$ for a molecule of its vapor, the difference in their energy consisting of a difference in E_A and E_E.

2. The assumption that the attraction was a mutual property of each pair of molecules, varying directly as the mass of the molecules (so long as the same chemical body is considered), and inversely as the square of the distance apart of the molecules. Later modified by 5 below.

3. The derivation of an equation expressing the energy relations necessitated by the above two conditions.

4. The experimental evidence deduced in favor of the equation.

5. The facts leading to the supposition that the molecular attraction is mutually absorbed by the attracting particles.

Examining these steps separately let us see which are open to doubt. Considering first the fourth—the experimental evidence in favor of the equation—we would here add nothing new. But we would put one portion of the evidence in a more striking form. We will use the equation derived by Helmholtz in 1854 as expressing the energy given out by the contraction of the sun, to calculate the energy given out by the contraction of isopentane from a gas to a liquid. The equation of Helmholtz has been given, equation 22, and is, for a change of volume corresponding to a change of density from D to *d*,

$$W = 0.9682K^2M^{5/3}. \tag{24}$$

To apply this equation to 1 gram of isopentane we have only to substitute for the constant in the above equation, the value for this constant that we have already found, 105.4. The equation then becomes,

(25) $$W = 105.4\,(\sqrt[3]{d} - \sqrt[3]{D}).$$

We give below in Table I the data and the results. The values given by equation 25 are in the column headed W. Under the heading $L-E_E$ we give the values of the internal heat of vaporization as actually determined from Young's measurements. It is inconceivable to us that the agreement between W and $L-E_E$ could be accidental.

TABLE I.—ISOPENTANE

Temperature	Density of liquid	Density of vapor	$\sqrt[3]{d} - \sqrt[3]{D}$	W	$L-E_E$
0° C	0.6392	0.001090	0.7585	79.9	81.3
20	0.6196	0.002358	0.7194	75.8	75.2
40	0.5988	0.004480	0.6781	71.5	70.7
60	0.5769	0.007819	0.6340	66.8	66.4
80	0.5540	0.01284	0.5871	61.9	61.8
100	0.5278	0.02022	0.5357	56.4	56.7
120	0.4991	0.03106	0.4788	50.5	50.9
140	0.4642	0.04728	0.4127	43.5	44.0
160	0.4206	0.07289	0.3316	34.9	35.4
180	0.3498	0.1258	0.2035	21.4	21.0
185	0.3142	0.1574	0.1399	14.7	14.0
187	0.2857	0.1833	0.0905	9.5	8.9
187.4	0.2761	0.1951	0.0712	7.5	6.9
187.8	0.2343	0.2343	0.0	0.0	0.0

The formula used by Helmholtz to represent the contraction of the sun does represent the contraction of isopentane from the gaseous to the liquid condition. And not only isopentane but essentially as well all of the non-associated substances examined by us. *For we have already published*[1] *similar comparisons for all of these substances,* the only difference being that we added to the energy given out by the contraction, the value of the energy due to the action of the external

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[1] See third paper of this series, Tables 1 to 21, and fifth paper, Tables 15 to 24.

pressure, and thus obtained the heat of vaporization. We have here republished the results for isopentane as coming from Helmholtz's formula only to emphasize the statement that we have not gone beyond the facts when we declare that, *as regards variation with the distance, the law of molecular attraction is identically the same as the law of gravitation, and precisely the same formula is applicable to both.*

The formula is,

$$E_A = \mu' (\sqrt[3]{d} - \sqrt[3]{D}), \tag{26}$$

where μ' has the meaning assigned previously in this and earlier papers.

As regards the third step mentioned above—the derivation of the equation—we can detect no flaw in the proof given by the author, or the proof given by Helmholtz, the basis of the mathematics as expressed in steps 1 and 2 being granted.

As regards the second step—the assumption of the law of the attraction—the fact that a true equation was deduced, entirely theoretically, from the assumption, is the surest evidence that the assumed law was the true one. One point remains to be examined here. Could any other law of attraction have produced the same equation, or one equally in accord with the facts?

To satisfy ourselves upon this point we have in a similar manner deduced the corresponding equations on the assumption that the attraction varied as the third, the fourth, the fifth, and the sixth powers of the distance between the molecules. These equations would take the form:

For the inverse third power of the distance,

$$\frac{M(L - E_E)}{d^{2/3} - D^{2/3}} = 0.4841\mu^2 M^{4/3} = \text{constant for a constant mass.} \tag{27}$$

For the inverse fourth power of the distance,

$$\frac{M(L - E_E)}{d - D} = 0.3227\mu^2 M = \text{constant for a constant mass.} \tag{28}$$

For the inverse fifth power of the distance,

$$(29)\quad \frac{M(L - E_R)}{d^{4/3} - D^{4/3}} = 0.2420\mu^2 M^{2/3} = \text{constant for a constant mass.}$$

For the inverse sixth power of the distance,

$$(30)\quad \frac{M(L - E_R)}{d^{5/3} - D^{5/3}} = 0.1936\mu^2 M^{1/3} = \text{constant for a constant mass.}$$

Applying these equations to isopentane, the constant given by equation 27 is shown in the column headed $\frac{1}{r^3}$, the constant given by equation 28 in the column headed $\frac{1}{r^4}$, etc. The values at the critical temperature, 187.8° C, were obtained by substituting for $L—E_R$ its value, $0.0_431833\,(V - v)\left(T\frac{dP}{dT} - P\right)$, and getting the limit of the resulting equation where V was equal to v. The resulting equations are:

For the limit of equation 27,

$$(31)\qquad \text{Constant} = 0.0_4477\; V^{5/3}\left(\frac{dP}{dT}T - P\right).$$

For the limit of equation 28,

$$(32)\qquad \text{Constant} = 0.0_431833\; V^{6/3}\left(\frac{dP}{dT}T - P\right).$$

For the limit of equation 29,

$$(33)\qquad \text{Constant} = 0.0_4239\; V^{7/3}\left(\frac{dP}{dT}T - P\right).$$

For the limit of equation 30,

$$(34)\qquad \text{Constant} = 0.0_4191\; V^{8/3}\left(\frac{dP}{dT}T - P\right).$$

The critical temperature is 187.8° C, the critical pressure is 25,020 millimeters of mercury, the critical volume is 4.268, and the $\frac{dP}{dT}$ at the critical temperature is 406, from the measurements by Dr. Sydney Young.

It will be seen that when the equation is deduced on the assumption that the attraction varies inversely as the square of the distance apart of the molecules *a constant is obtained, and on no other supposition does the corresponding equation give a constant.* It is evident therefore that *no simple change in the assumption as to the variation of the attraction with the distance will serve to explain the fact that the heat of vaporization does vary proportionately to the mass taken.*

TABLE II—ISOPENTANE.

Temperature	$L - E_E$	d	D	$\frac{1}{r^2}$	$\frac{1}{r^3}$	$\frac{1}{r^4}$	$\frac{1}{r^5}$	$\frac{1}{r^6}$
0°C.	81.35	0.6392	0.001090	107.2	111.2	127.5	147.8	171.5
50	68.62	0.5881	0.005967	104.5	102.6	117.9	139.6	166.3
100	56.67	0.5278	0.02022	105.8	97.9	111.6	134.6	165.1
150	40.13	0.4445	0.05834	106.9	92.9	104.0	126.7	160.5
180	21.04	0.3498	0.1258	103.4	85.7	93.9	114.7	148.1
187.8	0.0	0.2344	0.2344	107.2	86.9	94.0	114.4	148.3

The law of the attraction assumed, seems, therefore, to be the only assumption that will give an equation in accord with the facts.

As regards now the first step—the equality of the energy *per se* of a molecule of a liquid and of a molecule of its vapor—we have already stated in outline the facts which lead us to that belief. This first step is the most fundamental and important step in our work and is the most open to doubt. The fact that using this belief as a basis we derived an equation that appears to be true, is perhaps, again the best evidence that the belief expresses, at least partly, the truth. But only in part, for in attempting to derive a direct method for testing this belief we find that it will require some modification. An account of this work could not be introduced within the limits of this paper and we hope shortly to publish this investigation in a separate article. Recognizing the doubt, we would state that any errors introduced by our statement have undoubtedly canceled, since one is certainly able to calculate the energy given out by the contraction of a vapor into a liquid from the same formula used to calculate the energy given out by the contraction of the sun.

As regards now the fifth step—the conclusion that the molecular attraction is mutually absorbed or canceled by the attracting particles—we have only to say here that the conclusion is necessitated by the four previous steps and the further well-known facts, that the molecular sphere of action is small, and that the heat of vaporization of a liquid is proportional to the mass of the liquid taken for evaporation.

The Nature of the Attractive Forces

We would now return to a consideration of the idea proposed on page 151 of this paper, *that the attractive forces, whatever their nature, whether chemical, molecular, magnetic, electrical, or gravitational, which proceed from a particle are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount.*

We would call attention to what is actually known as to the action of attractive forces by the table on p. 158.

The general resemblance between these forces is so striking, we think, as to warrant a very serious consideration of any idea which leads to the belief that all of the forces do not follow the same law. Are they not perhaps all, in fact, one and the same force?

Considering the chemical force of attraction, the fact that this force does vary as some function of the distance apart of the atoms concerned has, we think, been already shown by the work of Richards[1] and Traube.[2] The latter says, "*Wie von mir zuerst festgestellt wurde, ist der Raum eines Atoms keine Konstante, sondern ändert sich von Stoff zu Stoff und ist um so kleiner, je grosser die Affinität des betreffenden Atomes zu den Atomen ist, mit welchen es in unmittelbarer Verbindung steht. Die Kontraktion der Atome ist daher*

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[1] Proc. Am. Acad., 37, 1 (1901); 15 (1902); 38, 7 (1902); 39, 23 (1904).

[2] Zeit. anorg. Chem., 40, 380 (1904).

Force	Medium of propagation	Effect of temperature	Is the attraction neutralized?	Is the attraction directive?	Law of distance, d	Numerator factor of force
Chemical	Ether	No effect	Neutralized	Yes	?	Nature of atom × Nature of atom
Molecular	Ether	No effect	Neutralized	?	$\frac{1}{d^2}$	Nature of molecule × Nature of molecule
Magnetic	Ether	?	Neutralized	Yes	$\frac{1}{d^2}$	Strength of pole × Strength of pole
Electrical	Ether	?	Neutralized	Yes	$\frac{1}{d^2}$	Charge × Charge
Gravitational	Ether	No effect	Not neutralized	No	$\frac{1}{d^2}$	Mass × Mass

ein unmittelbares Maass der Affinität." Concerning Traube's claim to priority in this discovery see remark by Richards.[1] While we prefer not to accept the conclusion of these investigators that the atoms themselves suffer a contraction, we cannot doubt from the evidence that they have brought

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[1] Proc. Am. Acad., 39, 23, 583 (1904).

forward that the chemical attraction between atoms is one of the deciding factors as to the distance apart of these atoms when combined into a molecule. That is to say, the distance apart of the atoms is some function of the chemical affinity. The problem is as yet too complicated to permit of finding the law of the attraction, and at present we must limit ourselves to the statement that the inverse square law of the distance is possible also with this force. When Newton discovered the law of gravitation others at once seized upon that law as a possible explanation of chemical affinity. Newton himself showed that the chemical attraction decreased more rapidly with the distance than was required by the inverse square law. But if the chemical attraction is mutually absorbed or canceled by the attracting particles, then it again becomes possible that the force itself varies inversely as the square of the distance from any particular atom, itself alone considered. Moreover, we know that this mutual absorption of the chemical attraction does take place.

We have made the statement that temperature has no effect upon chemical affinity. We have shown as a reason for this statement that 2.016 grams of H_2 and 16.00 grams of O_2 at the absolute zero possess at least 67,984 calories of chemical energy, while the total energy necessary to raise the H_2 and the O_2 from the absolute zero to 18° C is only 4301 calories. Now of this 4301 calories we can account for all but about 165 calories as necessitated by the changes in E_K, E_I, E_A and E_E. The details of this calculation will be given in the subsequent paper referred to above. At present we give the result only, as indicating the very minute influence that temperature has upon chemical affinity. It is possible that E_I is really the differential of the chemical energy. But even if this be true, it may more reasonably be referred to a slight alteration in the distance apart of the atoms composing the molecule, than to a real alteration of the chemical affinity.

In what form can the enormous amount of energy possessed by the hydrogen and oxygen at the absolute zero exist? Clausius has shown[1] that no system of particles could exist in stable equilibrium if all of the energy possessed by those particles was present as kinetic energy. Nor could all of the energy exist as potential energy. The energy must be partly kinetic and partly potential. Now it can be shown that when two particles exist under a mutual attraction varying inversely as the square of the distance apart of the particles, that the system composed of these two particles assumes the most stable equilibrium when one-half of the total energy is kinetic and one-half is potential. We cannot but believe it probable, that in a system of particles a similar distribution of energy would take place. The enormous amount of chemical energy that is existent at the absolute zero of temperature must, it seems to us, be present, one-half as potential and one-half as kinetic energy. That is to say, the hydrogen atoms and oxygen atoms at the absolute zero would revolve in pairs around a common center of gravity with enormous velocity, held in their orbits by the chemical attraction. This conception seems to us quite sufficient to explain the repulsive tendency referred to by Richards in his fourth paper above cited. We shall deal with this subject more fully later. We would only remark that the above conception of the mechanism of chemical affinity introduces no new assumption, save that the attraction obeys the inverse square law. This being true the other results follow if the principles underlying mechanics be true.

Our statement concerning the magnetic and electrical forces, not being the subject of dispute, may be passed over without comment.

As regards the gravitational force we meet the first and only exceptions to a complete similarity between the forces. The gravitational attraction is supposed not to be absorbed or neutralized by the attracting particles.

The questions involving the nature and laws of the attractive forces cannot, we are well aware, be settled by any appeal to our minds as to the relative difficulty or ease of the

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[1] See Meyer: Kinetic Theory of Gases, p. 344.

conception. But on the other hand such an appeal is *not without value*. If in the last analysis the testimony of consciousness cannot be trusted we had just as well give up the search for truth. We cannot hope to obtain to any absolute knowledge or full conception of any of the more elementary ideas such as time, space, matter, or motion. But we may attain to a partial knowledge of these ideas and this partial knowledge, we trust, may represent the reality truly, so far as it represents it at all. And in attempting to attain this partial knowledge, if one goes directly contrary to the testimony of one's mind as to the possibility or impossibility of a conception, one should not forget that the process of denying the truth of the testimony of consciousness once begun, can be as legitimately extended to an absolute agnosticism. Must be so extended, if one is consistent. One can refuse to examine the foundations for a house but one cannot undermine the foundations and yet continue to build the house. We do not believe, therefore, that the difficulties in the conception of the action of gravitational forces can longer be passed over as constituting no objection to the present statement of that law. Since Newton in 1682 deduced the law, all of the attempts—and they have been numerous—to formulate a sufficient cause for the law, have completely failed. The attempts have ended not alone in failure to formulate a cause for the law, but in emphasizing, most distinctly, the difficulty of forming such a conception at all.

May not the real cause of the trouble lie in the fact that scientists have been trying to explain how a force can be infinitely multiplied and absolutely unaffected by intervening matter, when force with such properties has really no existence? The line of apsides of Mercury's orbit has a slight motion unaccounted for by the law of gravitation. Dr. Asaph Hall pointed out that the observations could be satisfied by changing the law of gravitation by very slightly increasing the exponent of the distance factor. May not this slight divergence, explained as an *increase* in the exponent of the denominator, be explained rather by a *decrease* in the numerator, due to a neutralization of the attraction by the attracted particles. The planets are but dots in space, and the distortion of the field of force by the attraction which they would neutralize would be extremely small.

It will be further urged that we have no evidence of any shielding action in the case of gravitational forces and that, besides, gravitation is proportional to mass and not to surface in any way. In reply we would point out that we are dealing with a very fundamental question, and that we have, as yet, no explanation of mass. Mass is best represented perhaps, by the term "inertia," but the question is, What is "inertia?" Why has a molecule of lead more inertia than a molecule of aluminum? We have not, so far as the author knows, one iota of evidence, save in the suggestiveness of the periodic table of the chemical elements, that there is really more of the "ultimate material" in the molecule of lead than in the molecule of aluminum. For anything *we know* to the contrary, mass might be created at the same time as the attraction, a sort of action and reaction due to the same cause. And why this suggestion?

Because if one attempts to consider what changes must be made in the numerator factor of the forces in order to derive a common expression for all of the attractive forces, one starts with the broad idea that the force is measured by the effect which it produces. In producing this effect an opposite and equal effect must be produced on the force itself. This is according to Newton's third law of motion. Any other supposition would mean that the forces could be increased indefinitely. Force is transference of energy. We have no law as to the conservation of force but we have a law as to the conservation of energy. The amount of energy in the universe is constant. In a given time a constant amount of energy could not produce an infinite amount of force. But this production of an infinite, inexhaustible force is exactly what the law of gravitation necessitates, if it expresses the entire truth. We repeat *that one cannot believe that one particle of matter in the universe can attract every other particle* *of matter in the universe and itself suffer no diminution in its power to attract yet other particles of matter and hold also that the law of the conservation of energy is true. For these two beliefs necessitate that a constant energy, in a given time should be able to produce an infinite force, and this is impossible.* We reach therefore the conclusion that the attractive force given out by a particle in a given time is definite in amount. If therefore a portion of this attraction is expended upon one particle there remains exactly an equivalent amount less to be expended on the remaining particles. *Consequently, the attraction can be measured by the amount of the neutralized force.* This deduction we claim to be founded on the first law of thermodynamics, the conservation of energy. Now the amount of attractive force which can be neutralized will vary inversely as the square of the distance apart of the particles, because the surface front of the attractive wave of force increases as the square of the distance apart of the particles, and its intensity must correspondingly diminish, since the force cannot be infinitely multiplied. We can therefore write, attractive forces are measured by:

$$\frac{\begin{array}{c}\text{amount of attraction neutralized}\\ \text{at unit distance}\end{array} \times \begin{array}{c}\text{amount of attraction neutralized}\\ \text{at unit distance}\end{array}}{d^2}$$

Examining the numerator of the above fraction, there appears nothing improbable as regards its application as a general expression to take the place of the first four forces given in the table—chemical, molecular, magnetic and electrical. As regards gravitational force it makes mass proportional to the amount of attraction absorbed at unit distance. Is this idea necessarily wrong?

We doubt if the idea is necessarily opposed to established astronomical data. We might suggest that one reason why no shielding action had been detected among the heavenly bodies was because the mass really did vary with the amount of the shielding and exactly canceled the effect produced. Whether the idea is supported by molecular phenomena is more a subject of doubt. It might possibly explain the increased specific heat of a solid and liquid as compared with the corresponding vapor. We will return to this point in a later paper.

Chemical, magnetic, and electrical forces show decided evidence of directive action. We distinguish, moreover, positive and negative electricity, positive and negative poles of a magnet, and positive and negative elements, as indicating some difference in the kind of attractive force which they exert. As evidence of variation in the intensity of the molecular forces with their spatial relation around the molecule, might be cited the phenomena of crystalline form, of water of crystallization and molecular combinations in general, and also those cases where a liquid appears to show a definite and symmetrical structure. The evidence is not convincing, nor is there evidence indicating positive and negative molecular attraction. With gravitational forces similarly, there is no evidence showing directive, or positive and negative tendencies, unless the earth's magnetic field should be such an evidence.

The exceedingly close relationship between the electrical and chemical forces have often suggested their identity. The close relationship between electrical and magnetic forces is also recognized. There is also some evidence that molecular attraction is closely connected with electrical phenomena. Thus it has been pointed out by Abegg that liquids which cause dissociation are themselves most associated. We would note further a correspondence between the amount of dissociation produced by a liquid on a dissolved substance and the size of the molecular attraction, μ', as obtained by us. Perhaps it is also not without significance that the metals are the best conductors of electricity, are monatomic, and have a very great cohesion.

The amount of the molecular attraction, and the greater or less interpenetration of the molecular attraction among other molecules before it is neutralized, may, it seems to us, be the determining factor in the elasticity, ductility, malleability, brittleness, and hardness of substances in general, and of metals more particularly.

Our knowledge at present, is hardly sufficient to warrant speculation regarding the ultimate cause and nature of the attractive forces. They may be one and the same force—the molecular attraction being the unneutralized portion of the chemical attraction, magnetic attraction being a manifestation of the latter, and electricity closely connected with the former. Gravitation would be the unneutralized portion of the molecular attraction. We consider it possible that the attractive forces are one and the same force manifested under different conditions. We consider it likely that all of the forces are produced by some interaction between matter and ether. We consider it highly probable that the forces obey the same law whether their ultimate cause and identity be the same or not. We hope to develop the subject further in later papers.

Summary

1. The evidence that the molecular attraction varies inversely as the square of the distance apart of the molecules, and does not vary with the temperature, is reviewed and strengthened.

2. It is pointed out that the molecular attraction must be neutralized by the attracting molecules.

3. It is shown that the equation deduced by Helmholtz in 1854 to represent the energy given out by the contraction of the sun will, by changing the constant, represent accurately the energy given out by isopentane and other substances in changing from a saturated vapor to a liquid.

4. It is shown that a large amount of chemical energy is possessed by hydrogen and oxygen at the absolute zero, and that this energy is probably existent half as potential, half as kinetic energy.

5. It is shown that chemical attraction is probably unaffected by temperature.

6. The idea is introduced that the attractive forces, whatever their nature, whether chemical, molecular, magnetic, electrical, or gravitational, which proceed from a particle are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount.

7. The laws governing attractive forces are compared and it is suggested that all of the forces really obey the same law, *viz.*, the attractive forces are measured by the amount of the attraction neutralized, which is:

$$\frac{\begin{array}{c}\text{amount of attraction neutralized}\\ \text{at unit distance}\end{array} \times \begin{array}{c}\text{amount of attraction neutralized}\\ \text{at unit distance}\end{array}}{d^2}$$

8. The idea that the gravitational attraction of a particle could remain undiminished regardless of the amount of the attraction exerted upon other particles is shown to be contrary to the law of the conservation of energy.

Chemical Laboratory,
University of North Carolina,
December 10, 1906.

NEW BOOKS

Ice Formation; with Special Reference to Anchor-Ice and Frazil. *By Howard T. Barnes. First Edition. 15 × 23 cm; pp. x + 260. New York: John Wiley and Sons, 1906.*—"Nowhere can man witness a more wonderful sight of the delicate poising of the forces of Nature than in the spectacle of one of our northern rivers in winter. The full magnitude of the struggle which goes on between ice and water is only realized in its entirety where an engineering problem has to be met and the ice conditions studied. The steadiness of the temperature of the water throughout the winter is a matter of great interest. It never varies more than a few thousandths of a degree from the freezing-point, even though the temperature of the air may be 30° or 40° lower. As a constant temperature thermostat we have nothing to equal it even with all the appliances of one of our modern laboratories.

"Evidence shows that the greater bulk of our water-power lies in the northern portion of the American continent, from the great lakes and along the St. Lawrence valley through the snow belt. Hence, as water-power development advances, the circumstances under which ice formation takes place become more and more important. To the hydraulic engineer the question of ice formation is of vital importance, and too much attention cannot be given to this matter for a more thorough understanding of the problems involved. What presents itself during the summer months for consideration is nothing to what must be met during the winter months, when ice is forming rapidly, and ice bridges, dams, and shoves may change the whole character of the levels and channels in a single night. Rivers are thus known to have been turned entirely out of their course into new channels during a winter of unusual severity, and in some instances the reversal of a rapid is of yearly occurrence."

The intense cold of the Canadian winter gives rise to some types of ice formation which are either non-existent or of minor importance in regions where the cold weather is intermittent. The author distinguishes sheet ice, frazil, and anchor ice. Sheet ice is the solid ice which forms on the surface of the water. It is the only ice with which most people are familiar.

"Frazil is a French-Canadian term for fine spicular ice, from the French for forge-cinders, which it is supposed to resemble. It is always formed in an open channel, where the current is flowing too swiftly for the border-ice to meet over the service, and it is often called 'slush-ice'. It is a surface-formed ice, which cannot remain attached and freeze into a surface sheet. It occurs in varying degrees of fineness, depending on the degree of agitation of the water. On a smooth gliding surface flat plates of ice may be formed, and give rise to the term 'plate-ice'. In rapids or at the foot of waterfalls, only fine particles of ice are formed in minute needle crystals, which grow in bulk when carried far in open water.

"Artificial frazil-ice may be formed by subjecting water to rapid agitation in a cold atmosphere. A tub of water placed out-of-doors in winter and rapidly stirred, soon turns to slush by the copious growth of these fine crystals. It is safe to say that a long stretch of open water becomes loaded to the bottom with slush-ice during a period of intense cold and great wind agitation, frequently occurring in our northern rivers in winter. During such a time the water appears dull in color, presenting an appearance of being mixed with fine sand. At any time during cold weather, the water may be seen to be harboring numerous fine crystals by withdrawing a sample in a clear day for inspection. The amount it may contain will depend entirely on the weather conditions. A dull stormy day, with a wind that blows against the current, is productive of the greatest amount. This is the result of the surface agitation, together with the rapid extraction of heat. A bright, sunny day, although very cold, does not show much formation, on account of the absorption of the sun's rays near the surface, offsetting the cooling effect of the air. At night, under a clear sky with wind agitation, a large amount will be formed, depending on the temperature of the air. In this case both conduction to the air and radiation from the bottom and volume of the water are operating. Very little radiant heat is stopped by the atmosphere, on account of the minute amount of water-vapor present in the air under these circumstances. A stretch of open water makes a very much greater quantity of ice in the form of frazil crystals than could be produced as a surface-sheet, if the water were sufficiently quiet to allow such to grow. It is this which causes an open channel to be of so much trouble to engineering operations whenever frost occurs; for although a surface-sheet may form lower down, the fine ice is carried far under the surface-ice by the currents. Serious changes of level often occur in a river, by the damming up, or complete stoppage of a channel by frazil carried under the surface-ice, and building down on both sides of the channel. Great masses of frazil accumulate in the quiet bays by the drifting in of the fine crystals, and their subsequent settling upwards to the under side of the surface-sheet. The crystals soon become attached to the surface-ice, and attain depths reaching to the bottom of the river; in some cases we have observed a depth of 80 feet.

"In taking soundings through the ice, the lead may usually be sunk through the masses of frazil, but often these become frozen together so hard as to resist all efforts at penetration. The distance to which frazil-ice will be carried depends on the swiftness of the currents, and the amount of open channel above. In the St. Lawrence River, at Montreal, the frazil, generated for the most part in the Lachine Rapids, is found attached as far down as Verrans, some twelve miles below. In this case the river is open above the rapids, as far as Lake St. Louis, seven miles above."

Frazil is formed in the laboratory every time we make a freezing-point determination. Those who are not fortunate enough to be chemists become familiar with it as orange sherbet, which is frazil sweetened and flavored.

Anchor-ice is ice attached to the bottom of the river irrespective of the nature of formation. It is formed in two ways. Immense quantities of frazil become attached to the bottom by freezing to the layers of ice already formed there. The interesting problem is as to the formation of these original layers of ice or, in other words, as to the formation of anchor-ice *in situ*. Ice can form on the river bed only when the ground is colder than the water above it. Since conduction of heat away from the water to the ground is apparently not a factor to be considered seriously, the only other possible way in which heat can be lost is by radiation to the air through the water From this point of view the formation of ice on the river-bed is analogous to the formation of hoar frost on the surface of the earth. Since we know that the shorter heat waves are absorbed by water, we must assume that water is transparent for some of the longer heat-waves. While this is not definitely proved, there is evidence which makes it seem plausible and it certainly explains the formation of anchor-ice.

"If we sum up the various facts of common observation in connection with anchor-ice, we see that everything points to radiation as the prime cause. Thus we find that a bridge or cover prevents the ice forming underneath. Such a cover would act as a check to radiation, and reflect the heat-waves back again to the bottom. Anchor-ice rarely forms under a layer of surface-ice. It forms on dark rocks more readily than on light ones, which is in accord with what we know in regard to the more copious radiation of heat from dark surfaces. Anchor-ice never forms under a cloudy sky either by day or night, no matter how severe the weather, but it forms very rapidly under a clear sky at night. Anchor-ice is readily melted off under a bright sun. It seems highly probable, then, that radiation of heat supplies the necessary cooling to the bottom of a river to form the first layers of ice, after which the growth or building-up of the ice is aided by the entangling and freezing of frazil-crystals which are always present in the water.

"The growth of anchor-ice is exceedingly beautiful, taking place in arborescent forms and resembling bushy weeds. So hard and thick does it become that it is often very difficult to thrust a sounding-rod through it. It is very granular in structure, as is shown by an examination of the masses which rise to the surface. Through clear water the ice looks weed-like, with long tentacles rising up out of the mass. It often has immense power in lifting rocks and boulders up bodily, and many of these are carried far down-stream attached to irregular masses of ice."

These copious quotations are sufficient to show the interesting nature of the book. To the reviewer the chapter on sheet, frazil and anchor-ice is the most interesting in the book but there is much profitable reading in the other chapters, as may be seen from their headings: physical laws governing the transfer of heat; physical constants of ice; formation and structure of ice; precise temperature measurements; river temperatures; theories to account for frazil and anchor-ice; methods of overcoming the ice problem in engineering work.

Look at it from whatever point of view you may, it is a delightful paradox that the worst floods at Montreal occur when there is not very much water in the river. *Wilder D. Bancroft.*

A History of Chemical Theories and Laws. *By M. M. Pattison Muir. First Edition. 15 × 23 cm; pp. xx + 555. New York: John Wiley and Sons, 1907. Price: $4.00 net.*—"The more I try to understand chemistry, the more I am convinced that the methods, achievements, and aims of the science can be realized only by him who has followed the gradual development of chemical ideas. A just judgment can be passed on the relative importance of the methods which are used, the results which are obtained, and the problems which are being attacked by the chemists of to-day, only when a careful study has been made of the methods employed, the results gained, and the points of attack selected by the chemists of the past."

"What is meant in chemistry by the expression, 'a homogeneous substance?' In other words, what is 'a chemically distinct substance?' What happens when chemically distinct substances interact? These are the two main questions of chemistry; and these have always been the two main questions of chemistry, although the forms wherein these questions have been stated have differed much at different times.

"To trace the forms which the two fundamental inquiries of chemistry have presented at different periods, to describe some of the methods which have been used to find answers to these inquiries, and to set forth the general results of the application of these methods, is the object of this book."

The question as to what constitutes a homogeneous substance is treated under the following general headings: the recognition of homogeneous substances, and the description of chemical changes as the interactions of these substances; the marks of elements and compounds; the laws of chemical combination; the atomic hypothesis, the molecular and atomic theory; the more searching examination of the compositions of homogeneous substances, allotropy; elements which do not react; chemical nomenclature and notation.

The question as to what happens when homogeneous substances interact is dealt with under the headings: the classification of homogeneous substances; acids, bases, salts; radicals, types, dualism, the unitary hypothesis; chemical equivalency, isomerism and constitutional formulas; application of the hypothesis of ionization to the classification of homogeneous substances; the periodic law; the conditions and general laws of chemical change; chemical affinity; chemical equilibrium; the elucidation of chemical reactions by measurements of physical properties.

The book is well written and the typography excellent. Good books of this kind are too scarce and it would be well if we could have more of them. The closing paragraph of the book is an effective one.

"The study of the connexions between composition and properties has entered a new phase. The old questions remain. The answers which have been given by the labors of countless generations of naturalists, through more than two milleniums, have not solved these problems. Physicists and chemists have joined in the quest of finding new answers to the old questions: What is a homogeneous substance? What happens when homogeneous substances interact?"

Wilder D. Bancroft

Lehrbuch der Elektrochemie. *By Max Le Blanc. Vierte vermehrte Auflage. 14 × 22; pp. viii + 319. Leipzig: Oskar Leinder, 1906. Price: paper, 6 marks; bound, 7 marks.*—The author has succeeded in condensing his material to such an extent that there is only about 10 percent increase in the number of pages. The author cites Kahlenberg's work on stannic chloride and copper oleate in benzene to prove that 'instantaneous' reactions do take place between undissociated substances. In the fifth edition we shall probably learn that the dielectric constant is not always a measure of the dissociating power of a solvent. Billitzer's work on single potentials is taken up more in detail this time, though the objections to it are not urged. Altogether, we may welcome this edition as a distinct improvement over the preceding ones.

Wilder D. Bancroft

Physikalische Chemie für Anfänger. *By Ch. M. van Deventer. Mit einem Vorwort von J. H. van't Hoff. Dritte auflage, besorgt von Ernst Cohen. 15 × 21 cm; pp. xx + 161. Amsterdam: S. L. van Looy (Leipzig: Wilhelm Engelmann), 1905. Price: paper, $.80.*—This is rather an interesting little book because the method of presentation does not correspond at all to anything with which we are familiar in this country. After defining chemistry and substance, the author brings in the law of the conservation of weight (mass); the law of definite composition; the laws of constant and multiple proportions; the law of the equivalence of the elements and the laws of Gay-Lussac. Then comes a chapter on the behavior of gases followed by one on thermochemistry. One chapter is devoted to solutions and one to spectroscopy and photochemistry. The last chapter is on the periodic system.

Wilder D. Bancroft

Elektrolytische Alkalichloridzerlegung mit flüssigen Metallkathoden. *By R. Lucion. (Monographien über angewandte Elektrochemie. XXIII Band.) 17 × 24 cm; pp. viii + 206. Halle: Wilhelm Knapp, 1906. Price: paper, 9 marks.*—The book opens with a description of the general theory of electrolysis with a mercury cathode. Then comes a chapter on practical difficulties and a long one containing a description of the patented processes. The last section deals with the processes using a lead cathode, of which the Acker process is the only one in actual operation.

The reviewer would have liked to have seen a little more stress laid on the methods of purifying salt. The remarks on the life of carbon anodes, p. 13, seem a little inconsistent with the fact of the graphite anodes in the Castner process lasting about two years. These, however, are minor points. Taken as a whole, the book is an admirable one and contains a large amount of valuable information presented in a compact and convenient form.

Wilder D. Bancroft

Manuel de Manipulations d'Électrochimie. *By C. Marie. Préface de H. Moissan; Données numériques réunies par G. Noel. 16 × 25 cm; pp. viii + 166. Paris: H. Dunod et E. Pinat, 1906. Price: paper, 8; bound, 9.50 francs.*—This manual covers electrolytic work only and does not include electric furnace experiments. Seventy-four pages are devoted to a general introduction, twenty-two pages to inorganic preparations, and forty-one pages to organic preparations. This is followed by twenty-five pages of tables. The book does not differ essentially from the corresponding books in German. Making the compounds is the essential thing and the study of conditions is a very secondary matter.

Wilder D. Bancroft

Petrogenesis. *(Die Wissenschaft, Heft 13). By C. Doelter. 14 × 22 cm: pp. xii + 261. Braunschweig: Friedrich Vieweg und Sohn, 1906. Price: paper, 7 marks; linen, 7.80.*—The headings of the chapter are: vulcanism and the interior of the earth; the forms of volcanic rocks; the structure of volcanic rocks; relation between mineralogical and chemical composition of rocks; differentiation of the magmas; relative ages of plutonic rocks; occlusions in rocks; assimilation and corrosion; artificial rocks; solidification of fused magmas; contact metamorphosis; formation of crystalline slates; sediments.

This book brings out clearly the great need of proper experimental work such as the Geophysical Laboratory at Washington has undertaken. With only the facts that can be obtained from a study of geological formations, it is absolutely impossible to formulate any rational theory. There is nothing to show for instance whether the phenomenon of a basic lava followed by an acid one and still later by a basic one is purely a phenomenon due to fusibility or whether it must have been accompanied by a rise of temperature on the third eruption. This particular problem is really relatively simple but no one has yet gone at it the right way. *Wilder D. Bancroft*

Cours de Chimie organique. *By Fréd. Swarts. 16 × 24 cm. pp. 665. Paris: A. Hermann, 1906. Price: paper, 15 francs.*—This work is intended for students of medicine, engineering, and pharmacy, and in one sense is a very complete text-book—nothing (except an analytical table of contents, and references to the literature) being left out altogether.

Laboratory manipulation, *énergie superficielle*, stereochemistry, density-curves for solutions, dynamics of etherification (with an integration), tautomerism, theory of fractional distillation, the Geneva nomenclature, etc., etc., are taken up as occasion offers; structural formulas of alkaloids and camphors, of members of the indigo group, and of derivatives of uric acid, are given in full; and many more compounds are classified and more or less described than is at all usual in works written for the constituency to which the author addresses himself.

The method of treatment is as different as can be from that of Remsen's classical little book. Isomerism, and its explanation by structural formulas is brought in on page 6 (really page 2, not counting the preface); an alcohol is defined as "a hydrocarbon in which some of the hydrocarbonated hydrogen has been replaced by hydroxyl;" "organic acids are characterized by the presence in their molecule of one or more COOH groups;" and so on throughout.

The book is neatly printed, and the author has endeavored "to treat his subject as a branch of general chemistry;" but *Multa, non multum* should be written on the title-page. *W. Lash Miller*

Thermodynamique, *Lecons professées a la Faculté des Sciences. By G. Lippmann. Rédigées par A. Mathias et A. Renault. Seconde édition, conforme a la première. 16 × 25 cm; pp. vii + 251. Paris: A. Hermann, 1905. Price: paper, 3 francs.*—This second edition of Lippman's *Thermodynamique* is a reproduction of the Sorbonne lectures as originally edited by Mathias and Renault in 1889. The admirable qualities of the work as an introduction to the study of thermodynamics are well known. If the book is not to be rewritten, it is at least gratifying that it is not to be allowed to go out of print. *J. E. Trevor*

Die elektrochemischen Deutschen Reichspatente. *Auszüge aus den Patentschriften. By P. Ferchland and P. Rehländer. (Monographien über angewandte Elektrochemie. XXIV. Band.) 17 × 24 cm; pp. viii + 230. Halle: Wilhelm Knapp, 1906. Price: paper, 10 marks.*—The authors give brief abstracts of the German electrochemical patents. It is obvious that the book is not one to read through from beginning to end. As a reference work, however, it is very valuable. *Wilder D. Bancroft*

AN INVESTIGATION OF THE DOUBLE COBALT MALONATES[1]

BY RICHARD C. LORD

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I Introduction

The physico-chemical properties of a large number of inorganic double salts have been studied—the alums,[2] the double chlorides,[3] the double iodides, cyanides, nitrates and sulfates,[4] and others—but as yet we have seen no notice of any similar investigation of double salts of organic acids. Several double oxalates of chromium and recently those of the platinum group have been investigated. The double chrom-malonates were studied here a short time ago.[5] Of all these salts, however, no physico-chemical study has been made to our knowledge. In this paper the acid used was malonic acid, $C_3H_4O_4$, a dibasic acid of the general form $C_nH_{2n-2}O_4$, the next higher homologue to oxalic. The metal employed was cobalt in its bivalent condition, which readily

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[1] From a thesis submitted for the degree of Doctor of Philosophy at Washington and Lee University. This work was done under the direction of Dr. Jas. Lewis Howe.

[2] Jones and Mackay : Am. Chem. Jour., 19, 83 (1897).

[3] Jones and Ota : Ibid., 22, 5 (1899).

[4] Jones and Caldwell : Ibid., 25, 349 (1901).

[5] J. L. Howe : Jour. Am. Chem. Soc., 25, 445 (1903).

forms salts with malonic acid. The following salts were prepared and studied:

$CoMal.2H_2O$
$H_2CoMal_2.2H_2O$
$(NH_4)_2CoMal_2.4H_2O$
$K_2CoMal_2.4H_2O$
$Rb_2CoMal_2.4H_2O$
$Cs_2CoMal_2.4H_2O$
K_2CoMal_2

and probably also the anhydrous rubidium salt but this was not obtained in sufficient quantity to analyze. Several efforts were made to prepare a trivalent double salt, but these were unsuccessful. They will be described later.

While the main object of this work was a study of the properties of these double salts in solution, other properties have been studied and the general knowledge of these double salts made as complete as possible.

II Preparation

The salts have been prepared as follows:

The cobalt in a solution of cobalt nitrate is precipitated as $Co(OH)_2$ by KOH. A tall jar about 40 cm high and 10 cm in diameter was used for this purpose. The precipitate is at first blue, but soon changes to a pink. After being allowed to settle, the supernatant liquid is siphoned off and the jar filled with hot water and stirred. After a second settling the liquor is again decanted and the process of washing repeated twenty to thirty times till the supernatant liquid on evaporation of a few cubic centimeters on a watch glass shows no residue. The time required is from four to ten days, depending on the rapidity of the settling of the cobalt oxid or hydroxid. During the latter part of the washing when the water is very nearly pure the cobalt mud, as the compound is called, assumes a colloidal state and part of the mud remains suspended, it matters not how long the interval between successive decantations. Considerable mud is lost in this way: and, in testing for purity, the liquid must be boiled to coagulate the mud and then filtered. The suspension of the mud in colloidal form, however, indicates an approximate purity of the mud and generally two or three more washings suffice.

The pure mud is kept moist. On standing exposed to the air it gradually loses water and changes to a dark brown. The dark dry mud, while easily attacked by strong mineral acids, will not entirely neutralize malonic acid even after boiling for several hours in a solution of the acid.

To determine the action of malonic acid on some rather dry mud, which failed to act on the acid properly, the following series of experiments was performed:

Standard solutions of KOH and H_2Mal were prepared by titration with phenolphthalein as an indicator. A measured volume of H_2Mal was boiled with excess of the cobalt mud in a beaker with watch glass cover so as to keep the strength of the solution approximately constant. The solution was then filtered and titrated with KOH, precipitation of blue $Co(OH)_2$ being used as an end-point.

I. 30 cc 1.84N H_2Mal boiled with $Co(OH)_2$ three hours. 25.11 cc 1.84N KOH required to precipitate $Co(OH)_2$. $\frac{4.89}{30} = 16.3$ percent neutralized by mud.

II. 39.08 cc 0.95N H_2Mal boiled with $Co(OH)_2$ three hours. 31.74 cc 0.95N KOH required to precipitate $Co(OH)_2$. $\frac{7.34}{39.08} = 18.78$ percent neutralized by acid.

This shows the necessity of using fresh mud and of keeping it moist. Dilute nitric or hydrochloric acid dissolved the mud almost instantaneously.

$CoMal.2H_2O$
$H_2CoMal_2.2H_2O$

The formation of the simple cobalt malonate ($CoMal.2H_2O$) is effected by heating on a water bath the fresh mud with a solution of malonic acid at a concentration slightly above the solubility of the salt and evaporating to a supersaturated condition. When the mud used is dry, on evaporation a pinkish red salt crystallizes out, which caused some difficulty in its determination. It was found on analysis to be an acid cobalt malonate ($H_2CoMal_2.2H_2O$ or $CoMal.H_2Mal.2H_2O$). The neutral cobalt malonate, which crystallizes best from a slightly acid solution, is deep red in color, somewhat lighter if the salt is powdered. The neutral salt forms small but definite crystals, while the acid or pink salt crystallizes in the form of small clusters or balls, two or three millimeters in diameter. On attempting to dissolve the acid salt in water, it breaks up and leaves the red salt, $CoMal.2H_2O$, the excess of malonic acid going into solution. The water is colored very little by this method, the red salt being difficultly soluble in water.

$(NH_4)_2CoMal_2.4H_2O$
$K_2CoMal_2.4H_2O$
$Rb_2CoMal_2.4H_2O$
$Cs_2CoMal_2.4H_2O$

The four above salts are prepared by similar methods and so may be described together. Two equal amounts of malonic acid are weighed out and dissolved. One portion is treated on the water bath with an excess of the cobalt mud and filtered. The other is neutralized by the alkali hydroxid, using litmus paper as an indicator. The solutions are then mixed and evaporated to strong concentration. As the neutral cobalt malonate (CoMal) is rather insoluble. the solution before mixing must be comparatively dilute and is evaporated after union to about one-tenth its original volume. The color of the solution changes on mixing from a deep red to a red with a pinkish tinge. A small amount of free malonic acid should be added before evaporation as the salt ($M_2CoMal_2.4H_2O$) crystallizes better from a slightly acid solution.

Crystals for physical measurement can be obtained by continued evaporation on the water bath, but for the purpose of obtaining large and nearly perfect crystals for crystallographic measurement slow evaporation was necessary, and recourse was had to sulfuric acid under a bell jar. During the winter the bell jar and its plate were put on a large sand bath and a small gas flame kept burning continuously so that the temperature was approximately 25° C. For crystallizing purposes small deep beakers were found preferable to evaporating dishes and the extra depth of the liquor produced crystals less contorted than the shallow depth usually necessary in evaporating dishes.

During the latter part of the work, in preparing some of the potassium salt for chemical measurement, I evaporated it to supersaturation on the water bath and a pink salt separated out. On analysis it developed to be the anhydrous salt, K_2CoMal_2. One of the rubidium solutions showed a pink powder in addition to the hydrated crystals, but not sufficient for analysis. I judge it was analogous to the potassium salt.

III Analysis

I. $CoMal.2H_2O$
$H_2CoMal_2.2H_2O$

A portion of the salt is weighed into a porcelain crucible and heated to 150° to determine the water content, the color changing from red to a deep blue. There are no signs of decomposition of the malonate at this temperature, and below 130° there is no appreciable loss of water even if heated at that temperature for several hours. The anhydrous salt rapidly absorbs one-third of a molecule of water from the air and must be weighed rapidly. The water content of the acid malonate could not be determined in this manner as the unneutralized acid decomposes before all the water is driven off.

After determining the water, the anhydrous salt is transferred to a beaker, treated with conc. H_2SO_4 and heated till the malonic radical is decomposed. The solution of cobalt sulfate is then diluted and an excess of ammonia added till the solution colors to a deep orange-brown. The cobalt is determined by electrolysis on platinum electrode, the ammonium sulfate making the resistance low. A voltage of 2 to 3 is used and a current strength of about 0.8 ampere per 100 sq. cm. of electrode surface. From eight to twenty-four hours are required for complete deposition. When a drop of ammonium sulfid shows no dark coloration in the solution the cobalt is all removed. The electrode is removed from the solution, carefully washed with water and dilute alcohol and dried at 30°-40° to prevent oxidation, a trace of which is always present. The differential weight of the electrode gives the cobalt.

II. $CoMal.2H_2O$
$H_2CoMal_2.2H_2O$

In the salts containing no alkali the cobalt may be determined by reducing in a stream of hydrogen. The sample for analysis is weighed into a porcelain boat, the water content determined as in (I), similar phenomena being observed. The boat is then heated under a free Bunsen flame, roasting the cobalt to the oxide. During this roasting there is apparently a very slight sublimation of the cobalt as a bright mirror-like deposit on the side of the boat where the salt is most compact. Whether this is due to a formation of a cobalt carbonyl or not, I can not say, but the sublimation occurs only when the malonate is present and never when the reduced cobalt is roasted again to get a constant determination. There is no appreciable loss of cobalt, judging from the comparison of the results of this method with the electrolytic determination.

After roasting, the salt is heated in a combustion furnace to 300°-400° in a stream of hydrogen, and in fifteen to twenty minutes the cobalt is completely reduced. After weighing, the cobalt is roasted again, and again reduced till the cobalt is at a constant weight.

III. $M_2CoMal_2.4H_2O$

These salts are analyzed as in (I) with the following changes:

The water content is determined at 120°, the anhydrous salt formed being of a very light blue color. The salt loses water considerably under 100° but its total amount does not come off below 120°. These all rapidly absorb moisture to the extent of one-half of a molecule and must be weighed rapidly and immediately after cooling in the desiccator. In the ammonium salt the water content could not be determined as some ammonia volatilized before all the water came off.

For the determination of the alkali, the solution, after removal of the cobalt by electrolysis, is evaporated to a small volume and then transferred to a tared small platinum dish and evaporated to dryness. The dish must be heated very carefully to drive off the ammonium sulfate and then over the blast lamp to remove all free sulfuric acid at a red heat. The alkali sulfate, M_2SO_4, is then weighed to a constant and the alkali calculated.

IV. $M_2CoMal_2.4H_2O$

The alkali in the double salts can also be determined as the chlorplatinate, M_2PtCl_6. By this method the water content is obtained as in (III). The anhydrous salt is heated with conc. HCl, transferred to a beaker and an excess of H_2PtCl_6 added. The alkali chlorplatinate forms a precipitate varying from deep yellow for ammonium to cream colored for caesium. The supernatant liquid is then evaporated almost to dryness on a slow water bath and 10 cc of an 80 percent solution of alcohol added. It is allowed to stand for an hour or so and the precipitate is transferred to a prepared Gooch, washed several times with small amounts of the alcohol solution and dried at 105° and weighed to a constant. The filtrate is washed from the Erlenmeyer, a small amount of H_2SO_4 added and the solution is electrolyzed with a sheet of copper cathode at a voltage of three or four for an hour. The platinum from the excess of chlorplatinic acid separates and except for a small amount adhering to the cathode settles to the bottom of the beaker. The solution is then filtered off from the platinum, made alkaline by the addition of conisderable excess of NH_4OH and electrolyzed to determine the cobalt as in (I). The carbon and hydrogen contents were not determined, as the three factors—alkali, cobalt and water of crystallization—were sufficient to determine the salt.

The last two methods were both used in determining the alkali in the alkali malonates, $M_2Mal.2H_2O$, the water content being determined at 105°.

The following analyses were made:

$CoMal.2H_2O$

Weight		1	2	3	4
Assay		0.5260	0.3030	0.2980	0.2440
Co		0.1597	0.0925	0.0893	
H_2O					0.0448
Percent	**Theoretical**				
Co	29.95	30.36	30.52	29.96	
Mal	51.78				
H_2O	18.27				18.36

Analyses (1) and (2) were made by reducing in hydrogen.

Analysis (3) was made by electrolysis. Slight trace of oxidation on electrode.

$H_2CoMal_2.2H_2O$

Weight		1	2	3
Assay		0.2633	0.3053	0.2487
Co		0.0509	0.0601	0.0490
Percent	**Theoretical**			
Co	19.60	19.33	19.69	19.70
H_2Mal	68.44			
H_2O	11.96			

Above analyses were made by heating in hydrogen.

$(NH_4)_2CoMal_2.4H_2O$

Weight		1	2
Assay		0.2629	0.2513
Co		0.0408	0.0391
Percent	Theoretical		
NH_4	9.74		
Co	15.89	15.56	15.56
Mal	54.96		
H_2O	19.41		

Analysis (1) was made by electrolysis.

Analysis (2) was made by reducing in hydrogen

$K_2CoMal_2.4H_2O$

Weight		1	2	3
Assay		0.3048	0.4409	0.2828
K_2SO_4		0.1226		
Co		0.0435	0.0614	
H_2O				0.0502
Percent	Theoretical			
K	18.94	18.10		
Co	14.27	14.27	13.93	
Mal	49.36			
H_2O	17.43			17.75

$Rb_2CoMal_2.4H_2O$

Weight		1	2	3	4	5
Assay		0.2785	0.3355	0.3093	0.1551	0.2409
Rb_2PtCl_6				0.3478	0.1731	
Rb_2SO_4			0.1635			
Co		0.0326	0.0388			0.0288
H_2O		0.0387	0.0468			0.0345
Percent	Theoretical					
Rb	33.77		31.19	33.21	32.96	
Co	11.66	11.70	11.56			11.96
Mal	40.33					
H_2O	14.24	13.89	13.95			14.31

$Cs_2CoMal_2.4H_2O$

Weight		1	2	3	4
Assay		0.6489	0.6401	0.2898	0.5643
Cs_2SO_4					0.3317
Co		0.0661	0.0665	0.0289	0.0575
H_2O		0.0781		0.0340	0.0651
Percent	**Theoretical**				
Cs	44.25				42.91
Co	9.81	10.18	10.38	9.97	10.18
Mal	33.95				
H_2O	11.99	12.03		11.73	11.54

IV Physical Properties

(1) *Specific Gravity.*—The specific gravity of the salts under investigation was determined by weighing in benzene, which does not affect the salts, and also in air. The apparatus consisted of a pan of thin sheet platinum, suspended from the beam of the balance by three very fine platinum wires.[1]

The salt is immersed in benzene and stirred thoroughly to remove all air bubbles. It is then placed on the scale pan which has previously been immersed in the dish of benzene in which the weighings are made. The salt is weighed in benzene, drained against the side of the dish and dried in a vacuum desiccator for fifteen minutes, in which time all the benzene evaporates, and weighed in air. This process was repeated three times, care being taken each time to stir the salt in benzene before placing on the platinum pan. The results obtained were as follows:

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[1] This method, suggested by Dr. Howe, was tested in this laboratory by Mr. D. V. Guthrie and found to be very accurate. It is particularly advantageous where only a small quantity of a salt is available. The pan and its suspending wires are very light, and were kindly made and furnished for this work and that of Mr. Guthrie by Baker & Co., of Newark.

	Specific gravity	Molecular volume
$CoMal2H_2O$	2.279	86.5
$(NH_4)_2CoMal_2 4H_2O$	1.804	205.8
$K_2CoMal_2 4H_2O$	2.234	185.0
$Rb_2CoMal_2 4H_2O$	2.131	237.4
$Cs_2CoMal_2 4H_2O$	2.682	224.1

(2) *Solubility.*—The solubility was determined by allowing the solutions to remain in contact with the salt for one week or more. They were placed in small glass bottles and immersed in a thermostat at 18° C. As there was no access to a stirrer the bottles were shaken two to three times a day. After standing for the above-mentioned period the liquor was poured out, weighed, the cobalt content determined, and the solubility calculated.

	Weight of solution containing gram-molecule. Kilograms	Number grams anhydrous salt to 100 grams solution
CoMal	11.90	1.353
$(NH_4)_2CoMal$	2.82	10.61
K_2CoMal	8.01	4.26
Cs_2CoMal	3.72	14.23

V Properties in Solution

It is well known that when a mixture of two solutions of salts having a common negative ion is evaporated, we get in certain cases homogeneous crystals containing both the salts in some molecular ratio. That the solution of this mixture does not obey the law of mass action is very evident from the solubility of the mixture, which is always greater than that of the less soluble salt. The increase of the quantity of the negative ion in the solution should make the salt still less soluble instead of more so. For instance, in the case we have studied, cobalt malonate is much more soluble in a solution of potassium malonate than it is in water. This and other similar phenomena led to the inevitable conclusion that there was some rearrangement of the ions in the solution of the mixture—in short, that in the above case after the addition of the potassium malonate, the ions were no longer simply K, Co, and Mal, but some relation was established by which the tendency of the malonate ions associated with the potassium to throw down those of the cobalt malonate was not only nullified, but the cobalt malonate actually became more soluble. This led to the view of double salts in which the more positive ion, generally an alkali, forms the positive ion and the less positive metal unites to a greater or less degree with the acid radical to form a composite negative ion. In some cases this latter was so far true that the metal combining with the negative ion did not respond to its ordinary qualitative tests as is the case with the ferro- and ferricyanids.

Other of these double salts, while crystallizing out with the radicals in molecular proportions, still react for both of the positive radicals. This fact led Ostwald[1] to classify all these salts into two classes, double and complex. The double salts are those which in solution answer all the qualitative tests that a mixture of the salts would, of which the alums may be taken as an example. The complex salt is one in which the less positive element passes completely into the negative ion as the double iron cyanids. The line of demarcation between these two classes is by no means well defined and depends largely on several factors —concentration of solution, relative strength of basic and acid radicals, etc., and others. With an especial consideration of the importance of the strength of the acid in determining to which class the salt belongs, malonic acid was chosen for the present investigation. It belongs to the same series as oxalic—the dibasic acids—but contains a CH_2 group between the carboxyl radicals and hence is much weaker than oxalic, in every sense of the word.

The double salts of the mineral acids—principally the sulfates, nitrates, and halids—have been somewhat extensively studied recently by Jones and his students.[2]

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[1] Zeit. phys. Chem., 3, 596 (1889).

[2] Am. Chem. Jour., 19, 83 (1897).

This investigation of the double malonates was undertaken to see how far a double salt of an acid of this strength would be dissociated at high dilutions, and as a contribution to the larger question of how far the dissociation of complex ions depends upon the strength of the simple anion.

(1) *Electrolytic Dissociation.*—The most direct method of measuring the ionization is by comparing the electrical conductivities of equivalent solutions of the two salts constituting the double salt and comparing their sum with that of the double or complex salt itself. This was done for the four salts:

$(NH_4)_2CoMal_2$
K_2CoMal_2
Rb_2CoMal_2
Cs_2CoMal_2

The method of procedure was as follows:

A 100 cc solution was made up by weighing out a definite amount of the salt and standardized by determining the cobalt or the alkali content of a measured volume of the solution. In this way, the purity of the salt was always able to be checked from the definite quantity weighed out. All the water used in the determinations was distilled by the method of Jones and Mackay[1] and showed a conductivity of 2×10^{-6} mercury units or less.

The different strengths of the solution were made from the original 100 cc solution. Reading to 0.01 cc, twenty-five cc of this were measured from a 50 cc bottle, into a 100 cc flask and diluted to 100 cc. This amounted to a dilution of four. This was repeated for each succeeding dilution. For intermediate dilutions, 20 cc of the solution were poured into the measuring cell, and after determining its conductivity was diluted one-half by the addition of 20 cc of water. All burettes and pipettes in which any absolute measuring was necessary were accurately standardized.

The cell employed was the Arrhenius type, consisting of two circular electrodes of sheet platinum 32 mm in diameter.

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[1] Am. Chem. Jour., 19, 91 (1897).

These are welded to two short platinum rods, which are fused to small glass tubing, the latter acting as mercury cups for the connexions. For a description of the cell, see Ostwald, Physico-Chemical Measurements, p. 225. The electrodes were kept about 1 cm apart. They were carefully platinized before using.

The bridge for measuring the resistance was the direct reading Wheatstone bridge manufactured by Hartman and Braun, Frankfurt, a/M, Germany. Instead of using the regular resistances of 10, 100 and 1,000 ohms, a resistance box reading from 1 to 10,000 ohms was connected as the known resistance, and the minimum buzzing of the telephone determined as accurately as possible while the slide wire indicator stayed at 1, then the latter was adjusted and the proper factor applied to the reading of the resistance box.

All the determinations were made at the constant temperature 18°, and the cell was repeatedly standardized by a 1–50 normal solution of potassium chlorid throughout the series of experiments.

TABLE A

$CoMal.2H_2O$

Gram-molecules per liter	Volume	μ_v 18°
0.06	16.7	19.6
0.03	33.3	23.5
0.015	66.6	29.2
0.00934	107.0	35.0
0.00467	214.0	44.3
0.002405	416.0	60.7
0.002112	473.0	64.8
0.001202	831.0	78.9
0.00118	847.0	80.9
0.001056	947.0	84.4
0.0006012	1663.0	102.8
0.00059	1694.0	103.6
0.000295	3390.0	128.1

10 cc $CoMal.2H_2O$ solution gave 0.0354 gram Co = 0.06 gram-molecules per liter.

TABLE B

$(NH_4)_2Mal.2H_2O$

Gram-molecules per liter	Volume	μ_v 18°
0.1	10.0	158.0
0.05	20.0	177.0
0.025	40.0	187.6
0.0102	98.0	202.0
0.0051	196.0	212.0
0.00408	245.0	223.0
0.00204	490.0	230.0
0.00102	980.0	238.0
0.00051	1960.0	255.0

The ammonium malonate analyzed as follows:

Weight		1	2
Assay		0.2353	20.74
$(NH_4)_2PtCl_6$		0.5991	58.57
NH_4		0.0488	20.69
Percent	**Theoretical**		
NH_4	20.74	20.75	20.94
Mal	58.57		
H_2O	20.69		

10 cc of the standard solution gave 0.4412 gram $(NH_4)_2PtCl_6$ = 0.1 gram-molecules per liter.

TABLE C

$K_2Mal.2H_2O$

Gram-molecules per liter	Volume	μ_v 18°
0.0961	10.4	156.0
0.0480	20.8	171.0
0.0240	41.6	183.0
0.0120	83.2	196.0
0.00938	106.5	200.0
0.00469	213.1	211.0
0.00346	289.0	222.0
0.00173	578.0	229.0
0.00087	1156.0	236.0
0.00043	2312.0	245.0

10 cc $K_2Mal.2H_2O$ solution gave 0.1682 gram K_2SO_4 = 0.0961 gram-molecules per liter.

TABLE D

$Rb_2Mal.2H_2O$

Gram-molecules per liter	Volume	μ_v 18°
0.07	14.3	170.0
0.035	28.6	180.0
0.0175	57.2	194.5
0.00875	114.2	201.4
0.00433	228.8	208.2
0.00216	457.6	213.2
0.00108	915.2	216.9
0.00054	1830.0	223.3
0.00027	3660.0	237.9

10 cc $Rb_2Mal.2H_2O$ solution gave 0.4032 gram Rb_2PtCl_6 = 0.07 gram-molecules per liter.

TABLE E

$Cs_2Mal.2H_2O$

Gram-molecules per liter	Volume	μ_v 18°
0.342	29.2	179.0
0.171	58.4	189.0
0.0855	116.8	199.0
0.0427	233.6	205.0
0.0213	467.2	213.0
0.0106	934.0	220.0
0.0053	1868.0	236.0
0.0026	3736.0	264.0

10 cc of $Cs_2Mal.2H_2O$ solution gave:

0.2232 gram Cs_2PtCl_6 = 0.332 gram-molecules per liter
0.1272 gram Cs_2SO_4 = 0.352 " " " "

0.342

TABLE F
$(NH_4)_2CoMal_2.4H_2O$

Gram-molecules per liter	Volume	μ_v 18°
0.1022	9.78	135.0
0.0511	19.57	153.6
0.0256	39.13	172.6
0.0128	78.27	184.0
0.01014	98.6	203.1
0.00507	197.2	215.0
0.0036	278.0	222.4
0.00254	394.4	229.0
0.0018	555.0	235.0
0.0009	1111.0	254.0
0.00045	2222.0	282.0

10 cc of $(NH_4)_2CoMal_2.4H_2O$ solution gave:

0.0609 Co
0.0597

0.0603 = 0.1022 gram-molecules per liter.

TABLE G
$K_2CoMal_2.4H_2O$

Gram-molecules per liter	Volume	μ_v 18°
0.04	25	110.3
0.02	50	121.6
0.01	100	134.3
0.005	200	146.5
0.0025	400	159.6
0.0012	800	175.2
0.0006	1600	196.6
0.0003	3200	220.1

10 cc of $K_2CoMal_2.4H_2O$ solution gave 0.0302 gram Co = $^1/_{19.5}$ gram-molecules per liter—19.52 cc of solution diluted to 25 cc for above determinations.

TABLE H

$Rb_2CoMal_2.4H_2O$

Gram-molecules per liter	Volume	μ_v 18°
0.0893	11.2	152.7
0.0447	22.4	171.3
0.0223	44.8	190.0
0.0112	89.6	206.0
0.0056	179.2	223.0
0.0028	358.4	239.4
0.0014	716.8	261.8
0.0007	1433.6	294.2

10 cc of $Rb_2CoMal_2.4H_2O$ solution gave:

0.0527 gram Co
0.0527 " "

0.0527 gram Co = 0.0893 gram-molecules per liter.

TABLE I

$Cs_2CoMal_2.4H_2O$

Gram-molecules per liter	Volume	μ_v 18°
0.040	25.0	159.8
0.020	50.0	177.4
0.010	100.0	192.5
0.005	200.0	207.0
0.0025	400.0	224.8
0.00125	800.0	243.2
0.00062	1600.0	265.6
0.00031	3200.0	299.0

10 cc of $Cs_2CoMal_2.4H_2O$ solution gave 0.0236 gram Co = 0.040 gram-molecules per liter.

From the above tables the inserted diagrams have been made and curves plotted for the conductivity of the alkali malonate, cobalt malonate, their sum and the double salt. By interpolating, the following tables were obtained.

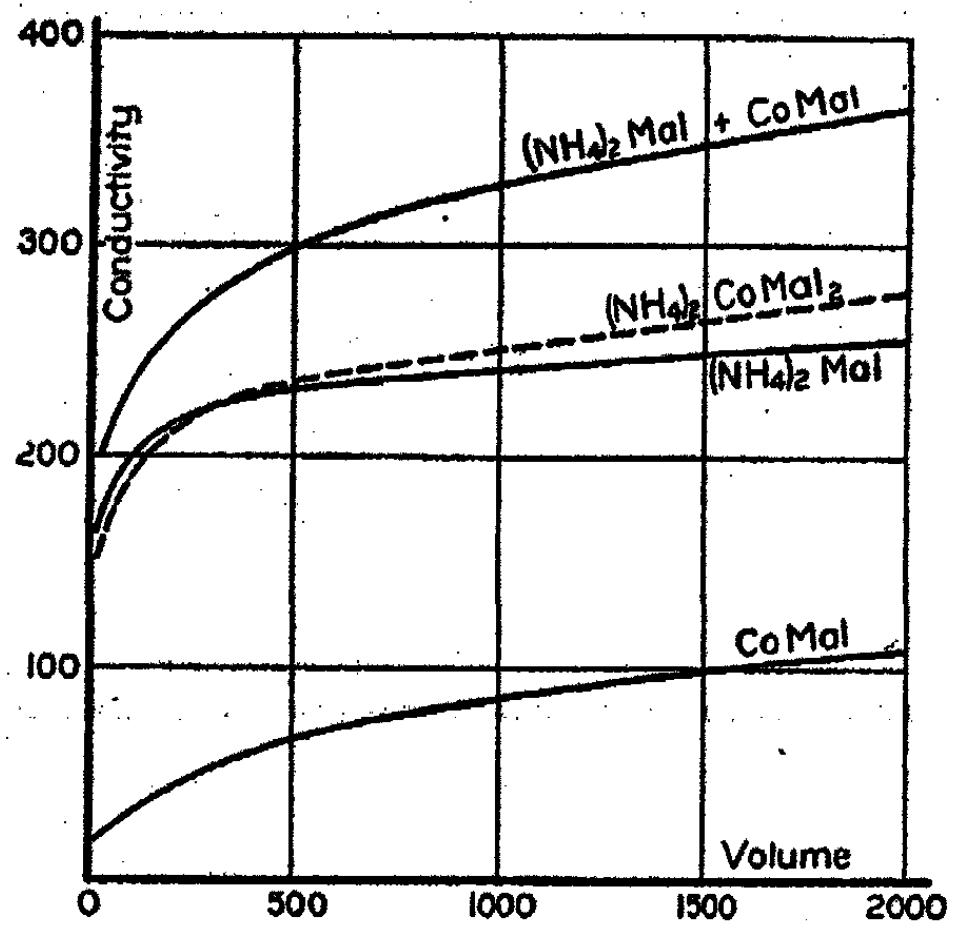
400
300
200
100
Conductivity
$(NH_4)_2$ Mal + CoMal
$(NH_4)_2$ CoMal$_2$
$(NH_4)_2$ Mal
CoMal
Volume
0
500
1000
1500
2000

Fig. 1

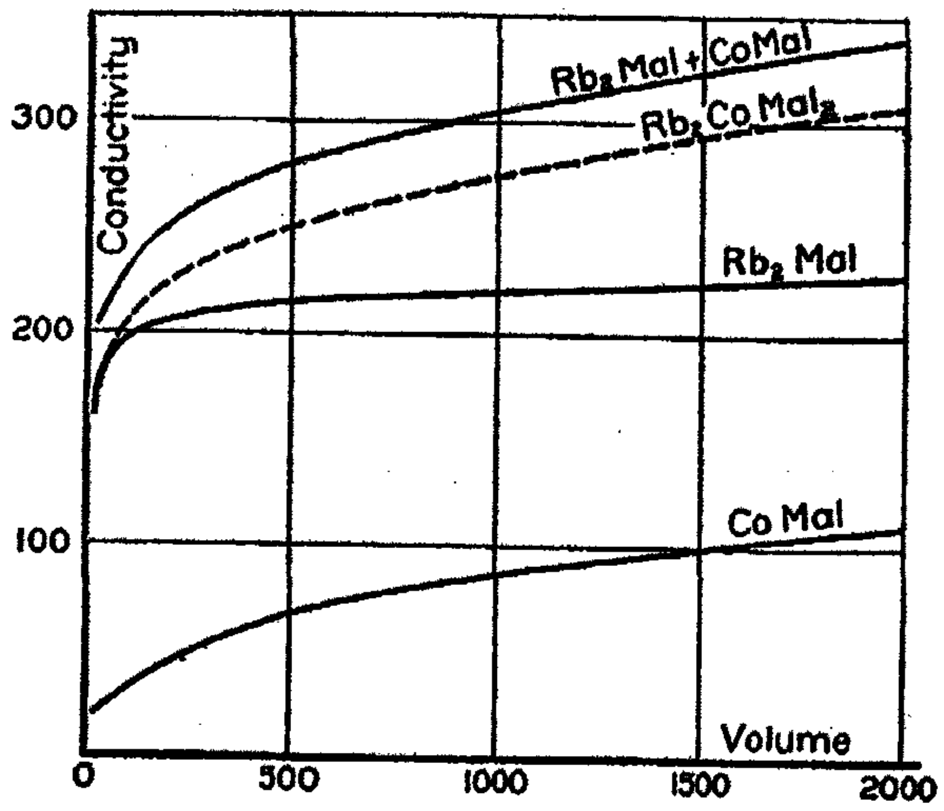
300
200
100
Conductivity
Rb_2Mal + CoMal
Rb_2CoMal$_2$
Rb_2 Mal
Co Mal
Volume
0
500
1000
1500
2000

Fig. 2

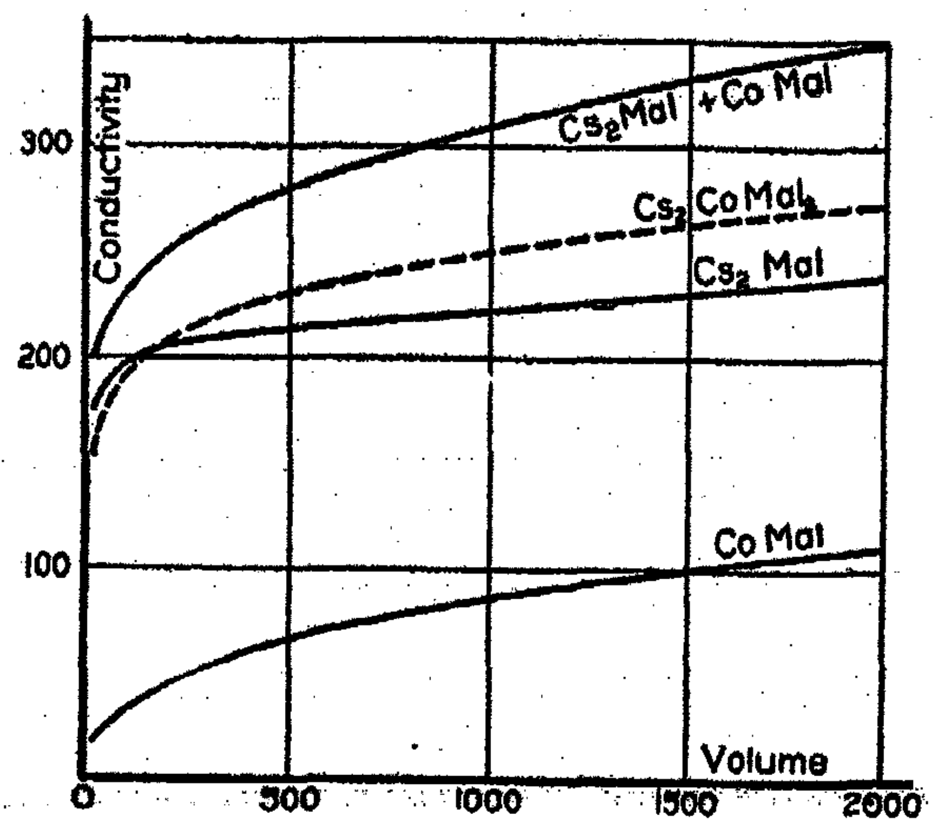

Fig. 3

TABLE J

$(NH_4)_2CoMal_2.4H_2O$

Volume	$\mu_{18}(NH_4)_2Mal$	μ_{18} CoMal	μ_{18} Sum	$\mu_{18}(NH_4)_2CoMal_2$	Difference
20	177	20.6	197.6	154.0	43.6
40	186	24.5	210.5	173.0	37.5
80	197	31.0	228.0	185.0	43.0
160	210	41.2	251.2	206.0	45.2
320	224	54.2	276.2	226.0	50.2
640	236	73.6	309.6	238.5	71.1
1280	245	94.5	339.5	258.0	81.5
2000	256	108.0	364.0	278.0	86.0

TABLE K

$K_2CoMal_2.4H_2O$

Volume	μ_{18} K_2Mal	μ_{18} CoMal	μ_{18} Sum	μ_{18} K_2CoMal_2	Difference
20	170	20.6	190.6	107.5	83.1
40	182	24.5	206.5	116.3	90.2
80	195	31.0	226.0	130.2	96.2
160	208	41.2	249.2	143.0	106.2
320	222	54.2	276.2	155.0	121.2
640	229	73.6	302.6	170.0	132.6
1280	238	94.5	332.5	189.0	143.5
2000	244	108.0	352.0	207.0	145.0

Table L

$Rb_2CoMal_2.4H_2O$

Volume	μ_{18} Rb_2Mal	μ_{18} CoMal	μ_{18} Sum	μ_{18} Rb_2CoMal_2	Difference
20	175	20.6	195.6	170.0	25.6
40	186	24.5	210.5	190.0	20.5
80	197	31.0	228.0	204.0	24.0
160	205	41.2	246.2	218.0	28.2
320	211	54.2	265.2	236.0	29.2
640	216	73.6	289.6	256.0	33.6
1280	221	94.5	315.5	287.0	28.5
2000	228	108.0	336.0	305.0	31.0

Table M

$Cs_2CoMal_2.4H_2O$

Volume	μ_{18} Cs_2Mal	μ_{18} CoMal	μ_{18} Sum	$\mu_{18}Cs_2CoMal_2$	Difference
20	174	20.6	194.6	156	38.6
40	184	24.5	208.5	172	36.5
80	195	31.0	226.0	187	39.0
160	203	41.2	244.2	203	41.2
320	210	54.2	264.2	217	47.2
640	216	73.6	289.6	232	57.6
1280	228	94.5	323.5	254	69.5
2000	238	108.0	346.0	276	70.0

As the result of the comparison of the above tables the following conclusions can be drawn regarding the conditions of the double cobalt malonates in solution.

(1) The large difference between the sum of the conductivities of the alkali malonate and cobalt malonate, and that of the double cobalt malonate is much too great to be accounted for by the ratio of the sum of the conductivities of two salts to that of a mixture.

(2) This large difference, taken in connection with the fact that the addition of an alkali malonate solution to that of one of cobalt malonate causes a change in color from a bright red to one with a slight purplish tinge, indicates some rearrangement of the molecule as far as the cobalt ion is concerned.

(3) The only arrangement possible, confirmed, as it is,

by a large number of analogous experiments, is that the cobalt is more or less associated with the negative ion.

(4) The great increase in the difference between the sum of the conductivities of the constituents and that of the double salt, as the dilution increases (which is marked in each case save the rubidium salts and in that the increase in conductivity with dilution is appreciable) indicates that the association of the cobalt with the anion does not diminish with increasing dilution and hence the salt approaches the "complex" type as defined by Ostwald—rather than the "double" salt.

(5) While the cobalt is precipitated to a considerable extent by the ordinary qualitative tests for cobalt in the cation, the dissociation is to some extent at least as follows: $\overset{+}{(NH_4)_2} \mid \overset{-}{Co}\overset{-}{Mal_2}$ and similarly for the other salts.

(6) The presence of a minimum point in the difference between the two means for measurement—the sum of the components and the double salt itself may probably be explained by the hydrated theory of solutions or the water of crystallization in solution, as has recently been propounded by Jones.

(7) Summing up—it seems undoubtedly true that the double salts of the alkalis and cobalt with malonic acid form solutions that are, to a considerable extent, associated into the ions $\overset{+}{M_2} \mid \overset{-}{Co}\overset{-}{Mal_2}$, while the presence of the ions $\genfrac{}{}{0pt}{}{\overset{+}{M_2}}{\overset{++}{Co}} \mid \overset{-\;-}{Mal_2}$ is also to some extent evident.

The ratio of the association of the former to the latter—that is, of the "complex" salt component to that of the "double" salt—is approximately the same for all dilutions.

(2) *Freezing-point.*—The lowering of the freezing-point of a liquid by the addition of a soluble salt was employed to determine the molecular weight of the cobalt malonates in a stronger solution than that for the conductivity measurements. The Beckmann apparatus was used. A strong

solution of brine was mixed with the ice to cool the temperature of the jar to —5° to —6° C. The overcooling varied from 0.5° to 3°, averaging about 2°. The tube containing the solution was inserted directly in the freezing mixture and stirred vigorously till ice crystals began to separate. It was then placed in the air jacket and allowed to rise to the maximum temperature and the reading made. For data see p. 196.

(3) *Migration.*—The solution of the alkali cobalt malonates dissociates in either one of two ways, 2K | $CoMal_2$ or 2K | 2Mal or partially according to both ways. The conductivity measurements showed that there was less conductivity for the double salt than for the sum of its components. The freezing-point determination indicated that the molecule does not average as many ions as required by the former of the above formulas if every molecule had completely dissociated. But the absolute constitution of the ions of the molecules were in neither case settled. The cobalt ion has a decided coloration and if we can determine in which direction it will travel when a current is passed through a solution of the double salt, the direction, whether towards anode or cathode, will determine the presence of the cobalt in the anion or the cation—a crucial point in our whole investigation. In performing this experiment, the following arrangement was adopted, for which credit should be given to Dr. S. C. Lind,[1] who employed it in some work on ruthenium salts at the Massachusetts Institute of Technology. A central dish contains a solution of the double salt, $(NH_4)_2CoMal_2$. Its strength was approximately one-tenth normal. Into this solution were dipped two inverted U-tubes. These had previously been filled with a 5 percent solution of the clearest jelly[2] obtainable. To the solution sufficient potassium chlorid was added to make it one-tenth normal. The U-tubes (3 or 4 inch) were filled with the hot solution of the jelly which was congealed in ice water.

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[1] A description of the apparatus is given in Jour. Am. Chem. Soc., 25, 931 (1903).

[2] Agar jelly was, at the time, unobtainable. If such is used, a 2 percent solution is sufficient.

FREEZING-POINT DETERMINATIONS.

Anhydrous salt, cc of solution	Gram-molecular volume Liters	Observed lowering	Corrected lowering	Mol. wt.	Ratio
		$(NH_4)_3CoMal_3$		299.2	
0.0553	5.4	1.010 1.009 1.018	0.984 0.981 0.989 0.985	106.1	2.82
		Rb_3CoMal_3		433.8	
0.0852	5.01	0.979 0.970 0.990 0.960	0.941 0.938 0.943 0.945 0.942	171.0	2.53
0.0484	8.95	0.613 0.615 0.579	0.573 0.574 0.573 0.573	160.0	2.71
0.0264	16.4	0.350 0.351 0.348	0.336 0.333 0.339 0.336	148.0	2.93
		Cs_3CoMal_3		529.0	
0.0956	5.03	0.893 0.899 0.908 0.905	0.891 0.885 0.890 0.887 0.888	213.0	2.48
0.0484	10.43	0.481 0.499 0.482 0.502	0.481 0.484 0.482 0.487 0.484	198.0	2.55

The tubes were dipped under the solution about ¼ of an inch. The other ends of the tubes were dipped, one into an acid solution, the other into an alkaline solution and a positive electrode inserted in the former and a negative electrode into the latter. The potassium chlorid is put into the jelly solution for conductivity purposes and the acid and alkali beakers are intended merely to neutralize the effect of the electrolysis at the opposite ends of the U-tubes. The voltage between the terminals was between 80 and 100. The current was very low, being about 0.03 ampere. This very high resistance caused almost entirely by the jelly in the U-tubes, caused considerable rise of temperature, to about 30°, sufficient to make the jelly liquid again and prevent the effect desired—the slow traveling of the cobalt in an ionized state in one direction or the other. To prevent this the solutions were kept surrounded by ice water and the U-tubes as far as possible also.

The result of the passage of the current was as follows: At the end of one hour, the jelly was assuming a red tinge at the point of immersion of the anode U-tube in the liquor. At this time there was no perceptible change in the cathode. The color at the anode intensified and lengthened till at the end of four hours the color had crept up the anode U-tube a distance of about 3 inches while the first ¾ of an inch was as intensely red as the solution itself. At the cathode U-tube a slight trace of color had by this time risen a distance of about 2 inches, but the tinge was so faint that considerable care was required to observe it.

From the above the following conclusions may be drawn:

(1) Since there is some color in both anode and cathode U-tubes the cobalt occurs in both anion and cation and the salt is ionized in both of the following ways:

$$2\mathrm{NH_4}|\mathrm{CoMal_2} \text{ and } 2\mathrm{NH_4}|\underset{\mathrm{Co}}{2\mathrm{Mal}}.$$

(2) The great intensity of the color in the anode tube and the fact that it is of the same shade of red as the solution

indicates that the cobalt is very largely in the anion and that the salt is principally ionized as

$$2NH_4|CoMal_2.$$

This is further strengthened by the change in color of a solution of cobalt malonate, when a solution of an alkaline malonate is added to it (see p. 176).

(3) The cobalt malonates are therefore salts with properties both of the "double" and the "complex" salts of Ostwald, but the salt is largely dissociated after the complex type.

VI Oxidation

As cobalt occurs both in the bivalent and trivalent state, it was thought that double cobalti-malonates could probably be prepared. Two chrom-malonic acids have been prepared in this laboratory, $HCrMal_2 2H_2O$ and $H_3CrMal_3 3H_2O$.[1] These form salts with the alkalis, the most pronounced being those with ammonium and potassium. Alums of cobalt with rubidium and caesium, $RbCo(SO_4)_2 12H_2O$ and $Cs_2CoSO_4 12H_2O$, have also been prepared in this laboratory.[2] These were prepared by the electrolytic oxidation of the bivalent cobalt salt.

A similar method was employed with the cobalto-malonates. A solution of these was electrolyzed in a cell consisting of a medium-sized platinum crucible for anode and a large platinum wire for cathode. A porous porcelain cup was put in the crucible to keep the main portion of the solution from coming in contact with the cathode wire. The solution in the anode or main portion was made as strong as possible and an excess of acid was added to it. The excess of malonate ions in the anode solution oxidized the cobalt ions to trivalent, unless the malonic acid was itself oxidized. This was very evident from the fact that no bubbles of oxygen came from the anode and that Co was deposited on the cathode while a blue precipitate of $Co(OH)_2$ was formed in the

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[1] Jour. Am. Chem. Soc., 25, 444 (1903).

[2] Ibid., 20, 759 (1898).

porous cup containing the cathode solution. A voltage of 3 to 5 was employed and the solution was electrolyzed for from one-half hour to two hours. The solution obtained was of a color varying from a bluish green to a very deep green, according to the extent of the oxidation. The intensity of the color of the green was several times stronger than that of the red solution from which it was obtained. The deep green solution was neutralized with the alkali of the double salt used in the electrolysis—most frequently cesium and ammonium—and allowed to evaporate. It was first dried over sulfuric acid at 30° as described previously for the bivalent salts. But after three or four days the solution changed back almost to its original color and no green salt was obtained by this method. The presence of the cobalti-malonate salt, corresponding as it does in color with that of the cobalt alum, indicates beyond doubt, I think, the presence of cobalt in the trivalent condition and as malonic acid was the only acid present, the cobalt must have been combined with that acid. Attempts were also made by rapid evaporation on the water bath to obtain the crystals of the salt, but before sufficient concentration could be obtained the color changed in this case also to the original red.

Several trials were made to prepare the trivalent cobalt salts by oxidation with ammonium and potassium persulfates. About 0.5 gram of the persulfate was added to 5 or 6 cc of a strong acid solution of the cobalto-malonate. The persulfate has no effect until the cobalt solution is heated to the boiling-point, when it changes color similarly to the electrolytic oxidation. The sulfuric acid can be precipitated by $Ba(OH)_2$ if added carefully. The deep green solutions produced by this method changed back to their original red color when allowed to stand for a few days or evaporated.

From the above attempts the following conclusions can be drawn:

(1) There is very strong probability of the existence of the alkali cobalti-malonates in solution, at least, from the fact

that its green color is similar to the color of the alkali cobalti-sulfates that have been prepared.

(2) It is probable that the crystals of this salt can be prepared under certain exacting conditions. It is possible that low temperature may be necessary for its stability for any length of time.

(3) The dark green color of the solution indicates that the cobalt is probably in a different state of relation to the other components as far as ionization is concerned, from the metal in potassium cobalti-nitrite. What this is cannot be surmised at present as the cobalt is probably to a considerable extent in the anion in the alkali cobalti-malonates as well as in the potassium cobalt nitrite.

Anchorage, Kentucky.

ON THE OPTICAL ROTATORY POWER OF SALTS IN DILUTE SOLUTIONS

BY FREDERICK LAFAYETTE SHINN

One of the most striking of the phenomena associated with the optical rotatory power of substances in solution is the change suffered by the specific rotation upon varying the temperature or the amount or nature of the solvent. The desire to find an adequate explanation for such changes has stimulated a large number of investigators to study optical activity; and their work has resulted in the accumulation of a vast quantity of valuable data. In this work it is easy to discern three different directions of effort, *viz.*: (1) An inquiry into the nature and cause of optical activity *per se*; (2) the desire to find an expression for the changes in the specific rotation in terms of other changes which take place simultaneously in the solution, (3) an attempt to gain some further insight into the nature of the process of solution itself. However, in spite of this marked activity resulting in various theories and formulations, it cannot be said that any generally satisfactory conclusions have been reached.

The theory of Le Bel and van't Hoff of the asymmetric carbon atom has given to the subject of optical activity of carbon compounds a scientific basis. But the theory concerns itself rather with the fixed internal molecular structure as the cause of activity and is not concerned with influences external to the active molecule, such as the action of the solvent is commonly conceived to be.

Ph. Guye,[1] starting with the LeBel and van't Hoff hypothesis, conceived the brilliant idea of expressing the degree of optical activity as a mathematical function of the degree of asymmetry of the carbon atom. According to this hypothesis, to which he was led by his work on the substituted tartrates and other compounds, the optical activity of a com-

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[1] Guye: Comptes rendus, 110, 714 (1890).

pound is modified by the entrance into the molecule of other elements or radicals, to an extent depending upon the mass of the entering groups. It is an important conception which, however, has not been found to be strictly applicable. It is easy to show[1] that the mass of the radicals attached to the asymmetric carbon atom is but one factor influencing the rotatory power and that their chemical nature and also the constitutive influences upon the compound formed must be taken into consideration.

Another generalization known as Oudemans' law[2] attempts to correlate a class of phenomena which do not conform to Guye's hypothesis. In 1873 Landolt observed that a number of the neutral salts of tartaric acid in solution in water possess very nearly the same rotatory power. A few years later Oudemans found a similar behavior in the case of the alkali and alkaline earth quinates and the salts of quinamine with various inorganic acids. His results were summed up in his well-known law that the specific rotatory power of alkaloids is modified in the same manner by different acids, provided the degree of saturation of the base by the acid is the same. This law was considerably modified and extended by Hädrich[3] who, interpreting his results from the standpoint of the theory of electrolytic dissociation, stated the law as follows: The rotating power, not only of salts, but of electrolytes in general, is, in approximately completely dissociated solutions, independent of the inactive ion. According to this rendering, the law would be valid only in the case of very dilute solutions.

Unfortunately, the measurement of the angle of rotation in solutions sufficiently dilute to conform to the conditions of the law is commonly associated with errors of observation so large as effectually to obscure the real relations sought. Prior to Hädrich's work a number of investigators from time

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[1] Frankland: Jour. Chem. Soc., 63, 1419 (1893).

[2] Liebig's Ann., 197, 48, 66 (1879).

[3] Zeit. phys. Chem., 12, 476 (1893).

to time had undertaken such measurements. The general result had been to cast doubt upon the validity of Oudemans' law. Hädrich, however, worked with much more dilute solutions than had previously been studied. He measured the rotations of very dilute solutions of hydrochlorides, nitrates, sulphates and amygdalates of some alkaloids and found closely agreeing values for salts of the same active base. He found in all cases that at high dilution (eightieth to one hundred sixtieth normal) the rotations attain a maximum or minimum constant value.

He also investigated a few substituted alkaloids. Morphine methyl salts gave a much lower value for the molecular rotation than the morphine salts at corresponding dilutions and, unlike the latter, the values decreased upon dilution. The same marked decrease in the rotation was shown by the methyl brucine salts.

Hädrich further examined some salts of tartaric acid; namely, the potassium arsenyl, boryl and antimonyl tartrates. The rotation of the potassium antimonyl tartrate was found to be incomparably greater than that of the other two salts, and also to be practically independent of the concentration, whereas the arsenyl and boryl tartrates showed rapidly diminishing rotations as dilution increased.

In spite of these contradictory results, and a few feeble protests, Oudemans' law has been commonly regarded as well established since the publication of Hädrich's work. However, the desirability of measuring the rotatory power of solutions at still greater dilutions has been recognized,[1] and in this paper are presented the results of a few such measurements.

In a review of the work which has been done on the rotation of dilute solutions, the fact that there are many substances which do not conform to Oudemans' law is readily apparent. Indeed, aside from the experiments of Hädrich

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[1] Landolt: Optical Rotation of Organic Substances, Long's translation, p. 196.

which I have been unable wholly to confirm, there are few substances which show a really satisfactory agreement with the law.

The deviations, when not too wide, are commonly ascribed to two causes, experimental error and incomplete ionic dissociation. The assumption is then made that, were it possible to measure solutions at such dilutions that ionic dissociation could be considered as approximately complete, identical values would be found for the rotations of the same active substance whether it exist in solution as the free base or free acid or as a salt.

To account for divergences which do not admit of the above explanations, other assumptions are invoked, such as polymerization, hydration, hydrolytic dissociation, secondary ionic dissociation and other influences[1] which are not sufficiently well understood to merit a name. A few efforts have[2] been made to prove the assumptions but more often no such attempts are recorded.

Experimental

At the suggestion of Professor Kahlenberg I undertook the measurement of the rotations of some active substances at very high dilutions in an endeavor to answer these questions: (1) Does the rotation of an active salt attain a constant value at high dilution and is this value independent of the inactive part of the salt? (2) Is there any relation between the change in the molecular rotation and the change in the electrolytic conductivity as dilution progresses?

Aqueous solutions of malates and tartrates were first tried, but were shortly abandoned on account of the small angle of rotation which these yield, and the relatively large experimental errors consequently introduced. Nevertheless, the few measurements made upon the tartrates are the result of very careful work and have been included in this paper.

Some of the active alkaloids show much larger rotations

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[1] Landolt: Optical Rotation of Organic Substances, p. 215.

[2] Ibid., p. 227.

than the tartrates and malates and are easy to obtain in a pure state. They were consequently chosen for further work, although they possess the distinct disadvantage of being almost insoluble in water in the form of the free base.

Description of the Instrument

The instrument kindly placed at my disposal was constructed for especially accurate work. It is the largest polariscope manufactured by Schmidt and Haensch and is of latest pattern. A long heavy cast bronze bench supported by three adjustable legs forms the base of the instrument. Two heavy bronze carriers support the optical parts. One, fixed at one end, bears the analyzer, telescope, scale and the two reading lenses. The other carries the polarizer and may be moved along the bench and rigidly fixed in any desired position by means of a set screw. The instrument is provided with an adjustment by means of which either a double or triple field, as desired, may be obtained. The maximum length of tube that may be used is 11 dm. The scale disc is protected by a case of hard rubber and is illuminated by small electric lights. The analyzer is provided with a micrometer screw by means of which the final setting is made. The scale is divided into tenths of a degree which are read off directly with the microscope, and by means of a graduated micrometer screw, which raises or lowers two parallel threads across the field of the lens, the angle may be read to thousandths of a degree.

As a source of light a powerful Bunsen burner was used, surrounded by a square chimney with a hole at one side. Within the chimney was supported horizontally, just above the inner cone of the flame, a piece of thin asbestos board having an opening through the center slightly narrower than the flame. This asbestos was impregnated with a saturated solution of sodium bromide and the flame playing through the opening became illuminated at the front and back. From time to time a little more of the sodium bromide solution was placed upon the asbestos. This proved to be a fairly satisfactory source of light. The period of maximum intensity lasted but a few minutes and the necessity of frequently replenishing the volatile sodium bromide, even during a single series of readings, proved somewhat annoying. I did not find the addition of either sodium chloride or carbonate to the sodium bromide of any advantage. The intensity of the light varied somewhat from day to day, depending upon the quality and pressure of the gas; but it was practically constant for any particular series of measurements.

The tube used in all the measurements was 11 dm long. The length was measured by means of a meter stick and can hardly differ from 11 dm by more than a quarter of a millimeter. It was deemed unnecessary to make any more refined measurement of the length of the tube inasmuch as the relative rather than the absolute values of the specific rotations were of prime interest for the purpose in hand. Moreover, assuming the tube to differ from 11 dm by 0.25 mm, the error thus introduced is but 25 units on 110,000 or 0.02 percent. This is of about the same order as the error of reading of the instrument in the case of the largest angle measured, *i. e.*, 50.34°. Hence for all angles of rotation less than 50 the error due to the uncertainty in the length of the tube falls below the error in setting the instrument and becomes, thereby, relatively insignificant. The tube was encased in a metal jacket through which water, maintained at the constant temperature of 25° C, was circulated. The tube was carefully adjusted on its supports in the axis of the instrument so that the light encountered no obstruction in its path. Care was always exercised to avoid producing any strains in the glass in screwing the end glass plates into position.

Considering the size and delicacy of the instrument, the results, in point of accuracy, were somewhat disappointing. In some cases successive readings differed from one another by one to four units in hundredths place, the eye being incapable of making closer settings. Several circumstances may be mentioned to account for this. In the first place the great length of the tube required that the source of light be placed at a correspondingly greater distance away in order to produce a distinct image on the analyzer diaphragm. This circumstance materially diminished the sensitiveness of the settings by decreasing the intensity of the light which reached the eye, and consequently necessitating the employment of a comparatively large angle of half shadow. That this is true is shown by the fact that by diminishing the distance between the analyzer and polarizer the settings became more accurate. This difficulty could perhaps be remedied somewhat by using a source of light of much greater intensity than I have employed.

In the case of dilute solutions the settings could be made quite as sharply with the tube in as with it out. The settings for dilute solutions were more satisfactory than for concentrated ones, owing to the fact that many of the stronger solutions were slightly colored, a difficulty that has been encountered by other investigators in working with the alkaloid salts. After a few dilutions the color disappears. Errors resulting from such coloration are partly offset by the fact that for strong solutions the angles of rotation are large.

In dilute solutions the average deviation from the mean of a series of readings was about fifteen thousandths of a degree. To illustrate the limits to which the eye was capable of setting the instrument when a tube of 11 dm was used, I append a few typical series for both strong and dilute solutions.

A consideration of the various sources of error, *e. g.*, errors of weighing, neutralizing, diluting the solutions and reading the polariscope, shows that the measurement of the angle of rotation is attended with by far the greatest relative degree of uncertainty. The vessels used in making the dilutions were carefully calibrated and much larger quantities of the substances than necessary to make the measurements were taken so as to reduce the errors of weight and volume to a minimum. By experiment I have satisfied myself that the errors of reading the instrument are much smaller than the differences observed in the molecular rotations upon diluting the solutions. Aside from one or two values which I have enclosed in parenthesis and which may be regarded as doubtful, and those for strychnine nitrate, the differences observed must be regarded as lying fully outside the limits of experimental error.

Strong solutions		Weak solutions	
(1)	(2)	(3)	(4)
147.015	146.115	149.620	157.738
0.020	0.100	0.633	0.740
0.020	0.070	0.626	0.745
0.040	0.070	0.626	0.744
0.015	0.125	0.626	0.750
0.010	0.060	0.634	0.738
0.010	0.045	0.628	0.738
0.010	0.075		
0.025	0.075	149.627	157.742
	0.065		
147.018	0.080		
	0.090		
	0.095		
	146.082		

Maximum deviations from the mean: (1) 0.022, (2) 0.043, (3) 0.007, (4) 0.008.

Experimental Data

In a few cases the electrolytic conductivities of the solutions were determined; in others the values found by Bredig[1] have been taken. Both rotations and conductivities have been tabulated to facilitate comparison. The rotations have been presented also in graphical form.

In calculating the molecular conductivities of the solu-

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[1] Kohlrausch: Leitvermögen der Elektrolyte, p. 174.

tions, that of the water, approximately 2×10^{-6}, has been deducted in the usual way.[1]

The equivalent rotations have been calculated from the formula

$$[M]_D^{25°} = \frac{\alpha V}{100\, l}.$$

α = the angle measured, and

V = the volume in liters containing a gram equivalent of the active substance.

l = eleven, the length of the tube in decimeters.

These designations hold also for the tables contained in this paper. In addition Λ is used to indicate the so-called equivalent electrolytic conductivity.

The tartrate solutions were made up by neutralizing a freshly prepared solution of tartaric acid with the calculated quantity of the hydroxide of the metal. The butylamine was weighed directly.

TABLE I

Potassium tartrate

v	α	$[M]_D^{25°}$
20	+1.686	+30.56
40	0.783	29.12

Sodium tartrate

v	α	$[M]_D^{25°}$
20	+1.709	+30.94
40	0.847	30.80

Lithium tartrate

v	α	$[M]_D^{25°}$
20	+1.627	+29.58
40	0.807	29.34

Ammonium tartrate

v	α	$[M]_D^{25°}$
20	+1.645	+29.90
40	0.780	28.35

Barium tartrate

v	α	$[M]_D^{25°}$
20	+1.344	+24.43
40	0.673	24.47

Butylamine tartrate

v	α	$[M]_D^{25°}$
40	+0.698	+25.38
60	0.456	24.87
80	0.302	21.96

It is evident that the rotations of the alkali tartrates and ammonium tartrate are very nearly equal at comparable

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[1] Professor Kahlenberg, in the Jour. Phys. Chem., 6, 452 (1902), calls attention to the fact that such a correction is scarcely rational. I have here simply followed common custom so as to make my data comparable with Bredig's.

concentrations; and also that the rotations decrease with increase of dilution up to fortieth-normal, the limit to which the dilutions could well be carried, owing to the small angle of rotation. The barium tartrate has a much lower rotatory power, and the results show it to be constant at the dilution measured. The twentieth-normal solution of the barium salt was supersaturated. Butylamine tartrate possesses a rotation of the same order as the barium salt. Its rotation decreases upon dilution.

In Table II are presented the results of the measurements of rotation of the alkaloid salts.

To ensure their purity the alkaloids were first recrystallized from water in the form of nitrate or sulphate, then dissolved in water and the free base precipitated with ammonia. The base was then recrystallized from alcohol and dried at 110° in an air bath.

The solutions were prepared by weighing out the free alkaloid base, dissolving it in the calculated quantity of normal acid, and making up to the desired volume. Whenever possible the reaction was allowed to complete itself in the cold,[1] though in some cases it was necessary to heat on the water bath.

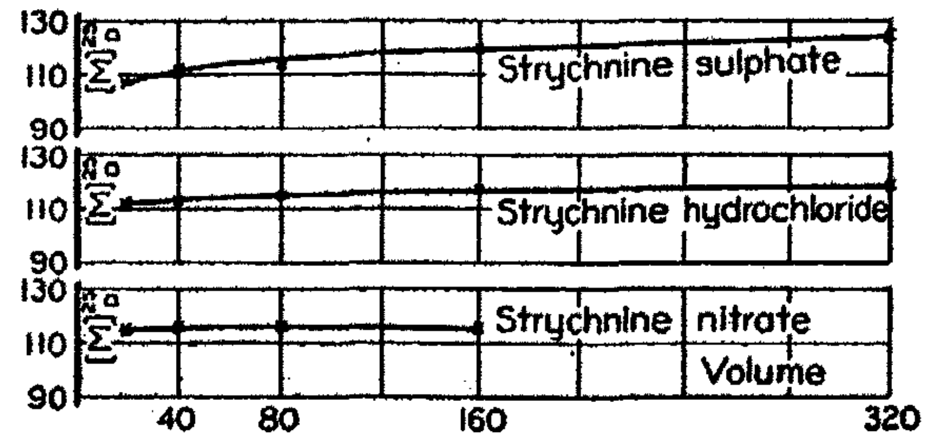

Fig. 1

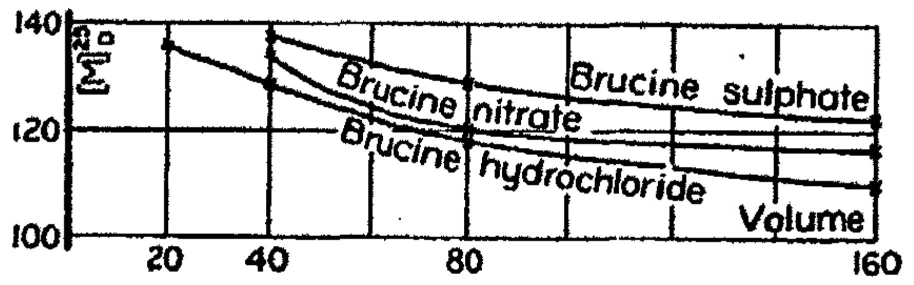

Fig. 2

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[1] This was done so as to avoid discoloration of the solution.

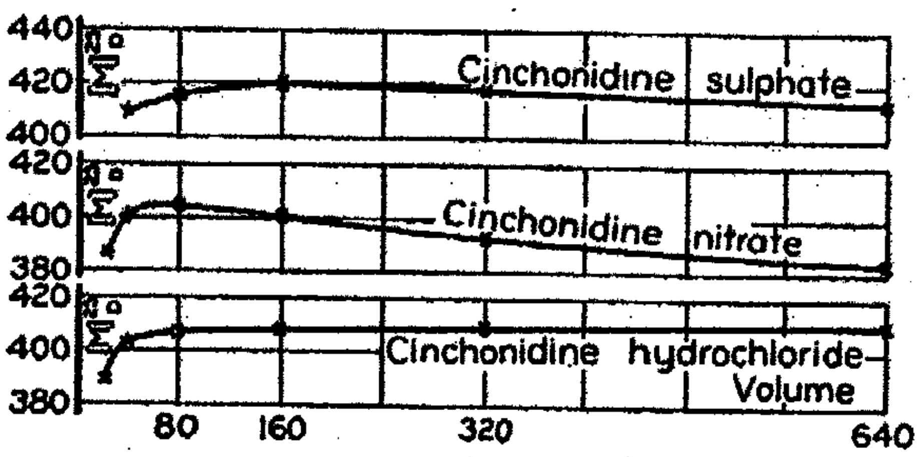

Fig. 3

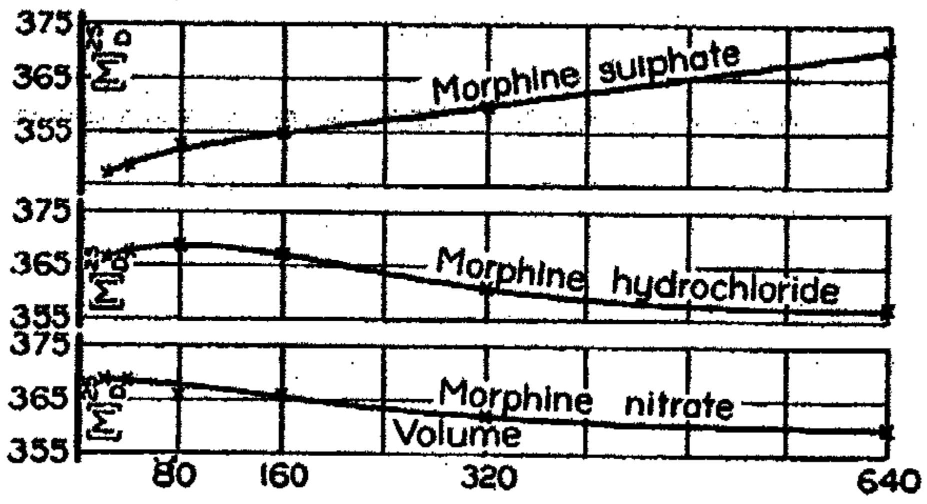

Fig. 4

TABLE II
Strychnine hydrochloride ($C_{21}H_{22}N_2O_2.HCl$)
Mol. wt. = 370.5

v	*α*	M	Λ
20	—6.122	—111.3	—[1]
40	3.089	112.3	86.0
80	1.555	113.1	90.3
160	0.793	115.3	93.5
320	0.400	116.3	95.8
640	—	—	97.0
1280	—	—	97.6

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[1] Bredig's data.

TABLE II—(*Continued*)

Strychnine nitrate, ($C_{21}H_{22}N_2O_2.HNO_3$)
Mol. wt. = 397.0

v	*α*	M	A
20	—6.237	—113.4	69.5
40	3.140	114.1	79.1
80	(1.547)	(112.5)	84.1
160	0.782	113.7	90.2
320	—	—	95.1
640	—	—	97.0
1280	—	—	98.1

Strychnine sulphate ($C_{21}H_{22}N_2O_2.{}^1/_2H_2SO_4$)
Mol. wt. = 383.0

v	*α*	M
20	—5.958	—108.3
40	3.062	111.3
80	1.535	111.6
160	0.8000	116.3
320	0.413	120.1

Brucine hydrochloride ($C_{23}H_{26}N_2O_4.HCl$).
Mol. wt. = 430.5

v	*α*	M	A
20	—7.530	—136.0	—[1]
40	3.544	128.9	84.1
80	1.621	117.9	87.3
160	0.755	109.8	90.8
320	—	—	92.8
640	—	—	94.0
1280	—	—	95.2

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[1] Bredig's data.

TABLE II—(*Continued*)

Brucine nitrate ($C_{23}H_{26}N_2O_4.HNO_3$)
Mol. wt. = 457.0

v	α	M	A
20	—	—	66.6
40	—3.679	—133.8	74.5
80	1.650	120.0	81.0
160	0.799	116.2	85.0
320	—	—	86.3
640	—	—	87.4

Brucine sulphate ($C_{23}H_{26}N_2O_4.{}^1/_2H_2SO_4$)
Mol. wt. = 443.0

v	α	M	A
20	—	—	—
40	—3.782	—137.5	63.5
80	1.772	128.9	73.8
160	0.840	122.0	82.0
640	—	—	88.5

Cinchonidine hydrochloride ($C_{19}H_{22}N_2O.HCl$)
Mol. wt. = 329.5

v	α	M	A
20	—21.37	—388.5	70.0[1]
40	11.053	401.8	84.1
80	5.581	405.9	88.2
160	2.791	405.9	91.6
320	1.398	406.6	94.3
640	0.700	407.2	95.7

Cinchonidine nitrate ($C_{19}H_{22}N_2O.HNO_3$)
Mol. wt. = 357

v	α	M
20	—21.260	—386.5
40	11.092	401.0
80	5.556	404.0
160	2.754	400.5
320	1.351	393.0
640	0.662	385.0

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[1] Bredig's data.

TABLE II—*(Continued)*

Cinchonidine sulphate ($C_{19}H_{22}N_2O.\frac{1}{2}H_2SO_4$).

Mol. wt. = 343

v	*α*	M	Λ
20	—	—	60.0
40	—11.206	—407.5	71.3
80	5.681	413.1	78.9
160	2.860	417.3	84.5
320	1.426	414.8	87.7
640	0.708	411.9	88.8

Morphine hydrochloride ($C_{17}H_{19}NO_3.HCl$)

Mol. wt. = 321.5

v	*α*	M	Λ
20	—20.146	—366.2	—[1]
40	10.107	367.5	85.4
80	5.060	368.0	89.4
160	2.524	367.1	92.4
320	1.238	360.1	94.6
640	0.608	357.0	95.7

Morphine nitrate ($C_{17}H_{19}NO_3.HNO_3$)

Mol. wt. = 348

v	*α*	M	Λ
20	—20.275	—368.6	72.4
40	10.154	369.2	78.8
80	(5.030)	(365.8)	82.3
160	2.515	365.8	84.9
320	1.245	362.2	89.4
640	0.614	360.0	90.7
1280	—	—	91.3

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[1] Bredig's data.

TABLE II—(*Continued*)

Morphine sulphate ($C_{17}H_{19}NO_3 . {}^1/_2 H_2SO_4$)

Mol. wt. = 434

v	α	M	Λ
20	—19.087	—347.0	65.2
40	9.573	348.1	70.7
80	4.853	352.9	77.6
160	2.430	354.7	83.4
320	1.237	359.8	87.0
640	0.637	370.6	89.2
1280	—	—	90.0

Quinine hydrochloride ($C_{20}H_{24}N_2O_2.HCl$)

Mol. wt. = 360.5

v	α	M	Λ
20	—31.80	—578.2	—[1]
40	16.277	591.9	83.0
80	8.155	592.8	87.3
160	4.075	592.7	90.6
320	2.007	583.8	92.6
640	0.929	540.8	93.8
1280	—	—	94.4

Quinine nitrate ($C_{20}H_{24}N_2O_2.HNO_3$)

Mol. wt. = 387

v	α	M	Λ
20	—31.951	—580.9	70.4
40	16.032	582.9	79.1
80	8.068	586.9	84.6
160	4.035	586.9	88.3
320	1.983	576.9	91.4
640	0.950	553.3	92.0
1280	0.452	526.0	92.3

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[1] Bredig's data.

Most of the salts mentioned in the above tables were also investigated by Hädrich. A comparison of his data with mine shows that the values found for the rotations are of the same general order, also the general directions of the changes in rotation with addition of solvent are the same, so far as Hädrich was able to carry the dilutions. On the other hand, differences in the magnitude of the rotation in specific instances are apparent.

In the case of one salt only, that of strychnine nitrate, did I find the molecular rotation to remain practically constant for different degrees of dilution, both the hydrochloride and sulphate of strychnine showing a slight increase in rotation up to a maximum constant value.

With the exception of the brucine salts, the molecular rotations of the alkaloid salts measured increase at first rapidly with the dilution Strychnine and cinchonidine hydrochlorides apparently reach a maximum constant value at a dilution of about eightieth normal. The rotations of strychnine and morphine sulphates increase with the dilution without reaching a maximum value, whereas the brucine salts show continuously decreasing rotations. The rotations of all the other salts measured, namely, morphine and quinine hydrochlorides and nitrates and cinchonidine nitrate and sulphate, reach maximum values which, upon further dilution, regularly decrease. The maximum value is reached in about eightieth normal solutions in all solutions which show this behavior, except that of cinchonidine sulphate, in which case one hundred sixtieth normal marks the turning point.

Oudemans[1] found very early in his work on the alkaloid salts that the acid salts possess much greater rotatory power than the neutral salts. Hädrich's experiments confirm this. To show what effect still greater dilution would have in such a case, the dihydrochloride of quinine was measured for dilutions up to twelve hundred eightieth normal.

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[1] Landolt: Optical Rotation of Organic Substances, p. 223.

TABLE III

Quinine di-hydrochloride ($C_{20}H_{24}N_2O_2.2HCl$)

Mol. wt. = 397

v	α	M
20	— 50.34	— 907.0
40	25.16	906.6
80	12.565	905.6
160	6.209	895.0
320	3.055	880.7
640	1.420	818.7
1280	0.632	728.7

From twentieth to eightieth normal the rotation changes very little and has a value about 60 percent higher than the corresponding monohydrochloride solutions. From eightieth normal the rotation decreases rapidly with increasing dilution.

One further experiment was made to determine what effect dilution would have upon an alkaloid salt in the case of a solution which is not an electrolyte. Chloroform was chosen as the solvent, but the salts of the alkaloids with inorganic acids are quite insoluble in that menstruum. Hence it was necessary to choose some organic acid with high carbon and hydrogen content. Oleic acid was selected and the oleate of quinine prepared.

A known quantity of normal quinine hydrochloride dissolved in water was treated with the calculated quantity of pure sodium oleate in aqueous solution. An oily precipitate formed which remained in suspension even after several days' standing. The emulsion was therefore extracted repeatedly with small quantities of chloroform, the chloroform solution evaporated at room temperature in a vacuum, and the residual oil of quinine oleate kept in a vacuum desiccator over calcium chloride for a week. It was then weighed, dissolved in chloroform, made up to definite volume and its rotation measured.

The extreme volatility of the chloroform necessitated very quick handling of the solution and as little exposure to the air as possible. The change in concentration resulting from evaporation was extremely slight. The results are presented in Table IV and Fig. 5.

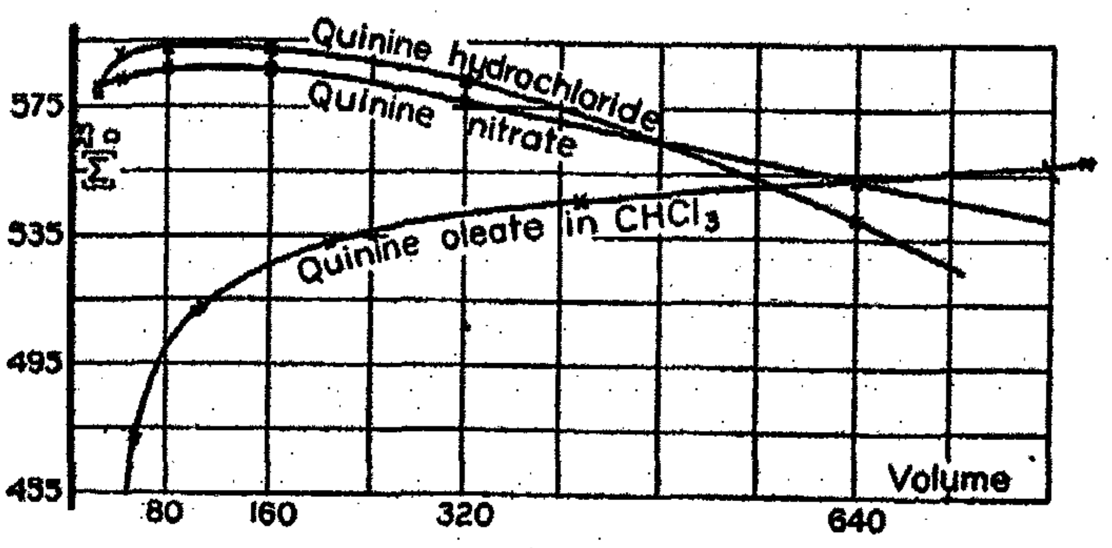

Fig. 5

TABLE IV

Quinine oleate ($C_{20}H_{24}N_2O_2.C_{18}H_{34}O_2$)

Mol. wt. = 606

v	*α*	M
12.68	—28.6	—334.3
25.36	—18.28	417.6
51.72	10.15	472.9
103.42	5.50	512.3
206.84	2.865	533.8
413.68	1.466	546.4
827.36	0.749	558.2

It will be observed that for strong solutions the values for the molecular rotations of quinine oleate dissolved in chloroform are somewhat lower than those of the hydrochloride and nitrate in water, all values at first increasing with the dilution. But very soon the molecular rotations of the nitrate and hydrochloride begin to fall off, and finally, at a dilution of about six hundred fortieth normal, become less than the rotation of the oleate in chloroform solution. The quinine oleate shows increasing rotations as far as the dilutions were carried.

Discussion

The difficulties encountered in endeavoring to explain the variations in rotation, shown in the above tables, on the basis of the theory of electrolytic dissociation, are at once apparent. In passing from saturated to dilute aqueous solutions of the alkaloid salts the qualitative trend of the changes in the rotatory power at first appears to accord with Oudemans' law. But at the highest dilutions measured, where the law should apply particularly well, the widest divergences from it are actually encountered. It consequently appears that, had Hädrich been able to measure the rotations of the solutions he used at still greater dilutions, he would have been led to quite different conclusions.

It is interesting to note that, among the limited number of experiments presented in the above tables, so many types of possible changes of rotation upon dilution have been encountered in solutions which are excellent electrolytes. (1) The rotations approach a *constant equal* value for different salts of the same base at high dilutions; *e. g.*, strychnine salts and morphine nitrate and hydrochloride. (2) The rotations show a *parallel* approach to *constant* but *different* values at high dilutions, *e. g.*, brucine salts. (3) The rotations *diverge* upon dilution; *e. g.*, morphine sulphate from the nitrate and hydrochloride. (4) A *maximum* rotation is reached, and upon further dilution, the values fall off more or less rapidly. (5) This *rate* of decrease of rotation with increasing dilution referred to in 4 may be the *same* for salts of the same base, as is true of morphine hydrochloride and nitrate where the rotations are very nearly identical for all dilutions, or it may be *different*, the rotations diverging at high dilution; *e. g.*, quinine nitrate and hydrochloride. The brucine salts suffer a decrease in molecular rotation from the first, but the curves suggest that at still higher dilutions than those measured the rotations very likely reach a minimum value. The results emphasize with what caution extrapolation formulae should be used, and the serious error which may result from predictions of the behavior of dilute solutions based upon phenomena occurring in more concentrated ones.

In looking over the literature, numerous examples are to be found in which the active acids (or bases) possess different rotations from their salts and show little or no tendency to approach identical values as dilution increases. But in many cases either the differences are too slight or the observations too incomplete to afford much ground for speculation. However, in this connection, mention may be made of some of the objections which have been made from time to time to Oudemans' law.

Frankland and Appleyard[1] found that the rotations of the alkali, alkaline earth and magnesium group salts of active glyceric acid possess marked differences in rotatory power. They found, for example, that the maximum rotations are shown by the magnesium and zinc salts, the minimum rotations by the alkaline earth salts, while the values for the rotations of the alkali salts lie intermediate between these two series. The fact that the salts do not possess approximately equal rotatory powers, but especially the order in which the rotations vary in passing from one group of metals to another, is entirely at variance with the theory of electrolytic dissociation. The authors also briefly review examples of other salts of active acids which do not conform to Oudemans' law, and cite as common examples tartaric, malic and camphoric acids. These acids possess very different rotations from their salts even in somewhat dilute solutions. The rotations of camphoric acid and its salts diverge upon dilution.

Similar behavior is to be found also among the optically active bases. The relation between nicotine and its salts is of especial interest. The free base in the pure state in aqueous solution is strongly levo-rotatory. Its salts with inactive acids, on the other hand, also in aqueous solution, dextro-rotatory. The rotation of the free nicotine, however, decreases rapidly with increasing dilution; and, according

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[1] Jour. Chem. Soc., 63, 296 (1893).

to the theory of electrolytic dissociation, it should, at high dilutions, tend to pass through zero and finally become identical with the rotations of the salts of nicotine. That it does not do so was shown by Hein,[1] who found that in solutions containing about 92 percent of water the rotation reached a minimum value, and upon further dilution increased.

The changes in the rotations of active salts, occasioned by a change of solvent, are, as often as otherwise, just opposite to what the theory of electrolytic dissociation would lead one to predict. One example will suffice. Organic quinates possess a larger molecular rotatory power than the metallic quinates, when the solvent is alcohol. When it is water the reverse is true. This fact led Cerkes,[2] on the basis of the theory of electrolytic dissociation, to the conclusion that in alcoholic solution the organic bases and quinic acid are uncombined, a conclusion which seems quite absurd.

Potassium antimonyl tartrate has a much greater rotatory power than other tartrates, and it remains practically constant upon dilution.[3] The same is true of potassium antimonyl malate. The slight hydrolysis which these salts undergo in aqueous solution is quite inadequate as an explanation for this behavior.[4]

That hydrolytic dissociation is unable to account for changes in the rotation of normal salts, has been pointed out by Carrara.[5] In the case of salts formed from weak bases with weak acids where hydrolytic dissociation takes place to a considerable extent in dilute aqueous solutions, one might expect the rotatory power to approach that of the free active acid or base, but this does not occur. Cinchonidine acetate affords an example of this in which the tendency is in the opposite direction.

The addition of even small quantities of any strong

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[1] Landolt: Optical Rotation of Organic Substances, p. 198.

[2] Cerkes: Comptes rendus, 117, 174 (1893).

[3] Hädrich: Zeit. phys. Chem., 12, 476 (1893).

[4] Landolt: Optical Rotation of Organic Substances, p. 227.

[5] Zeit. phys. Chem., 14, 562 (1894); 16, 244 (1895).

inorganic acid to aqueous solutions of the alkaloid salts of that same acid increases the rotation very greatly; whereas, on the basis of Arrhenius' theory it should, by decreasing the electrolytic dissociation, produce an effect on the rotation just opposite to that of simple dilution of the normal salt. Hädrich attributes such changes to hydrolytic dissociation occasioned by the addition of the acid. It is difficult to comprehend his line of argument. That acid salts undergo hydrolytic dissociation to a far greater extent than normal salts is well known, but is it not due to the ease with which the additional acid molecule splits off? There is certainly less free base present in the solution of an acid salt than in that of a neutral salt. One might expect therefore that the more complete the hydrolytic dissociation of the acid salt the more nearly would the rotatory power approach that of the neutral salt. Hence it appears that hydrolytic dissociation cannot account for the phenomenal *increase* in the rotation of the alkaloid salts upon the addition of an acid.

It is well known that active salts dissolved in solvents which either do not yield electrolytes or yield very poor ones show changes in the molecular rotatory power with dilution which are closely analogous to their behavior in solutions which are electrolytes. Absolute alcohol solutions of cinchonidine salts[1] afford examples of this, and even more striking are the changes in rotation suffered by quinine oleate in chloroform solution, as shown in Table IV.

Hädrich failed to carry the theory to its logical conclusion, namely, the calculation of the so-called degree of electrolytic dissociation from the molecular rotations of a salt at different dilutions. Rimbach[2] appears to be the first to seriously attempt such a calculation. He determined the rotations and the molecular conductivities of solutions of rubidium tartrate from saturated to about 1 percent solutions. The values of the degree of electrolytic dissociation

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[1] Schuster: Wien. Monatsheft, 14, 573 (1893).

[2] Zeit. phys. Chem., 16, 671 (1895).

computed from the rotations and from the conductivities were entirely discordant, and the more so the more dilute the solutions.

That the changes in rotation with dilution which most active substances undergo when in solution may, qualitatively and even quantitatively, be shown to be related to other concomitant changes occurring in the solution is altogether likely. Patterson[1] endeavors to associate such changes with changes in the specific volume of the solution. Winther[2] would consider in addition to the specific volume the changes in the molecular weight or degree of association of the dissolved substance. Winther, however, makes use of the theory of electrolytic dissociation to explain such changes in rotation occurring in electrolytes.

It appears to the writer that such methods, whatever their merit may be, must be applied consistently to all optically active substances and solutions whether they chance to conduct the electric current or not. May it not be that the phenomena from which we derive our conceptions of association and dissociation in solution, for example the lowering of the vapor pressure of the solvent, are really but measures of the affinities which are exercised between the solvent and the dissolved substance, the effects of which affinities vary with variations in the relative quantities of the components?

SUMMARY

The results of this paper may be summarized as follows:

(1) The measurements of the optical rotatory power of active salts in solutions considerably more dilute than have heretofore been studied are presented.

(2) The rotations of most of the salts studied, in solutions which are electrolytes, and whose molecular conductivities approach maximum constant values, do not, at high dilutions, tend to become identical for salts containing the same active base. Many of the values for the molecular

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[1] Jour. Chem. Soc., 79, 167 (1901).

[2] Zeit. phys. Chem., 35, 275 (1906).

rotations, on the other hand, diverge, some continuing to increase, others attaining a maximum value which afterward falls off as dilution progresses.

(3) The rotation of an alkaloid salt in a solution which does not conduct electricity suffers changes which are analogous to those found for conducting solutions.

The writer is unable to bring these experiments into harmony with the theory of electrolytic dissociation.

I gladly embrace this opportunity to express my sincere thanks to Professor Kahlenberg who suggested the work and placed at my disposal every facility including the use of his own private laboratory. He has followed the work with interest and I am indebted to him for inspiration and counsel.

Laboratory of Physical Chemistry,
University of Wisconsin,
Madison, December, 1906.

THE CHEMICAL KINETICS OF THE DECOMPOSITION OF OXALIC ACID IN CONCENTRATED SULPHURIC ACID

BY D. M. LICHTY

Introduction

A number of carbon compounds are known, which in contact with more or less concentrated sulphuric acid, split off carbon monoxide or a mixture of the monoxide and the dioxide. Potassium cyanide, for example, with ordinary concentrated sulphuric acid at room temperature yields almost pure carbon monoxide according to the equation

$$KCN + H_2O + H_2SO_4 = KHSO_4 + (NH_4)HSO_4 + CO.$$ [1]

Potassium ferrocyanide, heated with concentrated sulphuric acid, yields carbon monoxide according to the equation

$$FeK_4(CN)_6 + 11H_2SO_4 + 6H_2O = CO + 4KHSO_4 + 6(HH_4)HSO_4 + FeSO_4.$$

At first dioxide of carbon and sulphur are also formed.[2]

According to Markownikow and Purgold,[3] citric acid when heated with water, or better with diluted sulphuric acid at 160°, is changed to itaconic acid, water and carbon dioxide. Furthermore, a mixture[4] of one part of dried citric acid and two parts of concentrated sulphuric acid, heated in a water bath, produces at first formic acid and acetone dicarboxylic acid, then five volumes of carbon dioxide and three volumes of carbon monoxide, together with small quantities of other compounds.

Formic acid or its salts warmed with sulphuric acid splits into carbon monoxide and water,

$$HCO_2H = CO + H_2O.$$

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[1] Wade and Panting: Jour. Chem. Soc., 73, 255 (1898).

[2] Dammer: Anorg. Chem., II_1, 351.

[3] Zeit. für Chemie, 1867, 265.

[4] Beilstein: Handbuch der organischen Chemie, I, 836.

Heated with concentrated sulphuric acid, oxalic acid decomposes into carbon dioxide, carbon monoxide and water according to the equation

$$(CO_2H)_2 = H_2O + CO_2 + CO.$$

Döbereiner[1] showed that this decomposition occurs at room temperature in presence of slightly fuming sulphuric acid and that equal volumes of carbon dioxide and carbon monoxide are formed. In concentrated sulphuric acid the decomposition begins at 110°–115°, according to Gay-Lussac,[2] already at 100°–105°, according to Turner.[3] This difference in the temperature at which the evolution of gas begins, depends, as we shall see, on the degree of concentration of the sulphuric acid used. According to each author there are produced equal volumes of the two oxides of carbon. The two gases are evolved in the same proportions as well when the decomposition occurs in about 98.5 percent sulphuric acid as when it occurs in about 50 percent sulphuric acid, as is shown by the analyses recorded on pp. 24 and 25.

Anhydrous oxalic acid heated by itself sublimes undecomposed at 165.5° (Turner),[4] decomposes, however, at higher temperatures, when carbon dioxide, carbon monoxide and water are the only products.[5] Crystallized oxalic acid, on the other hand, when heated, melts at 98° (Gay-Lussac and Turner)[6] and decomposes above 110°–115°, into five volumes of carbon monoxide and 6 volumes of carbon dioxide. This excess of carbon dioxide arises through the simultaneous formation of formic acid.

The speed of the decomposition of formic acid, oxalic acid, and potassium ferrocyanide in concentrated sulphuric acid has already been studied by Veley,[7] but only in respect

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[1] Ann. Chim. Phys. (2), 19, 83 (1821).

[2] Ibid., (2), 46, 218 (1831); Liebig's Ann., 1, 20 (1832).

[3] Liebig's Ann., 1, 25 (1832); S. Archiv., 38, 159.

[4] Loc. cit.

[5] Comptes rendus, 82, 750 (1870).

[6] Loc. cit.

[7] Phil. Mag. [6], 6, 277 (1903).

to the supersaturation of the liquid with the gaseous products, through which the rate at which the gas is evolved increases from the beginning to a maximum and then decreases according to the bimolecular law. In my judgment this investigation permits conclusions only with respect to the velocity with which the gases voluntarily escape from the supersaturated solution, but nothing with certainty concerning the velocity with which the decomposition of the oxalic acid takes place.

In order to get some insight into the kinetics of the reaction between oxalic and sulphuric acid, and possibly into the constitution of concentrated sulphuric acid, the investigation detailed in the following pages was undertaken in the Physicochemical Division of the Chemical Laboratory of the University of Heidelberg under the direction of Prof. G. Bredig.

Purification and Dehydration of the Oxalic Acid

A good quality of commercial acid was dissolved in the smallest possible quantity of boiling water and filtered hot to free it from insoluble impurities. The product obtained from this filtrate was recrystallized three times from hot, about 12 percent, hydrochloric acid and then twice from hot water. During each crystallization the solution was cooled with moderate rapidity and stirred constantly to obtain the acid in a fine crystalline powder. After each crystallization the mother-liquor was well aspirated off and the crystals repeatedly washed with cold water. After pressing carefully between filter paper, the crystallized acid was allowed to lie spread out in the air, protected from dust, to dry. From these crystals the anhydrous acid was prepared by heating at 50°–60° until the weight was constant, and was then preserved in a desiccator over sulphuric acid.

A hot saturated solution of the oxalic acid, acidified with nitric acid, gave no turbidity with silver nitrate solution; another acidified with hydrochloric acid gave no reaction for sulphate. Spectroscopically, no potassium was found and only a trace of sodium. About 5 grams of crystals sublimed from a platinum crucible left no weighable residue. The oxalic acid used may therefore be considered as absolutely pure.

The Sulphuric Acid

Samples of sulphuric acid from different sources were used and will be described in detail later. Suffice to say here that the first trials were made with ordinary, about 96 percent, acid or with mixtures of such an acid and a fuming acid (see pp. 231–238). The more exact measurements were made with acid kindly furnished by the "Badische Anilin und Soda-Fabrik (p. 238)."

METHOD OF INVESTIGATION

A. General Considerations

The reaction was allowed to take place in long-necked Erlenmeyer flasks of Jena glass, having a capacity of 100 cc and carrying a charge of 50 cc of solution. These flasks were kept within ±0.1° at a constant temperature in a thermostat of the usual Ostwald type, which was filled with water covered with paraffin oil. Over the neck of each flask was slipped a rubber ring over which in turn was put a close fitting glass cap bearing a short 7 mm outlet tube, bent at right angles. This tube was connected with tubing which led to the hood or which had a drying apparatus attached for protection against the moisture of the air.

When samples for analysis were drawn into pipettes they became so filled with bubbles, disengaged from the solutions, saturated or perhaps supersaturated with the gaseous reaction products, that accurate measurements by this means were impossible. For this reason the samples were pipetted into weighing-glasses, cooled in running water, and then either accurately measured or more frequently weighed for the analyses. The oxalic acid was determined by means of potassium permanganate solution, the titration having been carried out between 70° to 90°, and at such a dilution that the total volume of liquid at the end amounted to 40 to 50 cc.

As the results given below, and obtained with an approximately one-fourth molar solution of oxalic acid in about 96 percent sulphuric acid, show, oxalic acid is but very slowly decomposed by sulphuric acid at room temperature. The figures express the number of cc of a permanganate solution required for 10 grams of oxalic acid solution.

Fresh solution	55.62 cc
After 5 days	55.52 cc
After 12 days	54.83 cc

In more concentrated sulphuric acid the decomposition proceeds so much faster that it was necessary to dilute the samples at once. This was done by pipetting them into tared and cooled glass stoppered weighing-glasses, containing diluted sulphuric (2 volumes 96 percent to 1 volume water), the quantity of diluted acid having been so chosen as to make the total water in the mixture at least 5 percent. The samples consisting of at least 10 grams were then weighed, and the volume of permanganate solution per 10 grams calculated from the titration values.

B. Method of Handling the Sulphuric Acid and of Diluting It with Water

The sulphuric acid was pipetted or siphoned directly from the supply bottle into one provided with a well-fitting glass stopper, and in amounts equal to 250 grams, or such as to make the weight of the water or of 40 percent sulphuric acid required for making the desired dilution, equal to at least 100 mg. In order to secure both the ready mixing of the two liquids and sufficient accuracy in weighing, the water was weighed in tubes open at both ends and widened somewhat in the middle, when the amount needed did not exceed 5 grams. These tubes were brought into the neck of the bottle and then pushed in ahead of the stopper, so that when water and acid came in contact with each other the bottle was securely closed and all loss by evaporation prevented. A number of trials abundantly satisfied me that although the weighing-tubes were open at both ends the loss of water by evaporation during the transference of the tubes from the balance to the bottle, which required less than 15 seconds, scarcely reached 0.5 mg. Care was always taken that the neck and stopper of the bottle remained free from liquid, thus better to preserve the concentration of the acid, which can be done with certainty for several days if not weeks. When more than 5 grams of water were used for diluting the sulphuric acid, the addition was made to a weighed quantity of acid from a pipette drawn to a small opening, which practically touched the surface of the acid. If the quantity of water needed was so large as to cause an evolution of much heat, approximately the correct amount of water was added while the acid was kept cooled in flowing water, and afterwards enough water or acid, according to necessity, to obtain a mixture of the desired concentration. The more concentrated mixtures were always taken from the bottle in which they were made, by means of a pipette provided with a calcium chloride drying tube. The use of sulphuric acid in the drying tube would undoubtedly have been more rational but certainly much less convenient. Considering, however, that 100 cc of air, saturated with water vapor at 18°, contain only 0.0016 gram of water, that the air is generally far from saturated and finally that the greater part of the small amount of moisture which was carried by the air that entered the pipette was surely absorbed by the calcium chloride, one sees that this arrangement fully served its purpose.

C. Preparation of the Oxalic Acid Solutions

The oxalic acid was weighed from a well-stoppered weighing-glass into a glass-stoppered bottle of suitable size, filled with dry air and containing several pieces of glass rod. The latter served to grind the difficultly soluble lumps, which always formed in the anhydrous oxalic acid, to a readily soluble powder. A little more than enough of the oxalic acid to make 100 cc of solution was taken and the necessary weight of sulphuric acid, calculated from the specific gravity at 20°,[1]

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[1] Domke and Bein: Zeit. anorg. Chem., 43, 176 (1905).

added, to give the solution the desired concentration. The specific gravity of 100 percent sulphuric acid is somewhat uncertain but is about 1.841 at 15°[1] while the minimum specific gravities 1.837 and 1.832 for concentrated sulphuric at 15° and 20° respectively correspond to about 99.6 percent acid. Calculated from these values, the specific gravity for 100 percent acid at 20° is 1.836. Although this value may differ slightly from the correct one, it is still exact enough for the present purpose. The specific gravities used in calculating the weights of diluted sulphuric acid are given in connection with the data of each experiment and are taken from the table of Domke and Bein.[2]

Preliminary Trials

The values of k, given in the annexed Table 1, were calculated from the data furnished by some preliminary measurements of the speed of the reaction by means of the equation

$$k = \frac{2.302}{t} \log \frac{a}{a - x}$$

for a monomolecular reaction. The data were obtained with a one-half molar oxalic aicd solution in about 96 percent sulphuric acid. The reaction is clearly monomolecular, when the initial amount of water present is four or more percent, the values of k decreasing rapidly with increase in the amount of water.

From an ordinary and a fuming sulphuric acid containing respectively 78.61 percent and 85.30 percent of sulphur trioxide, as determined by means of an approximately one-fifth molar solution of sodium hydroxide, free from carbon dioxide, a mixture was made which should contain 81.63 percent of sulphur trioxide, corresponding to 100 percent sulphuric acid. The weight of the ordinary acid required for each 100 grams of the fuming acid was calculated by means

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[1] Domke and Bein: Zeit. anorg. Chem., 43, 159, 160 (1905).

[2] Domke and Bein: Ibid., 43, 176 (1905).

of the equation $x = 100\dfrac{85.30-81.63}{81.63-78.61} = 121.5$.[1] An acid which should contain 1 percent of free sulphur trioxide was prepared in a similar manner.

While preparing a one-half molar solution of oxalic acid in the 100 percent sulphuric a slight evolution of gas was observed. At room temperature 7 percent of the dissolved oxalic acid had been decomposed in twenty-four hours, while at 98° after 12 minutes' heating, to bring the solution to the temperature of the thermostat, 10 grams of it required only 0.2 cc of approximately 0.1 molar solution of potassium permanganate, although the same weight of undecomposed solution should have required 28 cc of permanganate solution.

TABLE I

Time in minutes	Without addition of water *k*	1 percent of water added *k*	4 percent of water added *k*	8 percent of water added *k*
0	—	—	—	—
30	0.01607	0.01077	0.00418	0.00127
60	1578	1070	416	145
90	1571	1055	423	142
120	1544	1056	420	138
150	—	—	417	137
Means:	0.01575	0.01063	0.00423	0.00138
Total percent of the acid decomposed	82.29	71.86	46.48	18.60

In the sulphuric acid containing 1 percent excess of anhydride the decomposition of the oxalic acid proceeded so rapidly that the preparation of a solution was out of the question. At this time the work of Döbereiner (p. 226) was not known to me.

Even though the analytical error in determining the concentrations of the sulphuric acids used may be as high as

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[1] Lunge: Chem. Tech. Untersuchungen, I, p. 330; Gerster: Chem. Zeitung, 1887, 3.

0.2 of a percent, the results noted above still show that with an increase in the amount of anhydride or conversely a decrease in the amount of water held by the sulphuric acid the speed of decomposition of oxalic acid increases rapidly, and that with a slight excess of anhydride the speed becomes enormous.

Although the speed of the reaction in about 100 percent sulphuric is high at 98°, the fact that it is low at room temperature made it seem possible to measure it at 50°. To that end a slightly fuming acid and an ordinary concentrated one were analyzed and then mixed as before stated. To reduce the percentage error of weighing, from 7 to 10 grams of acid were diluted to 250 cc at 18°, then for titration 10 cc of this solution were measured out at the same temperature by means of a carefully calibrated, narrow stemmed pipette. In order to prevent loss of anhydride the fuming acid was drawn into a pipette-shaped tube and both ends sealed. The acid was allowed to flow a few centimeters away from the lower end before sealing, thus making it possible to open this end afterwards and bring it under water in a measuring flask without letting out acid before the upper end was also opened, and to mix the acid with water without the production of any fumes in the flask. On pouring rinsing water into the tube, fumes appeared in it however, and to avoid loss thereby its projecting end was again sealed and the final rinsing deferred until the fumes had entirely subsided. A volumetric analysis of the supposed 100 percent acid gave 99.89 percent as its concentration, a result which is well within experimental error. As molecular weights were used $H_2SO_4 = 98.08$, $H_2C_2O_4 = 90.02$.

Two parallel trials at 50° with an approximately one-fourth molar solution of oxalic acid (2.218 grams in 100 cc) in this at least nearly 100 percent sulphuric acid yielded the results recorded in Table 2, after a preliminary heating of 30 minutes. As calculated from the weight of the two acids used, 10 grams of the unchanged solution required 28.0 cc of a 0.01922 molar solution of potassium permanganate.

Here as well as in future trials unless otherwise stated the samples for analysis were handled as described on page 229 for the solutions in the more concentrated sulphuric acids.

TABLE 2

Time in minutes	cc of permanganate			Intervals in minutes	k	k_2
	I	II	Means			
$t_0 =$ 0	21.07	21.45	21.26	—	—	—
$t_1 =$ 30	17.17	17.60	17.38	$t_1 - t_0$ 30	0.00617	0.000350
$t_2 =$ 60	14.47	14.90	14.68	$t_3 - t_1$ 60	523	353
$t_3 =$ 90	12.51	12.89	12.70	$t_4 - t_1$ 90	502	366
$t_4 =$ 120	10.87	11.26	11.06	$t_4 - t_2$ 60	472	372

Two other trials with an oxalic acid solution of the same concentration in an independently prepared 100 percent sulphuric acid gave the results in Table 3.

TABLE 3

Time in minutes	cc of permanganate			Intervals in minutes	k	k_2
	I	II	Means			
t_0 0	19.61	20.33	19.97	—	—	—
t_1 30	15.74	16.53	16.13	$t_1 - t_0$ 30	0.00713	0.000397
t_2 60	13.23	13.67	13.45	$t_3 - t_1$ 60	546	401
t_3 90	11.08	12.17	11.62	$t_4 - t_1$ 90	514	405
t_4 120	9.70	10.63	10.16	$t_4 - t_2$ 60	468	401

Although the titration values in the first pair of trials are in better agreement with each other than is the case in the second, they are hardly satisfactory. The values of *k*, calculated by means of the equation for a monomolecular reaction (p. 231) decrease very noticeably with the progress of the reaction in both sets of trials, and are not concordant. The values of k_2 calculated by means of the integrated form of the equation for a bimolecular reaction

$$k_2 = \frac{1}{t}\frac{x}{a(a-x)},$$

are nearly constant in each case but the two sets of values lack concordance. Considering that if the sulphuric acid already contains about 4 percent of water the reaction goes monomolecular and that the value of k decreases with further addition of water (page 231) or that removal of water, *i. e.*, addition of anhydride accelerates the reaction (p. 232) it seems a fair inference that the disagreement in the values of k just mentioned is due to a small difference in the amount of water already present in the supposedly 100 percent sulphuric acids, and that the decrease in the values of k in each series is due to the water formed in the course of the reaction, which in two hours reached 0.14 percent. In order to render the amount of water formed during the reaction very small, measurements were made at 50° with one-fortieth molar oxalic acid solutions in 100 percent, 99.87 percent, 99.75 percent, 99.5 percent and 99.0 percent sulphuric acid prepared in the manner already explained. The permanganate solution used was 0.00456 molar. In calculating k and k_2, a was placed equal to the volume of permanganate solution used, at the time 0, which was 30 minutes after placing the solutions in the thermostat. Ten grams of the undecomposed solution should have required 11.95 cc of potassium permanganate solution.

As the reaction progresses the value of k_2 increases in each of the five concentrations of sulphuric acid used, so that no bimolecular reaction is involved. The values of k, although decreasing somewhat with the progress of the reaction in the first three trials, becomes constant in the last two where the amounts of water initially present are 0.5 percent and 1.0 percent respectively. A 1/40 molar oxalic acid solution contains 0.225 gram of anhydrous acid in 100 cc of solution, and this amount yields 0.045 gram of water, when it has been completely decomposed, equaling 0.0245 percent of the original solvent, calculated from the specific gravity, 1.8321[1] of 99.5 percent acid at 20°. At the end of the first interval of 30 minutes (Table 4) the amount of the water formed is only 0.0114 percent, at the end of the first

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[1] Domke and Bein: Zeit. anorg. Chem., 43, 159, 178 (1905).

60 minutes 0.014 percent. This small increase of only 0.0026 percent in the water content could not possibly be determined by the ordinary analytical means, yet it has an easily measur-

TABLE 4

$^1/_{40}$ Molar oxalic acid solution in 100 percent sulphuric acid at 50.0°

Minutes	cc permanganate			k	k_1
	I	II	Means		
0	8.91	8.89	8.90	—	—
30	6.17	6.33	6.25	0.01179	0.001588
60	4.51	4.24	4.58	0.01107	0.001766
90	3.25	3.42	3.33	0.01092	0.002088
120	2.66	2.67	2.66	0.01007	0.002197

TABLE 5

$^1/_{40}$ Molar oxalic acid solution in 99.87 percent sulphuric acid at 50.0°

Minutes	cc permanganate			k	k_2
	I	II	Means		
0	10.20	10.15	10.17	—	—
30	8.16	8.20	8.18	0.00725	0.000798
60	6.80	6.83	6.81	0.00668	0.000809
105	5.18	5.03	5.10	0.00657	0.000931
165	3.74	3.76	3.75	0.00605	0.001019
245	2.27	2.44	2.35	0.00598	0.001336
335	1.56	1.54	1.55	0.00562	0.001633

TABLE 6

$^1/_{40}$ Molar oxalic acid solution in 99.75 percent sulphuric acid at 50.0°

Minutes	cc permanganate			k	k_2
	I	II	Means		
0	11.01	10.88	10.94	—	—
30	9.71	9.97	9.84	0.00371	0.000358
60	8.86	8.66	8.76	0.00371	0.000379
105	7.67	7.70	7.68	0.00337	0.000369
165	6.44	6.27	6.35	0.00330	0.000410
245	4.90	4.90	4.90	0.00328	0.000460
335	3.57	3.65	3.61	0.00331	0.000554

TABLE 7

$^1/_{10}$ Molar oxalic acid solution in 99.5 percent sulphuric acid at 50.0°

Minutes	cc permanganate			k	k_2
	I	II	Means		
0	11.49	11.41	11.45	—	—
120	9.66	9.60	9.63	0.00144	0.000138
240	8.09	8.14	8.11	0.00144	0.000150
420	6.26	6.19	6.22	0.00145	0.000175
600	4.73	4.86	4.79	0.00145	0.000202
900	2.88	3.07	2.97	0.00150	0.000277
1440	1.45	1.44	1.44	0.00144	0.000325
			Mean:	0.00145	

TABLE 8

$^1/_{10}$ Molar oxalic acid solution in 99.0 percent sulphuric acid at 50.0°

Minutes	cc permanganate			k	k_2
	I	II	Means		
0	11.63	11.72	11.67	—	—
300	9.97	10.03	10.00	0.000515	0.0000477
600	8.62	8.60	8.61	0.000507	0.0000507
900	7.34	7.31	7.32	0.000518	0.0000566
1440	5.45	5.55	5.50	0.000522	0.0000667
1980	4.13	4.29	4.21	0.000515	0.0000763
			Mean:	0.000515	

able effect on the value of k, which changes from 0.0118 to 0.0111, a decrease of 6.3 percent. If we compare the value of k in Table 4, when the volume of permanganate used is 6.25 cc, with that in Table 5, when the volume of permanganate used is 6.81 cc, *i. e.*, when the oxalic acid concentrations are approximately the same, we see that an addition of about 0.13 percent of water to 100 percent sulphuric acid decreases the value of k from 0.0118 to 0.0067 or by about 40 percent.

Although the sulphuric acids used in these 5 measurements may not have been as concentrated by 0.1 or 0.2 percent as indicated by the analyses of the components, it is still evident that the speed of the reaction in approximately 100 percent sulphuric acid is very sensitive to exceedingly small quantities of water.

Since the speed of this reaction is affected by quantities of water which lie far and away below the limits of error in the analytical estimation of water in concentrated sulphuric acid it seemed important to secure a sulphuric acid which is absolutely pure and as nearly anhydrous as possible, and then find a method of defining it so that starting from it as a standard, any mixture of acid and water used could not only be defined itself but exactly reproduced at any time. Such a sulphuric acid was obtained in large quantity through the kindness of the now deceased Director Knietsch of the "Badische Anilin und Soda Fabrik," at Mannheim, for which I desire herewith to express my sincere thanks. For defining the sulphuric acids, as above stated, the specific electrical conductivity proved exceedingly satisfactory.

Testing and Preserving the Pure Concentrated Sulphuric Acid

The first sample of acid from the factory at Mannheim consisting of about two liters, is in later references designated by B. According to the description furnished by the factory its freezing-point was at +10.48° and it contained 100.01 percent H_2SO_4. As a check on this analysis I made duplicate gravimetric analyses by precipitating with barium chloride according to the directions given by Treadwell, Lehrbuch der analytischen Chemie, Vol. II, 3rd Ed., p. 338. The atomic weights used in the calculations are Ba = 137.4, S = 32.06 and O = 16. 8.8620 grams (corrected to vacuo) were weighed in a glass stoppered tube, diluted to 500 cc at 18° and at the same temperature two portions of 75 cc taken for analysis, with the following results:

$BaSO_4$ calculated for 100 percent H_2SO_4	$BaSO_4$ found	Percent H_2SO_4
3.1641 g	3.1639 g (corr.)	99.99
	3.1642 g "	100.00

The specific conductivity of the acid at 25° was found to be 0.01042 on December 6, 1905, and on the 10th of January, next, 0.01044, remaining unchanged for several weeks at least. This constancy was secured by preserving the acid in bottles with well-fitting stoppers having well-ground caps over them and by drawing the acid from the bottle by means of a pipette in such a way as to keep the stopper and neck both, always free from adhering acid.

The second supply of the pure acid (designated by B_2) was preserved in the carboy in which it was shipped. This was fitted with a doubly perforated rubber stopper for attaching a drying apparatus and a siphon tube, the latter being provided with a glass cock about 15 cm from its end. When the siphon was not in use, the free end was protected from moisture by slipping over it a test-tube, held in place by means of a rubber stopper. The drying apparatus, which served to dry the air entering when acid was siphoned off, consisted of a U-tube and a Drechsel gas washing-bottle, the former with unbroken glass connection with the stopper and provided with a stop-cock between it and the Drechsel bottle, both charged with concentrated sulphuric acid taken from the carboy. In order to make sure that none of the acid used in the measurements was contaminated through the siphon-cock, with moisture or any other foreign substance, the first 10 or 15 cc drawn were always rejected.

According to the statement from the factory, the freezing-point of this acid was at +10.43° and its content 100.01 percent H_2SO_4, determined volumetrically. According to my own analyses by the method just outlined, samples which, if the acid had been 100 percent H_2SO_4, should yield 3.1630 grams of barium sulphate, yielded 3.1671 grams and 3.1670 grams (both corrected to vacuo) representing a sulphuric acid content of 100.13 and 100.12 percent respectively.

An analysis, after closing the research, in which 14.8807 grams (corrected to vacuo) were made up to 500 cc and weighed and then two portions of about 50 cc, weighing respectively 50.943 grams and 51.0027 grams and representing 1.4881 grams (corrected) and 1.4889 grams (corrected) of the original acid, were precipitated with the following results:

$BaSO_4$ calculated for 100 percent H_2SO_4	$BaSO_4$ found	Percent H_2SO_4
3.5422 g	3.5416 (corr.)	99.99
3.5464 g	3.5489	100.07
	Mean:	100.03

The means of the four analyses is 100.08 per cent and I have taken the acid as 100 percent within the analytical error.

The specific conductivity at 25° was found to be 0.01043, *i. e.*, the same as that of B (p. 239), although the results of analysis differ by 0.08 percent. The measurement of the conductivity just mentioned was made on January 24, 1906. On February 6th, the conductivity of B_2 was again found to be 0.01043 and on May 7th, 0.01037, indicating that the acid had been preserved unchanged for three months.

One hundred grams of the acid B_2, vaporized from a platinum dish, left less than 2 mg of residue. Fifteen grams diluted to about 50 cc with very dilute manganese sulphate solution did not decolorize permanganate solution.

Conductivity Measurements

The conductivity measurements were made in a special apparatus. The electrodes are cylindrical in form, 10 mm high and as many in diameter, made of rather heavy sheet platinum, supported by stout platinum wires sealed into the wall of the vessel and projecting into tubes for holding the mercury for making connections with a source of current in the usual way, and rising about 4 mm above the ground joint. The electrodes were also well platinized.

The resistance capacity of the cell was measured at 25.0° with a one-tenth normal solution of purest potassium chloride and had not changed in seven months. Against 100 ohms in a Kohlrausch's universal measuring bridge, the mean of three readings was 2.48 on November 24, 1905, the same on December 11th, 2.472 on February 6th following, and 2.477 on June 11th following, although the cell had been subjected to temperatures varying from 25° to 98°. All these tests were made with the same potassium chloride solution which was preserved in a rubber-stoppered bottle.

Gasometric Determination

Fourteen grams of crystallized oxalic acid were decomposed in 337 grams of 100 per cent sulphuric acid at a temperature ranging from 85° to 100°. Fourteen grams of crystallized oxalic acid would, if completely decomposed, yield 6 grams of water which would dilute the sulphuric acid to 98.2 percent.. After the evolution of gas had continued for some time 3 portions were collected in gas burettes over water which had been saturated with the same gas, and then analyzed in a room over constant temperature.

	1	2	3
Measured volume of gas in cc	100.0	100.0	100.0
Absorbed by potassium hydroxide solution, cc.	49.5	49.4	48.5
" " pyrogallol, cc	0.2	0.2	0.6
" " ammonium cuprous chloride, cc.	49.6	49.8	48.7
Residue, cc	0.7	0.6	2.2

By means of 98 to 99 percent sulphuric acid, equal volumes of carbon monoxide and carbon dioxide are obtained.

The gaseous product obtained by means of about 50 per cent sulphuric acid was also analyzed. For this purpose 33 grams of 100 percent sulphuric, 24 grams of water and

25.2 grams of crystallized oxalic acid were heated to about 150 under an inverted condenser. If half of the oxalic acid were decomposed, then equal weights of water and sulphuric acid were present. The water added as such plus the water of crystallization were sufficient to dilute the sulphuric acid to 51.4 percent. The gas mixture was collected as before and then analyzed.

	1	2	3
Measured volume of gas in cc	100.0	100.0	100.0
Absorbed by potassium hydroxide solution, cc	46.7	46.4	40.8
" " phosphorus, cc	1.5	1.8	3.8
" " ammonium cuprous chloride, cc	46.1	46.1	40.5
Residue, cc	5.7	5.7	14.9

It will be seen that the product obtained by decomposing the oxalic acid in about 50 percent sulphuric acid as well as in about 98 percent sulphuric acid consists of equal volumes of carbon monoxide and dioxide. It is naturally highly probable that by means of any concentration of sulphuric acid between these two, the same proportions will hold, and perhaps also for acid above 100 percent.

Measurements at 25.0°

Not only the measurements at 25.0° but all others following were made with one-fortieth molar oxalic acid solutions in the acid B_2, except those recorded in Tables 15, 16, 20 and 21, which were made with acid B. The additions of water up to and including 0.05 percent, except those of 0.05 percent to the acid B_2, were made by means of 40 percent sulphuric acid (see p. 229). The acid B_2 was once mixed with 40 percent sulphuric and once with water, and the conductivities 0.01212 and 0.01210 respectively, were in close agreement. The latter mixture was used for the measurements given in Table 14. The oxalic acid solutions were prepared at 7° to 10°. In all cases the first sample for analysis was drawn 15 minutes after the solution was placed in the bath. k was calculated as mentioned on p. 231 for a monomolecular reaction, a being placed equal to the number of cc of permanganate solution used at the beginning of an interval (5th column of tables) and $a-x$ equal to the number used at the end of the same interval. The potassium permanganate solution used in all of the following measurements was 0.004751 molar, approximately one-fortieth normal. The meaning of k_w which was calculated after all the other data had been accumulated is explained on p. 264.

TABLE 9

Undiluted sulphuric acid

Assumed specific gravity, 1.8366; specific conductivity, 0.01043 at 25.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	8.16	8.09	8.13	—	—	—
15	5.83	5.96	5.89	15	0.02149	0.00000214
40	3.72	3.87	3.79	25	0.01677	0.00000382
75	2.34	2.44	2.39	35	0.01317	0.00000445
120	1.39	1.41	1.40	45	0.01189	0.00000523

TABLE 10

0.0100 gram water to 100.0 grams sulphuric acid

Specific conductivity, 0.01068 at 25.0°; specific gravity, 1.8366

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	8.89	8.88	8.88	—	—	—
15	7.08	7.03	7.05	15	0.01538	0.00000492
30	5.77	5.81	5.79	15	0.01312	0.00000597
60	4.01	4.07	4.04	30	0.01199	0.00000726
90	2.94	2.99	2.96	30	0.01037	0.00000793
150	1.74	1.70	1.72	60	0.00905	0.00000826

TABLE 11

0.0200 gram water to 100.0 grams sulphuric acid
Specific conductivity 0.01080 at 25.0°; specific gravity, 1.8366

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	9.65	9.61	9.63	—	—	—
20	7.99	7.95	7.97	20	0.00945	0.00000658
50	5.88	5.97	5.92	30	0.00991	0.00000916
90	4.42	4.43	4.42	40	0.00724	0.00000859
130	3.36	3.48	3.42	40	0.00641	0.00000873
180	2.38	2.43	2.40	50	0.00708	0.00000686

TABLE 12

0.0300 gram water to 100.0 grams sulphuric acid
Specific conductivity, 0.01122 at 25.0°; specific gravity, 1.8366

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	10.28	10.28	10.28	—	—	—
30	8.17	8.24	8.20	30	0.00753	0.0000095
90	5.71	5.84	5.77	60	585	096
210	2.99	3.32	3.15	120	504	107
390	1.55	1.60	1.57	180	387	118

TABLE 13

0.0400 gram water to 100.0 grams sulphuric acid
Specific conductivity, 0.01171 at 25.0°; specific gravity, 1.836

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	10.41	10.50	10.45	—	—	—
30	8.99	9.04	9.01	30	0.00494	0.0000098
90	6.66	6.73	6.70	60	494	118
210	3.97	4.06	4.01	120	429	127
390	2.12	2.17	2.14	180	349	123

TABLE 14

0.0500 gram water to 100.0 grams sulphuric acid
Specific conductivity, 0.01210 at 25.0°; specific gravity, 1.836

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	10.56	10.62	10.59	—	—	—
35	9.14	9.12	9.13	35	0.00429	0.0000126
95	7.27	7.33	7.30	60	369	127
205	5.07	5.09	5.08	110	329	129
420	2.92	2.83	2.87	215	266	123

TABLE 15

0.0500 gram water to 100.0 grams sulphuric acid
Specific conductivity, 0.01211 at 25.0°; specific gravity, 1.836

Minutes	cc permanganate			Intervals	k
	I	II	Means		
0	10.85	10.77	10.81	—	—
45	8.82	8.77	8.80	45	0.00457
105	6.84	7.04	6.94	60	396
255	3.99	4.28	4.13	150	346
465	2.30	2.44	2.37	210	264

TABLE 16

0.0500 gram water to 100.0 grams sulphuric acid
Specific conductivity, 0.01207 at 25.0°; specific gravity, 1.836

Minutes	cc permanganate			Intervals	k
	I	II	Means		
0	10.71	10.70	10.70	—	—
45	8.86	8.85	8.85	45	0.00423
105	7.17	7.18	7.17	60	351
225	4.75	4.77	4.76	120	341
420	2.81	3.16	2.98	195	263

The measurements recorded in Tables 15 and 16 were made with the acid B; the one in Table 14 with B_2. The data obtained show that the reactions in the three went closely parallel. This parallelism is graphically shown on Fig. 1. Concordant results are then obtainable, if one uses sulphuric acid having the same specific conductivity. The first two intervals on Curves (1) and (3) constructed with the data from Tables 15 and 16 are equal and therefore directly comparable. If the titration values corresponding to 225 and 420 minutes, respectively, are taken from Curve (3) then we have altogether comparable titration numbers and values for *k* for the four intervals 0 to 45, 45 to 105, 105 to 225 and 225 to 420 minutes. These are given in Table 17.

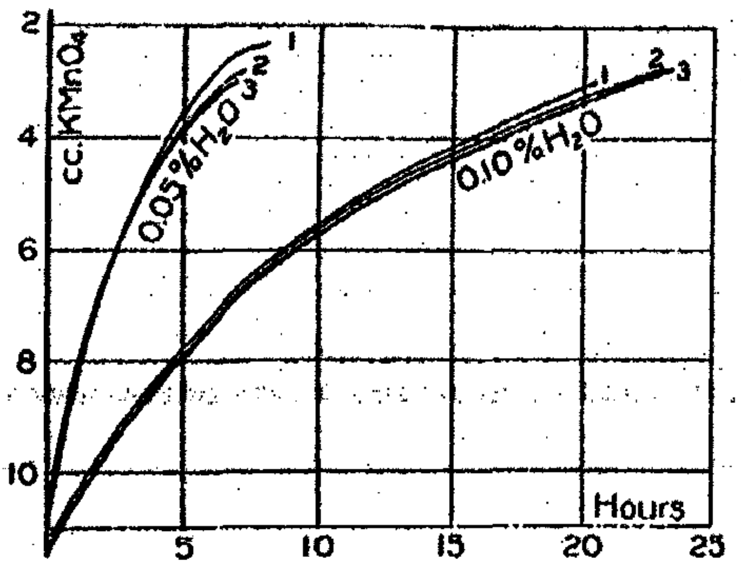

Fig. 1.—Temp. 25°

TABLE 17

Minutes	From Table 15		From Table 16 and Curve 3		Means of *k*
	cc permang.	*k*	cc permang.	*k*	
0	10.81	—	10.70	—	—
45	8.80	0.00457	8.85	0.00423	0.00440
105	6.94	396	7.17	351	373
225	4.55	352	4.76	341	346
420	2.62	283	2.98	263	280

The two series of titration numbers being nearly alike, the values of *k* also are approximately the same.

Table 18

0.0700 gram water to 100.0 grams sulphuric acid
Specific conductivity, 0.01352 at 25.0°; specific gravity, 1.836

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.18	11.12	11.15	—	—	—
60	9.45	9.45	9.45	60	0.00275	0.0000151
210	6.58	6.49	6.53	150	246	154
420	4.25	4.16	4.20	210	210	151
720	2.59	2.48	2.53	300	169	157

Table 19

0.100 gram water to 100.0 grams sulphuric acid
Specific conductivity, 0.01560 at 25.0°; specific gravity, 1.836

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.39	11.35	11.37	—	—	—
120	9.75	9.71	9.73	120	0.001297	0.0000141
360	7.34	7.38	7.36	240	1162	137
630	5.40	5.50	5.45	270	1113	142
1380	2.70	2.76	2.73	750	0921	085

Table 20

0.100 gram water to 100.0 grams sulphuric acid
Specific conductivity, 0.01552 at 25.0°; specific gravity, 1.836

Minutes	cc permanganate			Intervals	k
	I	II	Means		
0	11.36	11.29	11.32	—	—
120	9.69	9.71	9.70	120	0.001287
360	7.28	7.30	7.29	240	1191
630	5.40	5.37	5.38	270	1125
1195	3.06	3.12	3.09	565	0981

TABLE 21

0.100 gram water to 100.0 grams sulphuric acid
Specific conductivity, 0.01567 at 25.0°

Minutes	cc permanganate			Intervals	*k*
	I	II	Means		
0	11.40	11.40	11.40	—	—
120	9.73	9.79	9.76	120	0.001295
360	7.32	7.45	7.38	240	1186
630	5.49	5.62	5.55	270	1085
1195	—	—	3.25[1]	565	0968
1365	2.80	2.81	2.80	735[2]	0931

As will be seen in Tables 19 to 21, the reaction is already so much retarded by the addition of only 0.1 per cent of water, that, in order to follow it conveniently, it became necessary to increase the working temperature. This was then changed to 45°. The measurements in Tables 20 and 21 were made with the acid B and give concordant results, which are compared in Table 22.

TABLE 22

Intervals	*k*		
	From Table 20	From Table 21	Means
120	0.001287	0.001295	0.001291
240	1191	1186	1188
270	1125	1085	1105
565	0981	0968	0975

TABLE 23

Intervals	*k*			
	From Table 19	From Table 20	From Table 21	Means
120	0.001297	0.001287	0.001295	0.001293
240	1162	1191	1186	1180
270	1113	1125	1085	1108

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[1] From Curve (3), 0.1 percent water, Fig. 2.

[2] The experimental-interval, 630 to 1365 minutes.

Table 19 contains measurements made in acid B_2, and they agree well with those made with B. In Table 23 the three series of values of *k* and their means are given in so far as the intervals of measurement are alike.

The individual values of *k* for equal intervals do not differ far from their mean value. Here again concordant results are obtainable if one uses sulphuric acids with the same specific conductivity. As further evidence that the data are quantitatively reproducible, reference is again made to Fig. 1, in which the three curves approximately coincide. Curve (2) represents the result with the acid B_2. The results of the last three measurements and those with an initial addition of 0.05 percent of water, as well as the agreement in the specific conductivities given on p. 22, are good evidence that the acids B and B_2 were of the same concentration.

That even a trace of water in the sulphuric acid makes a measurable difference in the speed of the reaction, is clearly shown by the decrease in the value of *k* when only 0.01 percent of water is added, when the initial value falls from 0.0215 to 0.0154 (Tables 14 and 15), being a total decrease of 61 units, or of 6 units per 0.001 percent of water. With a progressive increase in the amounts of water added, at first by only 0.01 percent, the value of *k* decreases by easily measured amounts. Since the values of *k* depend not only on the amount of water originally added, but also upon the amount formed during the reaction, and since the values given in the preceding tables have not been calculated for the same changes in the oxalic acid concentrations, *i. e.*, between the same titration values, they are not strictly comparable. By means of the graphic method one can, however, easily obtain comparable values. For this purpose the curves in Fig. 2 were used, and the time determined which elapsed while the oxalic acid concentration changed from that represented by 8.13 cc of permanganate solution to that represented by 5.9 cc. By means of the intervals thus found and the titration values, *k* was calculated. The results are arranged in Table 24.

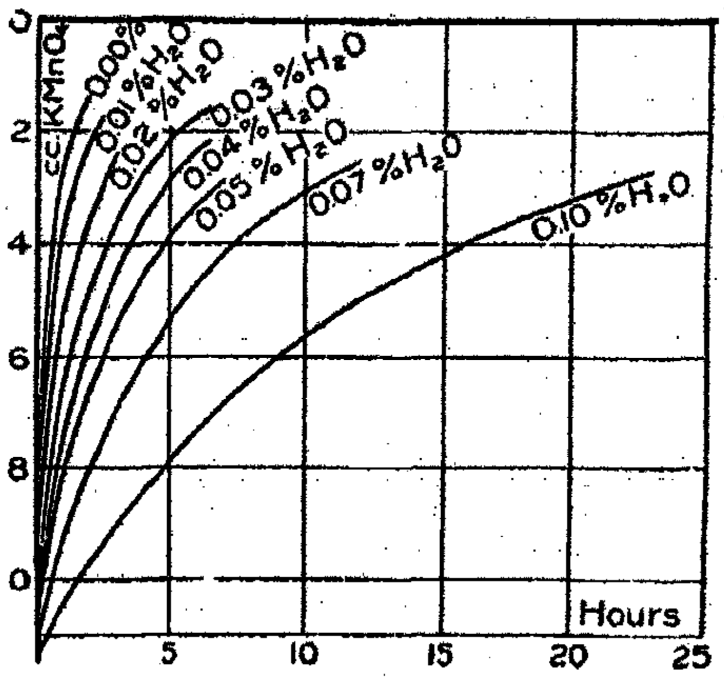

Fig. 2.—Temp. 25°

TABLE 24

Water added Percent	Specific conductivity in reciprocal ohms per cc	Minutes from time 0 to the titration value		Duration of the conversion 8.13 → 5.9	k	Difference per 0.01 percent of water
		8.13	5.90			
0.00	0.01043	0	15	15	0.02136	—
0.01	0.01068	5	28	23	0.01393	0.00743
0.02	0.01080	16	50	34	0.00943	450
0.03	0.01122	30	86	56	0.00572	371
0.04	0.01171	50	117	67	0.00478	94[1]
0.05	0.01210	64	159	95	0.00337	141
0.07	0.01352	117	256	139	0.00230	54
0.10	0.01560	273	558	285	0.00113	39

The differences in the values of k given in the seventh column show very strikingly, how sensitive the reaction is to very small additions of water, and the influence per 0.01 per cent of water added is still quite perceptible as far as a total addition of 0.1 percent. The very different periods of time required to secure the decomposition of equal quantities of oxalic acid, shown by column five, are also very striking. It will be seen, for example, that when 0.05 percent of water is added, the time increases to over sixfold of that required

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[1] Probably an experimental error.

when no water had been added, and that when the amount reached 0.1 percent the time required is increased to 19-fold. It will also be noticed that the value of k decreases much more rapidly than the conductivity of the sulphuric acid increases, and that there is no simple relation at any rate between the two magnitudes.

Measurements at 45.0°

These measurements were carried out like those at 25° with one-fortieth molar oxalic acid solutions, but only in acid B_2. In order to link this series of measurements with that made at 25°, it was begun with an addition of 0.1 percent of water, the same addition as that with which the series at 25° ended.

TABLE 25

0.100 gram water to 100.0 grams sulphuric acid

Specific conductivity, 0.01560 at 25.0°, and 0.02632 at 45.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	8.83	8.85	8.84	—	—	—
15	6.50	6.47	6.48	15	0.02070	0.000252
40	4.04	4.12	4.08	25	1850	247
75	2.04	2.15	2.09	35	1912	277
120	0.95	1.02	0.98	45	1683	258

TABLE 26

0.150 gram water to 100.0 grams sulphuric acid; specific gravity, 1.835

Specific conductivity, 0.01998 at 25.0°, and 0.03223 at 45.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	10.28	10.29	10.28	—	—	—
25	8.24	7.98	8.11	25	0.00947	0.000236
75	5.03	4.87	4.95	50	987	264
175	1.97	2.04	2.00	100	906	264
295	0.71	0.72	0.71	120	863	261

TABLE 27

0.200 gram water to 100.0 grams sulphuric acid; specific gravity, 1.834
Specific conductivity, 0.02404 at 25.0°, and 0.03848 at 45.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	10.84	10.87	10.85	—	—	—
40	8.66	8.66	8.66	40	0.00564	0.000241
100	5.92	5.95	5.93	60	631	285
180	3.87	3.86	3.86	80	537	255
300	2.07	2.07	2.07	120	519	256

TABLE 28

0.300 gram water to 100.0 grams sulphuric acid; specific gravity, 1.833
Specific conductivity, 0.03123 at 25.0°, and 0.04897 at 45.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.32	11.27	11.32	—	—	—
60	9.62	9.66	9.64	60	0.00265	0.000249
195	6.98	7.16	7.07	135	230	245
360	4.66	4.69	4.68	165	250	254
540	2.95	3.00	2.97	180	252	261

TABLE 29

0.400 gram water to 100.0 grams sulphuric acid; specific gravity, 1.832
Specific conductivity, 0.03758 at 25.0°, and 0.05834 at 45.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.48	11.45	11.46	—	—	—
120	9.60	9.58	9.59	120	0.00187	0.000246
360	7.01	6.86	6.93	240	135	231
750	3.99	4.04	4.01	390	140	245
1350	1.78	1.82	1.80	600	133	242

TABLE 30

0.500 gram water to 100.0 grams sulphuric acid; specific gravity, 1.833
Specific conductivity, 0.04303 at 25.0°, and 0.06662 at 45.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.45	11.42	11.43	—	—	—
255	9.24	9.28	9.26	255	0.000825	0.000214
735	6.04	6.02	6.03	480	894	237
1335	3.45	3.44	3.44	606	935	254
1860	2.23	2.24	2.23	525	826	228
				Means:	0.000870	0.000233

TABLE 31

0.600 gram water to 100.0 grams sulphuric acid; specific gravity, 1.833
Specific conductivity, 0.04820 at 25.0°, and 0.07476 at 45.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.43	11.49	11.46	—	—	—
255	9.89	9.89	9.89	255	0.000578	0.000233
735	7.50	7.42	7.46	480	588	223
1335	5.25	5.30	5.27	600	579	223
1860	4.00	3.89	3.94	525	554	217
				Means:	0.000575	0.000224

With an addition of 0.6 percent of water, k is certainly sufficiently constant for a reaction of the first order, *i. e.*, the influence of the water which forms during the reaction is practically nil as compared with that of the water initially added. On account of the greatly retarded speed with which the reaction proceeded during the last measurement, it was again desirable to increase the temperature. A few preliminary experiments showed that in order to get as far as possible with the additions of water and yet not have the reaction with an addition of 0.6 percent of water proceed too rapidly a temperature of 70° was suitable.

Table 32 is based on the measurements at 45° just as Table 24 on those at 25°. The graphic construction used for the purpose is found in Fig. 3.

In passing from 25° to 45° the values of k, calculated between the same titration values for an addition of 0.1 percent of water, rises from 0.00113 to 0.02003, *i. e.*, about to 17-fold (compare with Table 24). In passing from an addition of 0.10 percent of water to that of 0.6 percent, both at 45°, the time in which equal quantities of oxalic acid are decomposed increases to nearly 34-fold. The differences in the value of k are again very striking and at first somewhat larger for each addition of 0.05 percent of water than at 25° for 0.01 percent, but at the end of the series much smaller. The sensitiveness to water decreases with increase in the amount of water present. Here again no simple relation is found to exist between the conductivity of the sulphuric acid and the speed of the reaction.

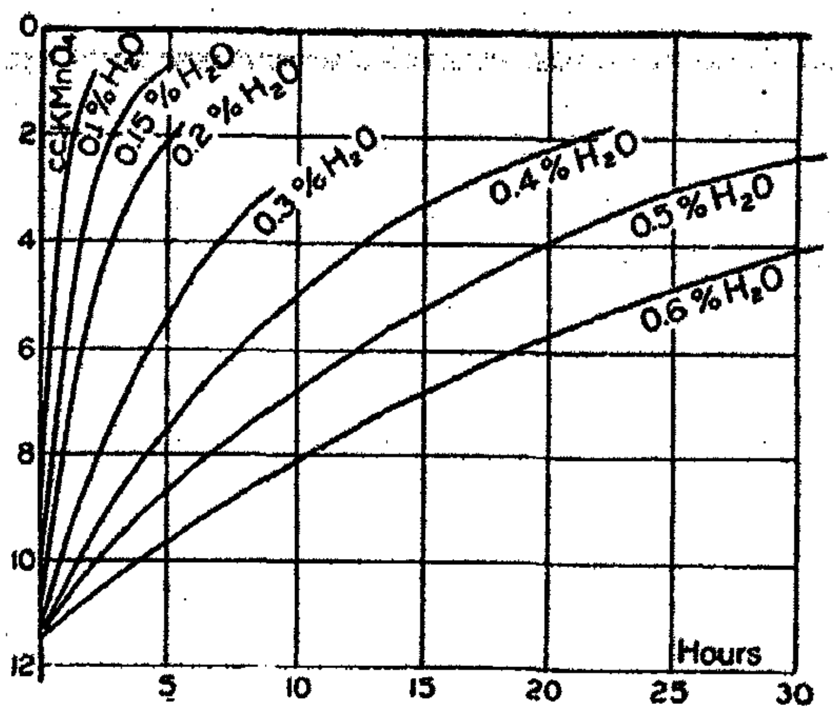


Fig. 3.—Temp. 45°

The specific conductivities of the sulphuric acids were also measured at 45°, giving the values below.

Addition of water, percent:	Specific conductivity, k:
0.10	0.02632
0.15	0.03223
0.20	0.03848
0.30	0.04897
0.40	0.05834
0.50	0.06662
0.60	0.07476

Measurements at 70.0°

These were also made with one-fortieth molar oxalic acid solutions in acid B_2 plus water, and were begun with an addition of 0.6 percent, the quantity with which the measurements at 45° ended.

TABLE 32

Water additions Percent	Specific conductivity at 25.0°	Minutes from the time 0 to the titration value		Duration of the conversion 8.13 → 5.90	*k*	Differences per 0.05 percent of water
		8.13	5.90			
0.10	0.01560	4	20	16	0.02003	—
0.15	0.01998	24	56	32	1016	0.00987
0.20	0.02404	50	102	52	616	400
0.30	0.03123	136	268	132	243	186
0.40	0.03758	242	479	237	135	54
0.50	0.04303	405	759	354	90	23
0.60	0.04820	591	1134	543	59	15

TABLE 33

0.600 gram water to 100.0 grams sulphuric acid; specific gravity, 1.833
Specific conductivity, 0.04772 at 25.0°, and 0.1142 at 70.0°

Minutes	cc permanganate			Intervals	*k*	k_w
	I	II	Means			
0	9.69	9.78	9.73	—	—	—
15	7.31	7.31	7.31	15	0.01906	0.00720
40	4.62	4.67	4.64	25	1820	700
75	2.41	2.44	2.42	35	1859	728
120	1.16	1.13	1.14	45	1673	666
				Means:	0.01814	0.00703

TABLE 34

0.700 gram water to 100.0 grams sulphuric acid; specific gravity, 1.834
Specific conductivity, 0.05284 at 25.0°, and 0.1259 at 70.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	10.14	10.07	10.10	—	—	—
15	8.26	8.35	8.30	15	0.01308	0.00665
40	5.95	5.92	5.93	25	1345	665
75	3.68	3.66	3.67	35	1370	718
120	2.08	2.07	2.08	45	1273	674
175	1.03	1.03	1.03	55	1269	678
				Means:	0.01313	0.00680

TABLE 35

0.800 gram water to 100.0 grams sulphuric acid; specific gravity, 1.834
Specific conductivity, 0.05679 at 25.0°, and 0.1344 at 70.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	10.35	10.39	10.37	—	—	—
25	8.00	8.04	8.02	25	0.01027	0.00681
60	5.58	5.67	5.62	35	1016	682
110	3.37	3.36	3.36	50	1029	698
180	1.63	1.67	1.65	70	1016	698
				Means:	0.01022	0.00690

TABLE 36

1.000 gram water to 100.0 grams sulphuric acid; specific gravity, 1.836
Specific conductivity, 0.06407 at 25.0°, and 0.1526 at 70.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	10.57	10.56	10.56	—	—	—
40	8.11	8.12	8.11	40	0.00660	0.00640
100	5.29	5.42	5.35	60	697	721
190	2.84	2.89	2.86	90	696	733
310	1.27	1.27	1.27	120	676	724
				Means:	0.00682	0.00686

TABLE 37

1.200 grams water to 100.0 grams sulphuric acid; specific gravity, 1.836
Specific conductivity, 0.07089 at 25.0°, and 0.1678 at 70.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.04	10.99	11.01	—	—	—
60	8.35	8.32	8.33	60	0.00465	0.00685
160	4.93	4.93	4.93	100	524	786
310	2.43	2.45	2.44	150	469	724
470	1.09	1.08	1.08	160	509	772
				Means:	0.0492	0.00743

TABLE 38

1.200 grams water to 100.0 grams sulphuric acid; specific gravity, 1.836
Specific conductivity, 0.07117 at 25.0°, and 0.1687 at 70.0°

Minutes	cc permanganate			Intervals	k
	I	II	Means		
0	11.02	11.05	11.03	—	—
60	8.28	8.34	8.31	60	0.00472
160	5.02	5.06	5.04	100	500
310	2.40	2.44	2.42	150	489
470	1.07	1.09	1.08	160	504
				Mean:	0.00491

TABLE 39

1.500 grams water to 98.5 grams sulphuric acid; specific gravity, 1.837
Specific conductivity, 0.07929 at 25.0°, and 0.1885 at 70.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.19	11.21	11.20	—	—	—
60	9.28	9.34	9.31	60	0.00304	0.00725
160	6.92	6.93	6.92	100	299	702
360	3.49	3.53	3.51	200	339	810
720	1.12	1.12	1.12	360	317	764
				Means:	0.00315	0.00750

TABLE 40

2.000 grams water to 98.0 grams sulphuric acid; specific gravity, 1.838
Specific conductivity, 0.09101 at 25.0°, and 0.2153 at 70.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.41	11.40	11.40	—	—	—
80	9.88	9.88	9.88	80	0.00179	0.00866
220	7.60	7.51	7.55	140	192	737
500	4.40	4.43	4.41	280	192	809
1160	1.22	1.21	1.21	660	196	832
				Means:	0.00190	0.00808

TABLE 41

3.00 grams water to 97.0 grams sulphuric acid; specific gravity, 1.838
Specific conductivity, 0.1069 at 25.0°, and 0.2533 at 70.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.44	11.46	11.45	—	—	—
110	10.35	10.35	10.35	110	0.00092	0.00863
310	8.52	8.58	8.55	200	95	898
730	5.74	5.75	5.74	420	94	897
1420	2.97	3.00	2.98	690	95	903
1900	1.88	1.92	1.90	480	94	890
				Means:	0.00094	0.00890

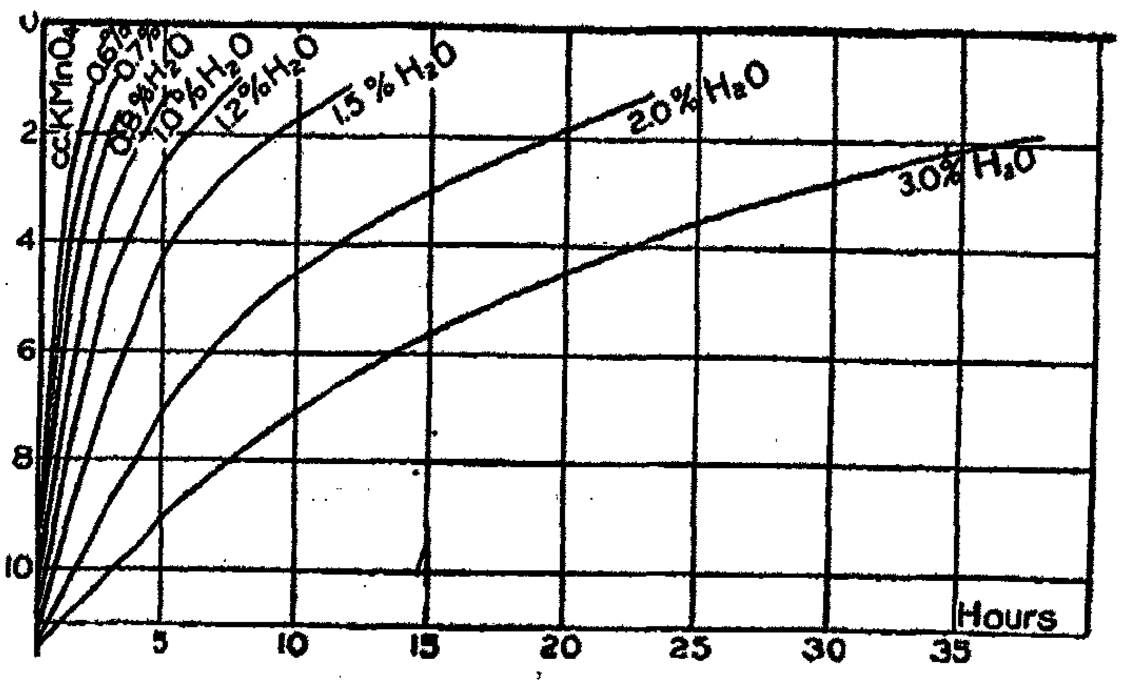


Fig. 4.—Temp. 70°

In Table 42 the additions of water, the values of *k* and the specific conductivities of the sulphuric acids used at 70°, are arranged. See also Fig. 4.

TABLE 42

Percent water per 100 grams H_2SO_4	*k*	Specific conductivity	
		at 25.0°	at 70.0°
0.6	0.01814	0.04772	0.1142
0.7	1313	0.05284	0.1259
0.8	1022	0.05679	0.1344
1.0	682	0.06407	0.1526
1.2	492	0.07089	0.1678
1.2	491	0.07117	0.1689
Percent water in 100 grams mixture			
1.5	315	0.07929	0.1885
2.0	199	0.09101	0.2153
3.0	94	0.1069	0.2533

For each pair of measurements at 70° *k* is a constant of the first order, whose value, however, still depends to a marked degree on the amount of the initial addition of water, as is seen clearly in the preceding table. While the conductivity increases to only a little over 2-fold in going from a water addition of 0.6 percent to one of 3.0 percent the speed constant *k* decreases to about one-nineteenth of its value for an addition of 0.6 percent of water. The first measurement with 1.2 percent of water was made early in March, 1906, the second in the following May. The agreement in the values of *k* and in those of the conductivity, *k*, prove that the stock of sulphuric acid had not changed noticeably during two months.

Measurements at 98.0°,

with one-fortieth molar oxalic acid in the sulphuric acid B_2 plus water.

TABLE 43

3.00 grams water to 97.0 grams sulphuric acid ; specific gravity, 1.838
Specific conductivity, 0.1069 at 25.0°, and 0.3635 at 98.0

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	9.13	9.30	9.21	—	—	—
15	6.49	6.56	6.52	15	0.02304	0.2173
35	3.82	3.90	3.86	20	2620	0.2481
60	2.06	2.28	2.17	25	2303	0.2187
90	1.11	1.12	1.11	30	2236	0.2127
				Means:	0.02365	0.2242

TABLE 44

4.00 grams water to 96.0 grams sulphuric acid ; specific gravity, 1.837
Specific conductivity, 0.1181 at 25.0°, and 0.4009 at 98.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	9.95	9.94	9.94	—	—	—
20	7.37	7.44	7.40	20	0.01476	0.2445
45	5.03	5.13	5.08	25	1504	0.2511
80	3.03	2.98	3.00	35	1505	0.2502
120	1.78	1.71	1.74	40	1361	0.2268
				Means:	0.01461	0.2432

TABLE 45

6.00 grams water to 94.0 grams sulphuric acid ; specific gravity, 1.833
Specific conductivity, 0.1293 at 25.0°, and 0.4489 at 98.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	10.86	10.86	10.86	—	—	—
30	8.96	8.82	8.89	30	0.00668	0.2324
90	5.83	5.85	5.84	60	700	0.2626
190	2.90	2.94	2.92	100	693	0.2602
370	0.86	0.86	0.86	180	679	0.2600
				Means:	0.00685	0.2538

TABLE 46

8.00 grams water to 92.0 grams sulphuric acid; specific gravity, 1.827
Specific conductivity, 0.1328 at 25.0°, and 0.4737 at 98.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.01	11.01	11.01	—	—	—
60	8.64	8.69	8.66	60	0.00400	0.3144
160	5.92	5.90	5.91	100	382	0.2544
340	2.95	2.79	2.87	180	401	0.2663
620	0.90	0.92	0.91	280	410	0.2727
				Means:	0.00398	0.2651

TABLE 47

10.00 grams water to 90.0 grams sulphuric acid; specific gravity, 1.816
Specific conductivity, 0.1300 at 25.0°, and 0.4933 at 98.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.42	11.50	11.46	—	—	—
100	9.30	9.28	9.29	100	0.00210	0.2135
285	6.03	6.15	6.09	185	228	0.2170
625	2.79	2.83	2.81	340	228	0.2320
1360	0.57	0.56	0.56	735	220	0.2254
				Means:	0.00222	0.2220

TABLE 48

15.0 grams water to 85.0 grams sulphuric acid; specific gravity, 1.780
Specific conductivity, 0.1226 at 25.0°, and 0.5240 at 98.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	11.84	11.80	11.82	—	—	—
210	10.23	10.23	10.23	210	0.00069	0.1527
690	7.14	7.08	7.11	480	76	0.1473
1530	3.92	3.89	3.90	840	72	0.1596
2730	1.60	1.56	1.58	1200	75	0.1660
				Means:	0.00073	0.1564

TABLE 49

20.0 grams water to 100.0 grams sulphuric acid; specific gravity, 1.727
Specific conductivity, 0.1390 at 25.0°, and 0.5704 at 98.0°

Minutes	cc permanganate			Intervals	k	k_w
	I	II	Means			
0	12.23	12.26	12.24	—	—	—
400	10.97	11.02	10.99	400	0.00027	0.0999
1270	8.43	8.43	8.43	870	31	0.1118
2710	5.45	5.38	5.41	1440	31	0.1132
4820	2.89	2.87	2.88	2910	30	0.1103
				Means:	0.00030	0.1088

Table 50 contained a summary of the results obtained at 98°.

TABLE 50

Percent water per 100 grams mixture	k	Specific conductivity at	
		25.0°	98.0°
3.0	0.02365	0.1069	0.3635
4.0	1461	0.1181	0.4009
6.0	685	0.1293	0.4489
8.0	398	0.1328	0.4734
10.0	222	0.1300	0.4933
15.0	73	0.1226	0.5240
20.0	30	0.1390	0.5704
50.0	3	0.5790	1.3304

The measurement in 50 percent sulphuric acid was made in stoppered flasks and was continued for 104 hours, during which time the decomposition reached only 15.82 percent. The value of k, 0.00003, is calculated from the titration values at the beginning and end of this long period and may not be very reliable. The decrease in the value of k is 0.00904 as the amount of water increases from 3 to 4 percent; *i. e.*, 0.00904 per 1 percent of water. When the amount of water is changed from 15 percent to 20 percent the decrease in k is 0.00043, or only 0.00009 per 1 percent of water, a change which is not measurable with any high degree of accuracy.

By raising the temperature from 70° to 98°, the value of the constant increases, for an addition of 3 percent of water, from 0.00094 to 0.02365 or to about 25-fold. Because of the large difference in the specific gravity of the sulphuric acid solutions used at 98°, the calculated titration values per 10 grams of oxalic acid solution are no longer comparable except when the additions of water were 3 and 4 percent. Consequently they were calculated over for a specific gravity equal to that when 3 percent of water was added, and on the basis that the titration values per 10 grams of the different solutions are universely proportional to the specific gravities of the solutions. Table 51 contains these corrected values.

TABLE 51

Percent water						
6.0	Minutes	0	30	90	190	370
	Titration values	10.82	8.86	5.82	2.91	0.86
8.0	Minutes	0	60	160	340	620
	Titration values	10.94	8.61	5.91	2.87	0.91
10.0	Minutes	0	100	285	625	1360
	Titration values	11.32	9.18	6.02	2.78	0.55
15.0	Minutes	0	210	690	1530	2730
	Titration values	11.45	9.90	6.88	3.78	1.53
20.0	Minutes	0	400	1270	2710	4820
	Titration values	11.50	10.32	7.92	5.08	2.70

Upon these corrected and now comparable titration values the curves in Fig 5 were constructed. For calculating

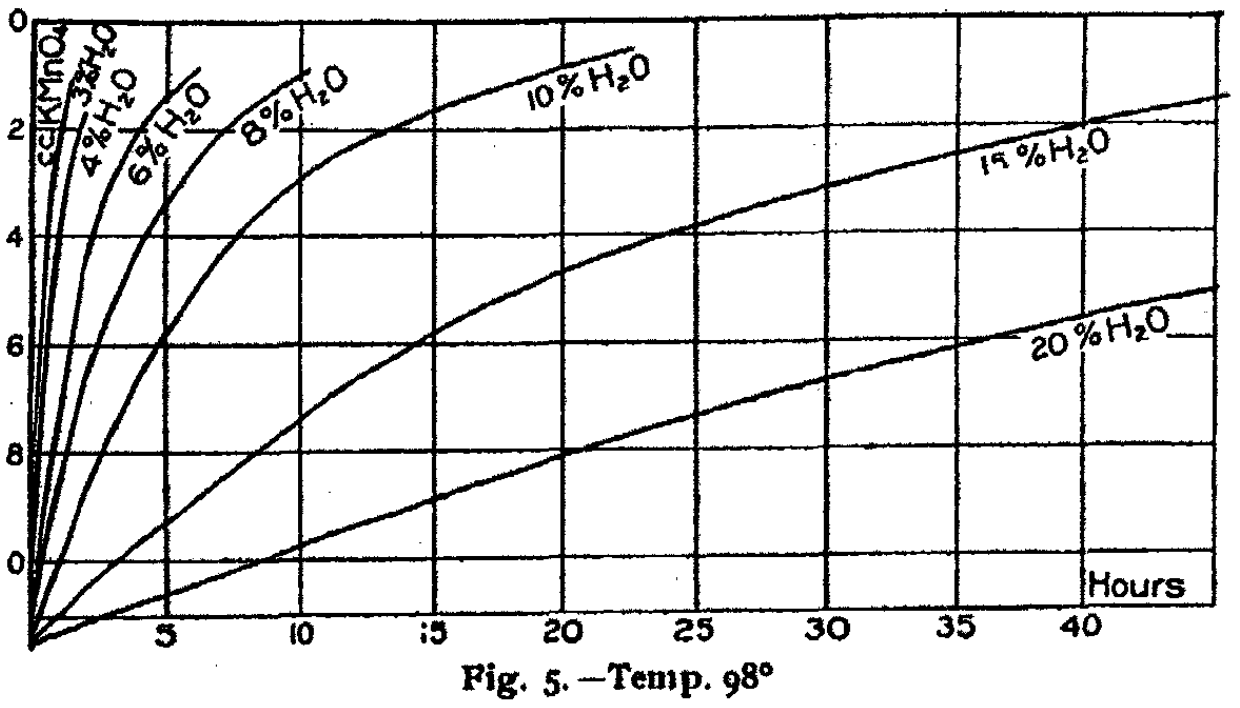


Fig. 5.—Temp. 98°

the constants of the first order, these corrections are of course without significance.

SUMMARY

In the following Table 52, are given the amounts of water added, the specific conductivities in reciprocal ohms

TABLE 52

Percent water to 100 grams H_2SO_4	Speed measurements		Specific conductivities, κ		
			at 25.0°	at	
0.00	$l_{8.13-5.90} = 15$	at 25.0°	0.01043		
0.010	23		0.01068		
0.020	34		0.01080		
0.030	56		0.01122		
0.040	67		0.01171		
0.050	95		0.01210		
0.070	139		0.01352		
0.100	285		0.01560		
0.100	16	at 45.0°	0.01560	0.02632	45.0°
0.150	32		0.01998	0.03223	
0.200	52		0.02404	0.03848	
0.300	132		0.03123	0.04897	
0.400	237		0.03758	0.05834	
0.500	354		0.04303	0.06662	
0.60	543 $k = 0.0005746$		0.04820	0.07476	
0.60	$k = 0.01814$	at 70.0°	0.04773	0.1142	70.0°
0.70	0.01313		0.05284	0.1259	
0.80	0.01022		0.05679	0.1344	
1.00	0.00682		0.06407	0.1526	
1.20	0.00492		0.07089	0.1678	
in 100 grams solution					
1.50	0.00315		0.07929	0.1885	
2.00	0.00199		0.09101	0.2153	
3.00	0.00094		0.10690	0.2533	
3.00	0.02365	at 98.0°	0.1069	0.3635	98.0°
4.00	0.01461		0.1181	0.4009	
6.00	0.00685		0.1293	0.4489	
8.0	0.00398		0.1328	0.4734	
10.0	0.00222		0.1300	0.4933	
15.0	0.00073		0.1226	0.5240	
20.0	0.00030		0.1390	0.5704	

and cc and the speed constant k, where constants were obtained for a monomolecular reaction, and where not, the time in minutes required to change the titration values from 8.13 to 5.9, expressed by $t\ 8.13 \Rightarrow 5.9$.

The table shows that the percentage decrease in the speed of the reaction (*i. e.*, the increase in the duration of the reaction from 8.13 to 5.9 and the decrease in the speed constant) is very much larger than the percentage increase in the specific conductivity for equal additions of water. Accordingly, measuring the speed with which oxalic acid decomposes in concentrated sulphuric acid, appears to be a much more delicate means, than the conductivity measurement, for the analytical estimation of very small amounts of water in pure concentrated sulphuric acids; on the other hand, the electric conductivity can generally be more accurately and quickly measured. Contamination with alkali sulphates has, as is seen in Tables 54 and 56, only one-tenth as great a retarding influence as the same percentage of water.

Temperature Coefficients

For the temperature interval 25° to 45° and an addition of 0.1 percent of water, using in place of the speed constants, the inverse of the time in minutes required to secure equal transposition (Table 52), the value of A in the integrated form of the van't Hoff-Arrhenius equation, $\log \frac{k_1}{k_2} = \frac{A}{2.302} = \frac{T_1 - T_2}{T_1 T_2}$ was found to be 13,650. The temperature coefficient $\left(\frac{k_1}{k_2}\right)$ for the interval 25°–35°, calculated with this value of A is 4.42. By means of the experimental data for an addition of 0.6 percent of water at 45° and 70° (Table 52). A was found equal to 14,380 and the temperature coefficient from 45°–55°, equal to 3.97. For an addition of 3 percent of water at 70° and 98°, A was equal to 14,650 and the temperature coefficient for the interval 70°–80° equal to 3.35. The temperature coefficient is therefore quite high and decreases with rise in temperature, but in view of the fact that the different values belong to acids of different dilutions they are not strictly comparable.

Application of the General Equation

$$\frac{dx}{dt} = \frac{k_w(a-x)}{(w+x)^2}.$$

Since there were indications that the speed of the reaction was approximately proportional to the square of the weight of the water added, the values of k_w already presented, were calculated by means of the integrated form of the differential equation given above, in which

w is the weight of water added,

a, the amount of oxalic acid dissolved,

x, the amount of oxalic acid which was decomposed at the end of t minutes, or the amount of water formed in the same time,

$a-x$, the amount of oxalic acid left undecomposed after t minutes, all expressed in moles per liter.

If we let $a - x = \mu$ and $w + a = b$ then

$$k_w\int dt = -\int \frac{(w+a-\mu)^2}{\mu}\,d\mu = -\frac{(b-\mu)^2}{\mu}\,d\mu,$$

$$= -b^2\int\frac{d\mu}{\mu} + 2\,b\int d\mu - \int \mu\,d\mu,$$

and

$$k_w t = -b^2 ln\mu + 2\,b.\mu - \frac{\mu^2}{2} + c$$

$$= -(w+a)^2 ln(a-x) + 2(w+a)\,(a-x) - \frac{(a-x)^2}{2} + \text{C}.$$

Hence,

$$k_w = \frac{1}{t_2 - t_1}\left\{(w+a)^2 ln\frac{a-x_1}{a-x_2} - 2(w+a)\Big[(a-x_1)-(a-x_2)\Big] + \frac{(a-x_1)^2-(a-x_2)^2}{2}\right\},$$

or using Briggian logarithms instead of Naperian,

$$k_w = \frac{1}{t_2 - t_1}\left\{2.302\,(w + a^2)\log\frac{a - x_1}{a - x_2} - 2\,(w + a)\Big[(a - x_1) - (a - x_2)\Big] + \frac{(a - x_1)^2 - (a - x_2)^2}{2}\right\}.$$

a = 0.0250 moles, corresponding to 11.5 cc of permanganate solution. From these two values and the titration values at the end of t minutes, the oxalic acid concentration at the end of the same period (*i. e.*, the value of $a - x$) was calculated.

For an addition of x gram water to 100 grams sulphuric acid the value of w was calculated by means of the equation

$$w = \frac{1000\,x}{100 + x} \cdot \frac{\text{sp. gr.}}{18},$$

and for x gram of water in 100 grams of mixture of sulphuric acid and water w was calculated by means of the equation

$$w = \frac{1000\,x}{100} \cdot \frac{\text{sp. gr.}}{18}.$$

In both cases the specific gravities already given in the tables of data were used.

Table 53 gives the values of k_w in order as the reaction proceeded in each set of measurements, the values of w and the temperature, together with the numbers of the tables from which the data are compiled. Up to and including the addition of 0.04 percent of water the value of k_w, for each measurement, increases, in general, with the progress of the reaction, but for additions above that amount they are approximately constant for each set of measurements, and at the same temperature are all of the same order of magnitude. k_w, therefore, appears to be a function of w or of $w + x$.

Influence of the Alkali Sulphates

To learn what effect the alkali sulphates have on the speed with which oxalic acid decomposes in concentrated sulphuric acid, potassium and sodium sulphates were carefully recrystallized and then dried to constant weight by

TABLE 53

Temperature	Percent water added	*w*	Table No.	k_w					k_w Means
25°	0.0000	0.0000	9	0.0_5214	0.0_5382	0.0_5445	0.0_5523	—	—
	0.0100	0.0102	10	0.0_5492	0.0_5597	0.0_5726	0.0_5793	0.0_5826	—
	0.0200	0.0204	11	0.0_5658	0.0_5916	0.0_5859	0.0_5873	0.0_5686	—
	0.0300	0.0306	12	0.0_4095	0.0_4096	0.0_4107	0.0_4118	—	—
	0.0400	0.0408	13	0.0_4098	0.0_4118	0.0_4127	0.0_4123	—	—
	0.0500	0.0510	14	0.0_4126	0.0_4127	0.0_4129	0.0_4121	—	0.0000126
	0.0700	0.0713	18	0.0_4151	0.0_4154	0.0_4151	0.0_4157	—	0.0000153
	0.100	0.1020	19	0.0_4141	0.0_4137	0.0_4142	0.0_4085*	—	0.0000140
45°	0.100	0.1020	25	0.0_3252	0.0_3247	0.0_3277	0.0_3258	—	0.000259
	0.150	0.1527	26	0.0_3236	0.0_3264	0.0_3264	0.0_3261	—	0.000256
	0.200	0.2034	27	0.0_3241	0.0_3285	0.0_3255	0.0_3256	—	0.000259
	0.300	0.3047	28	0.0_3249	0.0_3245	0.0_3254	0.0_3261	—	0.000252
	0.400	0.4056	29	0.0_3246	0.0_3231	0.0_3245	0.0_3242	—	0.000241
	0.500	0.5065	30	0.0_3214	0.0_3237	0.0_3254	0.0_3227	—	0.000233
	0.600	0.6080	31	0.0_3233	0.0_3223	0.0_3233	0.0_3217	—	0.000224
70°	0.600	0.6080	33	0.0_2720	0.0_2700	0.0_2728	0.0_2666	—	0.00703
	0.700	0.7090	34	0.0_2665	0.0_2665	0.0_2718	0.0_2674	0.0_2678	0.00680
	0.800	0.8090	35	0.0_2681	0.0_2682	0.0_2698	0.0_2698	—	0.00690
	1.000	1.010	36	0.0_2640	0.0_2721	0.0_2733	0.0_2724	—	0.00686
	1.200	1.210	37	0.0_2685	0.0_2786	0.0_2728	0.0_2666	—	0.00743
	Percent water in mixture								
	1.500	1.531	39	0.0_2725	0.0_2702	0.0_2810	0.0_2764	—	0.00750
	2.000	2.041	40	0.0_2866	0.0_2737	0.0_2809	0.0_2832	—	0.00808
	3.000	3.063	41	0.0_2863	0.0_2899	0.0_2897	0.0_2903	0.0_2890	0.00890
98°	3.000	3.063	43	0.2173	0.2481	0.2187	0.2127	—	0.2242
	4.000	4.083	44	0.2445	0.2511	0.2502	0.2268	—	0.2432
	6.000	6.110	45	0.2324	0.2626	0.2602	0.2600	—	0.2538
	8.000	8.120	46	0.3144	0.2544	0.2663	0.2727	—	0.2651
	10.00	10.09	47	0.2135	0.2170	0.2320	0.2254	—	0.2220
	15.00	14.84	48	0.1527	0.1473	0.1596	0.1660	—	0.1564
	20.00	19.17	49	0.0999	0.1118	0.1132	0.1103	—	0.1088

glowing gently in a platinum crucible. The measurements recorded in Tables 54 and 55 were made at 25° with one-fortieth molar oxalic solution in sulphuric acid to which there had been added 0.10 percent of water and weights of the sulphates equivalent to 0.185 percent of water.

TABLE 54

0.10 gram water and 1.812 grams K_2SO_4 to 100 grams H_2SO_4

Minutes	cc permanganate			Intervals	*k*
	I	II	Means		
0	11.25	11.31	11.28	—	—
1380	9.39	9.47	9.43	1380	0.000129
2820	7.87	7.88	7.87	1440	126
4240	6.58	6.63	6.60	1420	124

TABLE 55

0.10 gram water and 1.480 grams Na_2SO_4 to 100 grams H_2SO_4

Minutes	cc permanganate			Intervals	*k*
	I	II	Means		
0	11.36	11.36	11.36	—	—
1380	9.34	9.43	9.39	1380	0.000141
2820	7.91	7.81	7.86	1440	124
4240	6.60	6.63	6.61	1420	122

It will be seen that the influence of equivalent quantities of the two sulphates is nearly the same and that they decrease the value of *k* to about one-tenth of that obtained with 0.1 percent of water alone (compare with Table 19).

A third measurement in which only an amount of potassium sulphate equivalent to 0.10 per cent of water was added is given in Table 56.

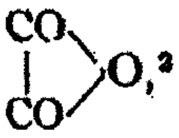
TABLE 56

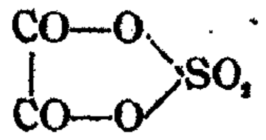
0.968 gram K_2SO_4 to 100 grams H_2SO_4 at 25.0°

Minutes	cc permanganate			Intervals	*k*
	I	II	Means		
0	11.01	11.04	11.02	—	—
75	9.62	9.64	9.63	75	0.001797
225	7.60	7.62	7.61	150	1569
465	5.61	5.69	5.65	240	1242

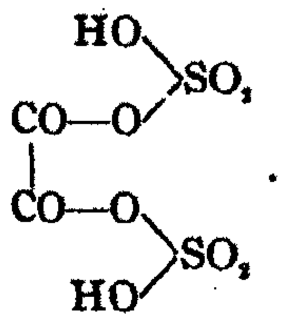
These data show that the influence of potassium sulphate on the speed of the reaction is about the same as that of an equivalent quantity of water (see Table 19), but is for 0.1 percent of potassium sulphate about one-tenth as great as that of the same percent of water.

CONCLUSION

Upon what chemical equilibrium in the concentrated sulphuric acid the influence of water makes itself felt, can not now be determined, but at all events there is no maximum or minimum in the action on oxalic acid coinciding with the minimum[1] conductivity of concentrated sulphuric acid. Between 0.05 and 4 percent of water the speed of the decomposition of oxalic acid seems to be approximately inversely proportional to the square of the amount of water added. It depends on a component of the concentrated sulphuric acid (perhaps sulphur trioxide or pyrosulphuric acid) or on an intermediate product of the reaction, whose active mass is strongly repressed by the addition of water. In terms of the hypothesis of intermediate reactions, one might perhaps conceive of the first stage of the reaction as resulting in an unstable oxalic acid anhydride  $(CO)_2O$,[2] or in the formation of a compound between oxalic and sulphuric acid,[3]



with liberation of water, or one of the following form:



These intermediate products could then themselves decompose according to an irreversible reaction. Since, in the

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[1] Knietsch: Ber. chem. Ges. Berlin, 34, 4069 (1901).

[2] Compare O. Diels and B. Wolf: Ber. chem. Ges. Berlin, 39, 689 (1906).

[3] Compare H. Meyer: Wiener Monatsh. f. Chemie, 24, 840 (1903); O. Stillich: Ber. chem. Ges. Berlin, 38, 1242 (1905).

formation of these hypothetical compounds, water is formed, water which is added at the start or that which forms during the reaction, could retard the speed with which the intermediate product forms, and of course thereby retard the speed with which the oxalic acid decomposes. This, however, is to be regarded as pure theorizing.

SUMMARY

1. In this research, I believe, a dehydrating action by means of concentrated sulphuric acid has for the first time been measured quantitatively.

2. Addition of water causes a progressive decrease in the speed of decomposition of oxalic acid.

3. With very concentrated sulphuric acid the reaction is very sensitive to exceedingly small additions of water.

4. For additions of water up to 0.6 percent the law of reaction is complex.

5. From 0.6 percent upward, constants for a monomolecular reaction have been obtained.

6. The equation for a monomolecular reaction can be replaced from 0.05 percent to 20 percent of water by a more complex one in which the reaction constant is approximately inversely proportional to the square of the total water present.

7. The temperature coefficient of the reaction is strikingly high.

8. The measurement of the specific conductivity, as a means of defining the sulphuric acid, has proved very gratifying.

9. The alkali sulphates have about one-tenth of the retarding influence upon the speed of the reaction, which an equal weight of water has.

10. Both the measurement of the speed of decomposition of oxalic acid in concentrated sulphuric acid and the measurement of the specific conductivity of the sulphuric acid, far exceed in delicacy, the ordinary analytical method of determining the amount of water in very concentrated

sulphuric acid. Although the speed of the reaction under consideration is far more sensitive to traces of water in very concentrated sulphuric acid than is the conductivity, the latter is much more readily measured.

Ann Arbor, Mich.,
December, 17, 1906.

THE SYSTEM, LIME, NITRIC ACID AND WATER[1]

BY F. K. CAMERON AND W. O. ROBINSON

Recently mixtures composed of lime and nitric acid have become prominent in agriculture as proposed fertilizers. Cultural tests[2] have indicated that these mixtures have probably a great value, and at least the one produced under the patents of Birkeland and Eyde[3] is now assuming considerable commercial importance. Consequently, it has been deemed advisable to determine the solubility curves and corresponding solid phases for the system, lime (CaO), nitric oxide (N_2O_5) and water. The data here presented were obtained at a temperature of 25° C, and refer to that part of the system only in which lime is present in excess of its equivalent of nitric acid. The solutions were all alkaline to phenolphthalein.

The calcium nitrate used, contained some calcium carbonate, though otherwise quite pure. To free from carbonates, a saturated solution of this preparation was boiled, a slight but decided excess of nitric acid having first been added. A series of solutions of varying concentrations was then prepared by the addition of boiled distilled water and to each solution an excess of freshly prepared lime was added in excess. The solutions were kept in 8-ounce sterilizer bottles, tightly stoppered, and constantly rotated in a water-bath which was maintained at 25° C.

From time to time small portions of the solutions were withdrawn and titrated with a standard solution of nitric acid, until successive titrations showed that equilibrium had been reached. Upwards of a month and a half was required to bring the whole series to a constant state.

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[1] Published by permission of the Secretary of Agriculture.

[2] See, for example, Bellenoux : Comptes rendus, 140, 1190 (1905); and Schloesing : Ibid., 141, 745 (1905).

[3] Among the many descriptions, which have appeared, that of O. N. Witt, Chemische Industrie, 28, 699 (1905), will be found very complete and satisfactory.

At the end of this period the precipitates in the bottles were allowed to settle and the clear solution drawn off and analyzed for total calcium and calcium in excess of that required for the formation of the normal nitrate with the nitric acid present. As this quantity never exceeded more than four-tenths of 1 percent of the solution and was in most cases less than two-tenths of 1 percent, the experimental difficulties of the analysis are obviously great.

Two methods were possible. First, one might determine the total calcium and the nitric acid and calculate the calcium as calcium hydroxide by difference. It was found that the experimental error in such a proceeding might easily amount to a hundred percent in the final results and so this method had to be given up. The second method was to estimate the calcium present as hydroxide by titrating the solution to the neutral point with a standard nitric acid solution. This second method is open to two objections. No two indicators give quite the same neutral point and for the same indicator no two widely different concentrations of the same solution give strictly comparable titration figures, owing to the hydrolysis which takes place with a salt of this character. If, however, the solutions be titrated at the same dilution and using the same indicator (in this case phenolphthalein), the results are comparable and dependence can be placed upon them as far as breaks in the solubility curve are concerned. The data obtained are given in Table I, and are shown graphically in Fig. 1.

From inspection of the chart it will be seen that there are four distinct curves with three inversion points. As this is a three-component system there can be only one stable solid phase in equilibrium with solutions along each of the branches of the isotherm and the triangular diagram method, or the method of residues may be used to determine the solid phases.[1] Accordingly, the solution was freed as completely as possible from certain precipitates along the different curves and the

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[1] Schreinemakers: Zeit. phys. Chem., 11, 81 (1893); Bancroft: Jour. Phys. Chem., 6, 181 (1902).

TABLE I

Density $\frac{25°}{25°}$	CaO as $Ca(OH)_2$		$Ca(NO_3)_2$	
	In 100 cc	In 100 g H_2O	In 100 cc	In 100 g H_2O
1.0249	0.095	0.096	3.35	3.38
1.0484	0.105	0.109	8.18	8.52
1.0940	0.120	0.125	12.91	13.42
1.1383	0.170	0.181	19.43	20.73
1.1840	0.171	0.187	26.49	28.98
1.2101	0.180	0.198	29.82	32.84
1.2287	0.190	0.212	32.97	36.83
1.2290	0.191	0.213	33.27	37.55
1.2541	0.200	0.224	35.87	40.25
1.2581	0.203	0.230	37.04	41.98
1.2826	0.226	0.260	40.88	47.00
1.2905	0.229	0.263	41.08	47.16
1.3337	0.277	0.332	48.99	58.67
1.3735	0.346	0.429	50.88	69.40
1.4195	0.440	0.545	63.93	83.03
1.4840	0.331	0.449	73.58	99.70
1.5330	0.263	0.371	81.91	115.50
1.5809	0.203	0.303	90.38	135.30
1.5842	0.000	0.000	91.84	139.30

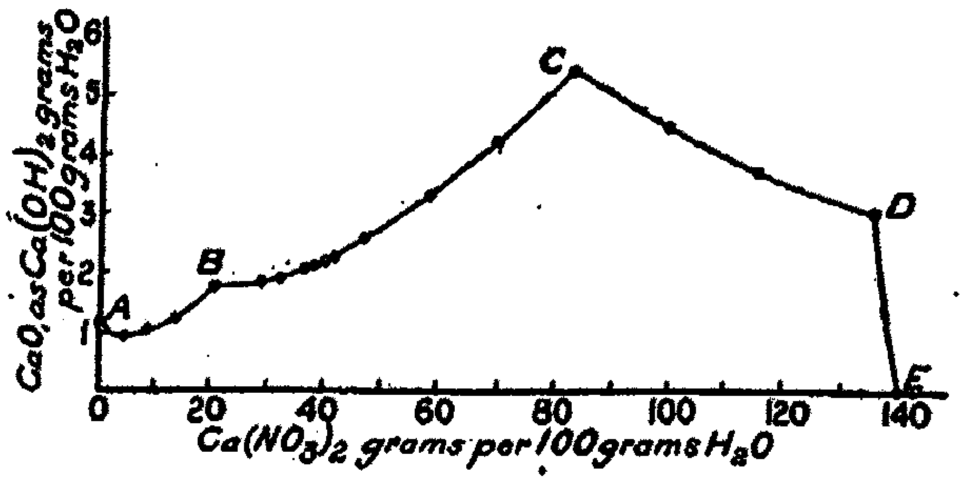

Fig. 1

points obtained by charting the analytical results, Table II, were joined with those of their respective solutions as plotted on the triangular diagram, Fig. 2.

In the analysis of the precipitate with adhering mother-liquor the total calcium was determined gravimetrically and the free calcium hydroxide was determined by titration with

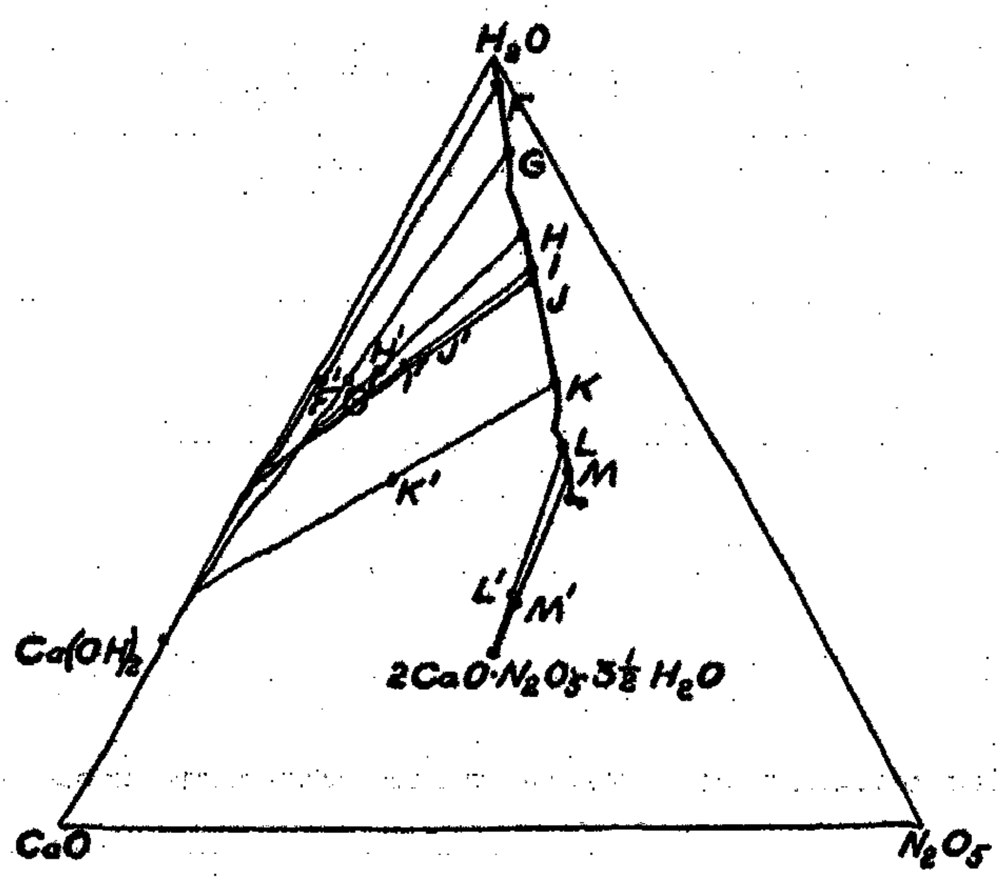

Fig. 2

standard nitric acid. The following table gives the compositions of the solutions and of the corresponding precipitates with adhering mother-liquor.

TABLE II

Point	Solution		Point	Precipitate with adhering solution	
	CaO Percent	N_2O_5 Percent		CaO Percent	N_2O_5 Percent
F	1.21	2.15	F'	40.85	1.00
G	4.16	7.80	G'	37.70	4.09
H	7.77	14.70	H'	33.26	7.20
I	9.34	17.84	I'	29.73	9.87
J	9.83	18.77	J'	27.49	11.60
K	14.21	26.87	K'	38.59	15.71
L	17.20	33.32	L'	31.64	36.36
M	18.50	35.33	M'	31.72	37.21

From the diagram it will be seen that the extension of the lines F F' and G G' meet in a point corresponding to solid calcium hydroxide. This substance therefore was the solid phase in contact with the solutions represented by the curve A B.

The following experiment shows conclusively that calcium hydroxide and not a solid solution containing calcium hydroxide, nitric acid and water, is the stable solid phase along this portion of the curve. A mixture was made up containing 20 grams of calcium nitrate to 100 grams water and after shaking a few days with lime the solid was washed several times by decantation and finally by suction, excluding the carbon dioxide of the air. No nitrates were found in the precipitate when treated in this way. If it were the solid solution no amount of washing would completely free it from nitric acid.

It is evident that the lines joining the points representing the composition of the solutions and their corresponding precipitates for the second branch of the curve, when extended, do not meet at a common point. The precipitate is therefore of variable composition and since there can be only one phase present it must be a series of solid solutions containing calcium oxide, nitric oxide, and probably water.

The residues along the third branch of the curve proved to be a substance occurring in long acicular crystals. As scaled off from the diagram its percentage composition is CaO, 39.5; N_2O_5, 38.0; and 22.5 H_2O, corresponding to the compound, $2CaO.N_2O_5.3\frac{1}{2}H_2O$, and is identical with the one described by Werner.[1]

Crystals of this basic nitrate were freed from adhering mother-liquor by pressing between filter-papers. On standing exposed to the air, or more quickly by washing with alcohol, the crystals gradually lost water, but retained their external forms.

It would seem that this more or less completely dehydrated residue corresponds pretty closely to the product of the Birkeland and Eyde process. Owing to the fact that it is absolutely opaque under the microscope it is not possible to say whether it be a definite compound or a mixture, but it is probably the latter. It is obvious that the basic nitrate of calcium is stable at 25° C, only when in contact with an aqueous solution containing between 83 and 135 grams of

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[1] Ann. Chim. Phys., 27, 570 (1892).

calcium nitrate—$Ca(NO_3)_2$—to 100 grams of water, and cannot therefore persist in the dry form.

The solid phase in contact with the solutions along the fourth branch of the curve was undoubtedly the well-known normal nitrate $Ca(NO_3)_2.4H_2O$, and no further attempt was made to determine its composition.

Finally, the data for the "constant solutions" have been brought together in Table III.

TABLE III

Points	Solid phases in contact with solution	Concentration of solutions, grams per 100 grams H_2O	
		CaO as $Ca(OH)_2$	$Ca(NO_3)_2$
A	$Ca(OH)_2$	0.118	0.0
B	$Ca(OH)_2$, and solid solution $CaO.xN_2O_5.yH_2O$	0.170	20.73
C	Solid solution $CaO.xN_2O_5.yH_2O$ and $CaO.N_2O_5.3\frac{1}{2}H_2O$	0.440	83.03
D	$CaO.N_2O_5.3\frac{1}{2}H_2O$ and $Ca(NO_3)_2 4H_2O$	0.203	135.3
E	$Ca(NO_3)_2.4H_2O$	0.0	139.30

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ON THE LATENT HEAT OF FUSION OF ICE

BY LEO FRANK GUTTMANN

While engaged in some calorimetric determinations I required to know the latent heat of fusion of ice with some accuracy, and consulted the data given in Landolt and Börnstein's tables. It was surprising to find that the most trustworthy figures, those of Regnault (79.24 calories) and of Bunsen (80.03), differed by nearly 1 per cent. As each of these experimenters could be trusted to work to 1 part in 1,000, the difference was too great to strike a mean value. After all the papers on the subject had been carefully studied to find a cause for this discrepancy, it appeared that A. W. Smith[1] had been similarly struck by this fact and been led to redetermine the latent heat of fusion of ice. Smith gives a critical survey of the previous determinations in his paper, but as there is some difference in our conclusions, I will state the results of my investigation.

A very careful series of determinations had been made by de la Provostaye and Desains,[2] using dry ice at its melting-point, and they found 79.25 as the mean of 17 experiments. (Landolt and Börnstein erroneously give 79.01.) Regnault made two sets of experiments,[3] and found 79.06 using dry solid ice, and 79.24 using pure snow. A considerable quantity of snow was used, and on account of its finely divided state and subsequent rapid melting in the calorimeter, the duration of each experiment was only from 1 to 1½ minutes. The cooling correction was very small and could have produced no sensible error in the results. The snow was always at a temperature below 0°, and could have contained no water. There seems to be no source of error in this series of measurements, and the value 79.24 should be very accurate. As Smith (*l. c.*) has already pointed out, ice at its melting-point is sure

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[1] Physical Review, 17, 193 (1903).

[2] Ann. Chim. Phys. [3], 8, 5–19 (1843).

[3] Ibid. [3], 8, 19–27 (1843).

to contain some water, and the values 79.25 and 79.06 cited above may be dismissed as being too low. But on p. 21 of his memoir Regnault states: "La temperture de la glace était inférieure à zèro, mais seulement d'une fraction de degré, par consequent, la glace, avant de se fondre, absorbait une certaine quantité de chaleur pour monter à zèro. La determination de cette quantité exige la connaissance de la capacité calorifique de la glace, j'ai admis qu'elle était la même que celle de l'eau." The specific heat of ice near its melting-point has been determined by Person[1] and does not differ sensibly from 0.500. I have therefore recalculated Regnault's results, using 0.500 for the specific heat of snow, and find the mean value for the latent heat of fusion of ice, as determined from his experiments, to be 79.41.[2]

Now as to Bunsen's value: The accuracy of the ice calorimeter has been rather overestimated, but should certainly be 1 in 1,000. After a careful study of Bunsen's paper,[3] only trifling sources of error could be found. The latent heat of fusion of ice was determined by dropping into the inner tube of the ice calorimeter a small glass tube containing 0.333 gram of water, previously heated to 100° in a steam jacket. The specific heat of the glass had been determined from only two experiments, but the error thus introduced is negligible. Two consecutive experiments were made, and the results naturally only differed slightly from each other. A greater source of error is introduced by the variation of the density of the ice in the calorimeter. The peculiar alteration in structure which the calorimeter ice

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[1] Compt. rend., 23, 162 (1846); Ann. Chim. Phys. (3), 21, 307 and 312 (1847).

[2] In Ann. Chim. Phys. [3], 30, 80 (1850), Person states that Regnault found 79.43 for the latent heat of fusion of ice, his experiments being corrected for the specific heat of ice, which is taken to be 0.48. He does not mention that he (Person) applied the correction, and the recalculated value does not appear in Landolt and Börnstein's tables. Smith, in his paper, mentions that Regnault assumed the specific heat of ice to be equal to that of water, and yet uses the figure 79.24 in taking the mean of previous determinations.

[3] Pogg. Ann., 21, 1-31 (1820).

undergoes in course of time, has been noticed by all experimenters. It is extremely likely that this change is accompanied by a variation of density, and the values obtained by different observers for the weight of expelled mercury equal to 1 calorie, vary from 15.44 to 15.57 mg, one experimenter even finding 15.26.

Nichols,[1] has fully investigated this subject and concludes that old and new ice differs greatly in density. He obtained 0.91661 for the density of pure ice, and 0.9161 for ice frozen by means of a mixture of CO_2 and ether, although after twenty-four hours this attained the above value. Bunsen's value is 0.91685 and differs by 2 in 10,000 from Nichols', introducing an error of 2 in 1,000 in the amount of ice supposed to have been melted in the calorimeter. Zakrzewski,[2] using an improved form of Bunsen's dilatometer, found 0.91660. Nichols moreover found pure natural ice to be denser by 1 part in 1,000 than calorimeter ice. Barnes[3] finds that the difference between the densities of old and new ice may amount to as much as 2 in 1,000, and depends on the age of the ice. As Bunsen used the same mantle of ice in the calorimeter for many weeks, an uncertain and appreciable error is introduced in the value found by him for the latent heat of fusion of ice. The specific heats of various metals determined by Bunsen are throughout lower than the values obtained by Regnault, a fact to which he himself drew attention.

Regnault's recalculated value 79.41 is therefore the most accurate and trustworthy of the older determinations.

One other correction can be applied. Regnault tabulates all his experimental data in full, and on recalculating his figures I obtained the value he gives if the specific heat of the water in the calorimeter is taken to be unity at all temperatures. There is some difficulty in reducing many of Regnault's experiments to a definite heat unit, on account of the error in his

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[1] Physical Review, 8, 21-37 (1899).

[2] Wied. Ann., 47, 157 (1892).

[3] Physical Review, 13, 55-59 (1901).

formula for the variation in the specific heat of water at ordinary temperatures. This does not apply in this case, and I was able to reduce his results substituting the values for the specific heat of water given by Griffiths (Thermal Measurement of Energy, Table VII). When this is done, the true mean value for the latent heat of fusion of ice as determined by Regnault is found to be 79.59.

The value found by Smith (l. c.) is 334.21 joules = 79.90 mean calories, assuming 1 Clark (15°) = 1.434 volts, and 1 calorie = 4.1832 joules. The value now generally adopted for 1 Clark (15°) = 1.433 volts, and Smith's value must be decreased in the ratio of (1.433 : 1.434). This is also the correction applied by Professor Kohlrausch. (Private communication to the author.) The value adopted for J has, however, also undergone a change, and the Berlin Congress in 1903 fixed 0.23872 calories as the most probable value (4.1890 joules = 1 calorie). Recalculating Smith's value for 1 Clark (15°) = 1.433 volts, and 4.1890 joules = 1 calorie, we get 79.67 calories for the latent heat of fusion of ice. I could find no source of error in Smith's accurate experiments, and have therefore adopted 79.67 as the most accurate value. Regnault's corrected value 79.59 is in good agreement with this, and again shows the skill and accuracy of this classic experimenter.

It had been intended to publish this note together with other experimental work, but it has not yet been found possible to complete all the calculations. The frequency with which Regnault's old value is quoted, for instance see Leduc (*Compt. rend.*, **142**, 46–48, 1906), has necessitated publication.

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ELECTROMOTIVE FORCES OF CONCENTRATION CELLS

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CONTENTS

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The problem

For the electromotive force of a concentration cell of the type

$$\mathrm{M} \mid \mathrm{MCl,I} \mid \mathrm{HgCl.Hg.HgCl} \mid \mathrm{MCl,II} \mid \mathrm{M},$$

Helmholtz, in 1882, under certain simplifying assumptions, deduced the equation

$$(1) \qquad \mathrm{A_I} - \mathrm{A_{II}} = q.r_2\theta \int_{h_{II}}^{h_I} h \frac{\partial \log p_1}{\partial h} \partial h.$$

Here q denotes the mass of salt dissolved on the passage of unit current in unit time, r_2 the specific gas-constant of water vapor, θ the absolute temperature, $h = \mathrm{M_2/M_1}$ the mass of water per unit mass of salt in the solution, and $p_1(\theta,h)$ the vapor pressure of the solution.

For comparison with experiment, Helmholtz evaluated the integral in (1) by means of an empirical relation giving the vapor pressure of solutions of zinc chloride as a function of the concentration at constant temperature. The object of the present note is to integrate Helmholtz's differential equation under the assumption that the relation between vapor pressure and concentration is given by the equation of the theory of dilute solutions,

$$\log \frac{p_0}{p_1} = (1 + \alpha) \frac{n_1}{n_2},$$

together with Ostwald's dilution law

$$k\frac{1-\alpha}{U}=\left(\frac{\alpha}{U}\right)^2;$$

and to determine how the result is altered when Ostwald's equation is replaced by van't Hoff's modification

$$K\left(\frac{1-\alpha}{U}\right)^2=\left(\frac{\alpha}{U}\right)^3$$

of the form proposed by Rudolphi for the dilution law. In these equations, $p_0(\theta)$ denotes the vapor pressure of water, n_1/n_2 the number of mols of salt in the solution per mol of water, α the degree of electrolytic dissociation of the (binary) salt, and U the volume of the solution per mol of salt.

The electromotive force of the cell

For the purpose of making apparent the assumptions involved by (1), I shall begin by deducing the general thermodynamic equation for the electromotive force of the cell. Let $F(p,\theta,M_1,M_2)$ be the free energy of the solution composed of the masses M_1, M_2 of salt and water under the pressure p at the temperature θ. The change of the free energy of the system composed of these masses, when the separated masses at p,θ reversibly or irreversibly form the solution stable at p,θ, is

$$\Delta F = F - M_1 f_1 - M_2 f_2,$$

where $f_j(p,\theta)$ is the specific free energy of the j-th component. Since this function ΔF of the variables p,θ,M_1,M_2 is homogeneous and of the first degree in M_1, M_2, we have

$$\Delta F = M_1\frac{\partial\Delta F}{\partial M_1}+M_2\frac{\partial\Delta F}{\partial M_2};$$

whence, differentiating with regard to either M_1 or M_2,

$$\frac{\partial}{\partial h}\frac{\partial\Delta F}{\partial M_1}+h\frac{\partial}{\partial h}\frac{\partial\Delta F}{\partial M_2}=0. \tag{2}$$

This general equation may be employed to connect the electromotive force of the concentration cell with the concentrations of the two solutions. For $\partial\Delta F/\partial M_1$ may be expressed by means of the electromotive force of the single cell, two of which constitute the concentration cell; and $\partial\Delta F/\partial M_2$ may be expressed by means of the vapor pressure of the solution and thus by means of the concentration; wherefore integration between the two concentrations of the double cell will yield the relation desired.

Let the current in the single cell flow from the metal M to the mercury. When the current J flows in the time dt, the electromotive force A does the work $AJdt$. The work added to the solution is $-AJdt$. This work may also be expressed as $\partial\Delta F/\partial M_1 . Jqdt$. This work being exclusively electrical work,

$$-AJdt = \frac{\partial\Delta F}{\partial M_1} Jqdt$$

$$\frac{\partial\Delta F}{\partial M_1} = -\frac{A}{q}$$

$$\frac{\partial}{\partial h}\frac{\partial\Delta F}{\partial M_1} = -\frac{1}{q}\frac{\partial A}{\partial h}, \tag{3}$$

as was shown by Helmholtz.

On p. 399 of a paper[1] on the thermodynamic theory of solutions, I have shown, equation (15*a*), that

$$\frac{\partial\Delta F}{\partial M_2} = p^2\frac{\partial}{\partial p}\frac{1}{p}\left\{\int_{p_1}^{p_0}\left(v_a - \frac{\partial V}{\partial M_2}\right)dp + \int_{p_0}^{p}\left(v_2 - \frac{\partial V}{\partial M_2}\right)dp\right\},$$

where $v_a(p,\theta)$ is the specific volume of saturated water vapor, $v_2(p,\theta)$ is the specific volume of liquid water, and $V(p,\theta,M_1M_2)$ is the volume of the solution of M_1 in M_2. Executing the indicated differentiation,

$$\frac{\partial\Delta F}{\partial M_2} = p\left(v_2 - \frac{\partial V}{\partial M_2}\right) - \int_{p_1}^{p_0}\left(v_a - \frac{\partial V}{\partial M_2}\right)dp - \int_{p_0}^{p}\left(v_2 - \frac{\partial V}{\partial M_2}\right)dp;$$

whence

$$\frac{\partial}{\partial h}\frac{\partial\Delta F}{\partial M_2} = -p\frac{\partial}{\partial h}\frac{\partial V}{\partial M_2} - \frac{\partial}{\partial h}\int_{p_1}^{p_0}\left(v_a - \frac{\partial V}{\partial M_2}\right)dp - \frac{\partial}{\partial h}\int_{p_0}^{p}\left(v_2 - \frac{\partial V}{\partial M_2}\right)dp. \tag{4}$$

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[1] This Journal, 10, 392 (1906).

Substituting (3) and (4) in the general equation (2), solving for $\partial A/\partial h$, and integrating between h_{II} and h_I, where $h_I > h_{II}$,

$$(5)\quad A_I - A_{II} = -qp\int_{h_{II}}^{h_I} h\frac{\partial}{\partial h}\frac{\partial V}{\partial M_2}\,dh - q\int_{h_{II}}^{h_I} h\frac{\partial}{\partial h}\int_{p_1}^{p_0}\left(v_a - \frac{\partial V}{\partial M_2}\right)dp.dh$$

$$- q\int_{h_{II}}^{h_I} h\frac{\partial}{\partial h}\int_{p_0}^{p}\left(v_2 - \frac{\partial V}{\partial M_2}\right)dp.dh.$$

This is the wholly general thermodynamic equation for the electromotive force of the concentration cell at p,θ. When the cell functions under the pressure $p = p_0$, the last of the three terms of the second member disappears.

Helmholtz's equation

If we assume that $p = p_0$, and also that $\partial V/\partial M_2$ is independent of h and is negligible in comparison with v_a, the equation (5) becomes

$$A_I - A_{II} = -q\int_{h_{II}}^{h_I} h\frac{\partial}{\partial h}\int_{p_1}^{p_0} v_a dp.dh.$$

If we further assume that the saturated water vapor may be regarded as an ideal gas, *i. e.*, that $v_a = r_2\theta/p$, we find

$$(5a)\quad A_I - A_{II} = q.r_2\theta\int_{h_{II}}^{h_I} h\frac{\partial \log p_1}{\partial h}\,dh,$$

which is Helmholtz's equation as cited at the beginning of this article.

Integration of Helmholtz's equation

Our present problem is to effect the integration of (5*a*), under the assumption that the form of $p_1(\theta,h)$ is given by

$$(6)\quad \log\frac{p_0}{p_1} = (1+\alpha)\frac{n_1}{n_2},$$

where the form of $\alpha(\theta,h)$ is to be obtained from

$$(7)\quad k\frac{1-\alpha}{U} = \left(\frac{\alpha}{U}\right)^2.$$

We thus require to find the form of $\partial \log p_1/\partial h$ in h, through elimination of α between (6), (7), and determination of the forms of the functions n_1/n_2 and U.

Solving (7) for α,

$$\alpha = -\frac{k\mathrm{U}}{2} + \left\{k\mathrm{U} + \left(\frac{k\mathrm{U}}{2}\right)^2\right\}^{\frac{1}{2}}.$$

Here, both k and U being positive, the positive square root must be taken to make α positive. Eliminating α,

$$(8) \qquad -\log\frac{p_0}{p_1} = -\frac{n_1}{n_2} + \frac{k\mathrm{U}}{2}\frac{n_1}{n_2} - \frac{n_1}{n_2}\left\{k\mathrm{U} + \left(\frac{k\mathrm{U}}{2}\right)^2\right\}^{\frac{1}{2}}.$$

It remains to express n_1/n_2 and U in terms of h. Writing w_j for the molecular weight of the j-th component of the solution,

$$(9) \qquad \frac{n_1}{n_2} = \frac{\mathrm{M}_1}{\mathrm{M}_2}\frac{w_2}{w_1} = \frac{w_2}{w_1}\frac{1}{h}.$$

Identifying the volume V of the solution with the mass of water in the solution, V = M_2; whence U, the volume of the solution per mol of salt, becomes

$$(10) \qquad \mathrm{U} = \frac{\mathrm{V}}{\mathrm{M}_1/w_1} = \frac{w_1\mathrm{M}_2}{\mathrm{M}_1} = w_1 h.$$

Eliminating n_1/n_2 and U, (8) becomes

$$(11) \quad -\log\frac{p_0}{p_1} = -\frac{w_2}{w_1}\frac{1}{h} + \frac{kw_2}{2} - \frac{w_2}{w_1}\frac{1}{h}\left\{kw_1h + \left(\frac{kw_1h}{2}\right)^2\right\}^{\frac{1}{2}}.$$

Differentiating,

$$(12) \qquad \frac{\partial \log p_1}{\partial h} = \frac{w_2}{w_1}\frac{1}{h^2} + \frac{w_2}{w_1}\frac{kw_1}{2h(kw_1h + k^2w_1^2/4.h^2)^{\frac{1}{2}}}.$$

Substituting this expression in (5*a*), and noting that w_2r_2 is the molecular gas-constant r,

$$\mathrm{A}_{\mathrm{I}} - \mathrm{A}_{\mathrm{II}} = \frac{q}{w_1}.r\theta.\log\frac{h_{\mathrm{I}}}{h_{\mathrm{II}}} + \frac{kq.r\theta}{2}\int_{h_{\mathrm{II}}}^{h_{\mathrm{I}}}\frac{dh}{(kw_1h + k^2w_1^2/4.h^2)^{\frac{1}{2}}}$$

$$(13) \quad = \frac{q}{w_1}.r\theta.\log h\left\{1 + \frac{kw_1}{2}h + \sqrt{kw_1h + \left(\frac{kw_1h}{2}\right)^2}\right\}\Bigg|_{h_{\mathrm{II}}}^{h_{\mathrm{I}}}.$$

This result assumes a simpler form when the composition of the solution is expressed by means of α instead of by means of h. From (7) and (10), namely

$$kU = \frac{\alpha^2}{1-\alpha}, \qquad U = w_1 h,$$

we find $h(\alpha)$ to be

$$\frac{1}{kw_1}\,\frac{\alpha^2}{1-\alpha}.$$

Replacing h in (13) by $h(\alpha)$, we find

$$A_{I} - A_{II} = 2\,\frac{q}{w_1}.r\theta.\log \frac{\alpha}{1-\alpha}\Big|_{\alpha_{II}}^{\alpha_{I}}$$

$$= 2\,\frac{q}{w_1}.r\theta.\log \frac{\alpha_{I}}{\alpha_{II}}\,\frac{1-\alpha_{II}}{1-\alpha_{I}}. \tag{13a}$$

Integration with regard to the degree of electrolytic dissociation

As is indicated by the simple form of the result (13*a*), the above integration of Helmholtz's differential equation is more readily effected when α instead of h is employed as the concentration variable. This shall now be shown. From the general thermodynamic equation

$$\Delta F = M_1 \frac{\partial \Delta F}{\partial M_1} + M_2 \frac{\partial \Delta F}{\partial M_2},$$

by differentiation with regard to M_2 we find

$$\left(M_1 \frac{\partial}{\partial \alpha}\frac{\partial \Delta F}{\partial M_1} + M_2 \frac{\partial}{\partial \alpha}\frac{\partial \Delta F}{\partial M_2}\right)\frac{\partial \alpha}{\partial M_2} = 0.$$

Noting that $\partial\alpha/\partial M_2$ does not vanish, and that

$$\frac{M_2}{M_1} = h = \frac{1}{kw_1}\,\frac{\alpha^2}{1-\alpha},$$

as just shown, we obtain

$$\frac{\partial}{\partial \alpha}\frac{\partial \Delta F}{\partial M_1} + \frac{1}{kw_1}\,\frac{\alpha^2}{1-\alpha}\,\frac{\partial}{\partial \alpha}\frac{\partial \Delta F}{\partial M_2} = 0. \tag{14}$$

Now, as before

$$\frac{\partial \Delta F}{\partial M_1} = -\frac{A}{q};$$

whence

(15) $$\frac{\partial}{\partial \alpha}\frac{\partial \Delta F}{\partial M_1} = -\frac{1}{q}\frac{\partial A}{\partial \alpha}.$$

Again as before, and under the same assumptions,

$$\frac{\partial \Delta F}{\partial M_2} = -\int_{p_1}^{p_0} v_a(p,\theta)\,dp$$
$$= -\phi\Big(p_0(\theta),\theta\Big) + \phi\Big(p_1(\theta,\alpha),\theta\Big);$$

whence

$$\frac{\partial}{\partial \alpha}\frac{\partial \Delta F}{\partial M_2} = \frac{\partial \phi}{\partial p_1}\frac{\partial p_1}{\partial \alpha}$$
$$= v_a(p_1,\theta)\,\frac{\partial p_1}{\partial \alpha}$$

(16) $$= r_2\theta\,\frac{\partial \log p_1}{\partial \alpha}.$$

Again assuming (6), we have

$$\log\frac{p_0}{p_1} = (1+\alpha)\,\frac{n_1}{n_2}$$
$$= (1+\alpha)\,\frac{w_2}{w_1}\,\frac{1}{h}$$
$$= w_2 k\,\frac{1-\alpha^2}{\alpha^2}$$
$$\frac{\partial \log p_1}{\partial \alpha} = \frac{2w_2 k}{\alpha^3};$$

wherefore (16) becomes

(16*a*) $$\frac{\partial\,\partial \Delta F}{\partial \alpha\,\partial M_2} = \frac{2k.w_2 r_2.\theta}{\alpha^3}.$$

Substituting (15) and (16*a*) in (14),

$$\frac{\partial A}{\partial \alpha} = 2\,\frac{q}{w_1}\,r\theta\,\frac{1}{(1-\alpha)\alpha}.$$

Integrating over the difference of the concentrations in the concentration cell,

$$A_I - A_{II} = \Big|\, 2\,\frac{q}{w_1}\,r\theta \log\frac{\alpha}{1-\alpha}\Big|_{\alpha_{II}}^{\alpha_I}$$

the same result (13*a*) as before.

The assumptions made

From the above work it is clear that Helmholtz's differential equation (1) involves the assumptions:

The salt is involatile ;
The cell functions under the pressure $p_0(\theta)$;
$\partial V/\partial M_2$ is independent of h, and negligible
in comparison with v_a;
The form of $v_a(p,\theta)$ is $r_2\theta/p$.

And it is clear that the further assumptions made in the integration, and thereby involved in the equivalent formulations (13), (13*a*), are:

$$\log \frac{p_0}{p_1} = (1+\alpha)\frac{n_1}{n_2}$$

$$k\,\frac{1-\alpha}{U} = \frac{\alpha^2}{U^2}$$

$V = M_2$. I. e. the volume of the solution in cm^3 is sensibly the same as the mass of the water in grams.

It will not be overlooked that the first of these further assumptions introduces the hypothesis that the heats of dilution of the solutions are negligibly small. The general equation (5) for the electromotive force of the concentration cell involves only the assumption of the involatility of the salt.

Integration assuming the dilution law of Rudolphi-van't Hoff

It is not without interest to determine the manner in which the foregoing result is modified when the assumption of Ostwald's dilution law is replaced by that of Rudolphi's equation as modified by van't Hoff,

$$K\left(\frac{1-\alpha}{U}\right)^2 = \left(\frac{\alpha}{U}\right)^3.$$

The formulation $U = w_1 h$ of equation (10) converts this to

$$h = \frac{1}{w_1 K}\,\frac{\alpha^3}{(1-\alpha)^2}; \tag{17}$$

wherefore the general relation

$$\frac{\partial}{\partial\alpha}\frac{\partial\Delta F}{\partial M_1}+h\frac{\partial}{\partial\alpha}\frac{\partial\Delta F}{\partial M_2}=0$$

becomes

$$\frac{\partial}{\partial\alpha}\frac{\partial\Delta F}{\partial M_1}+\frac{1}{w_1K}\frac{\alpha^3}{(1-\alpha)^2}\frac{\partial\Delta F}{\partial M_2}=0.$$

As before, equations (15), (16), we have

$$\frac{\partial}{\partial\alpha}\frac{\partial\Delta F}{\partial M_1}=-\frac{1}{q}\frac{\partial A}{\partial\alpha},\qquad \frac{\partial}{\partial\alpha}\frac{\partial\Delta F}{\partial M_2}=r_2\theta\frac{\partial\log p_1}{\partial\alpha};$$

wherefore

$$\frac{\partial A}{\partial\alpha}=\frac{q}{w_1}\frac{r_2\theta}{K}\frac{\alpha^3}{(1-\alpha)^2}\frac{\partial\log p_1}{\partial\alpha}. \tag{18}$$

Now, by (6), (9), (17),

$$\log\frac{p_0}{p_1}=w_2K\frac{(1+\alpha)(1-\alpha)^2}{\alpha^3}$$

$$\frac{\partial\log p_1}{\partial\alpha}=w_2K\frac{(3+\alpha)(1-\alpha)}{\alpha^4};$$

which converts (18) to

$$\frac{\partial A}{\partial\alpha}=\frac{q}{w_1}r\theta\frac{3+\alpha}{(1-\alpha)\alpha};$$

wherefore, integrating between α_{II}, α_I,

$$A_I-A_{II}=\frac{q}{w_1}r\theta\left(3\log\frac{\alpha}{1-\alpha}+\log\frac{1}{1-\alpha}\right)_{\alpha_{II}}^{\alpha_I}.$$

This is the formulation sought. It may be written

$$A_I-A_{II}=\frac{q}{w_1}r\theta\log\frac{\alpha^3}{(1-\alpha)^4}\Bigg|_{\alpha_{II}}^{\alpha_I} \tag{19}$$

$$=\frac{q}{w_1}r\theta\log\frac{\alpha_I^3}{\alpha_{II}^3}\frac{(1-\alpha_{II})^4}{(1-\alpha_I)^4}.$$

Cornell University,
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THE REACTION BETWEEN BROMIC, HYDRIODIC AND ARSENIOUS ACIDS, AND THE "INDUCTION" BY HYDROGEN BROMIDE OF THE REACTION BETWEEN BROMIC AND ARSENIOUS ACIDS

BY FRED C. BOWMAN

The reduction of bromates by bromides or iodides in acid solution has been studied by Ostwald,[1] Burchard,[2] Meyerhoffer,[3] Scott and Noyes,[4] Magnanini,[5] Judson and Walker,[6] Schilow,[7] and lastly by Mr. R. H. Clark.[8] The net result of these researches is that the rate is proportional to the first power of the concentration of the bromate, the first power of that of the bromide or iodide, and the second power of that of the acid.

The ordinary chemical equations for the reactions of the bromate with the bromide and iodide are:

$$\begin{aligned} KBrO_3 + 5KBr + 3H_2SO_4 &= 3K_2SO_4 + 3Br_2 + 3H_2O \\ KBrO_3 + 6KI + 3H_2SO_4 &= 3K_2SO_4 + 3I_2 + 3H_2O + KBr \end{aligned} \qquad (1)$$

or in the ionic notation:

$$\begin{aligned} BrO'_3 + 9Br' + 6H^\bullet &= Br' + 3Br'_3 + 3H_2O \\ BrO'_3 + 9I' + 6H^\bullet &= Br' + 3I'_3 + 3H_2O \end{aligned} \qquad (2)$$

Since these do not square with the kinetic hypothesis, which demands equations of the form

$$BrO'_3 + Br' + 2H^\bullet = \text{(products of the reaction)} \qquad (3)$$

resort has been had to the usual method of "explaining" discrepancies between theory and practice in kinetic measurements, by assuming the temporary existence of hypothetical

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[1] Zeit. phys. Chem., 2, 127 (1888).

[2] Ibid., 2, 796 (1888).

[3] Ibid., 2, 585 (1888).

[4] Ibid., 18, 128 (1895).

[5] Gazz. chim. Ital., 20, 390 (1890).

[6] Jour. Chem. Soc., 73, 410 (1898).

[7] Zeit. phys. Chem., 27, 512 (1898); 42, 641 (1903).

[8] Jour. Phys. Chem., 10, 679 (1906).

intermediate compounds, such as the HBrO and $HBrO_2$ of the following equation.

$$\begin{aligned} BrO'_3 + Br' + 2H^{\cdot} &= HBrO_2 + HBrO \\ BrO'_3 + I \ + 2H &= HBrO_2 + HIO \end{aligned} \qquad (4)$$

Independent evidence of the formation of these intermediate acids would, of course, be very welcome;[1] and even the confirmation by experiment of conclusions based on the assumption that they exist would be of value.

One such conclusion has been drawn by Luther,[2] who points out that compounds which *ex hypothesi* react quickly with certain reducing agents, may naturally be expected to react quickly with others; and suggests that new cases of chemical induction are apt to be found by a study of the reactions whose kinetic equations lead to the assumption of such hypothetical "primary" products.

The only induced reaction in which bromic and hydrobromic acids are known to take part, is that in which arsenious acid acts as acceptor; and, in accordance with the view just set forth, the induction is ascribed—both by Luther and by Schilow who discovered the reaction—to the oxidation of the arsenious acid by the hypothetical primary products of Equation 4.

It is not necessary, however, to have recourse to these hypothetical acids in order to account for the results of Schilow's measurements. The bromine liberated by the oxidation of the hydrogen bromide (Equation 1) acts instantaneously on arsenious acid, and all the experimental data are in full accord with the assumption that the "induced" oxidation of arsenious acid is due to this action alone.[3] There are thus two explanations of Schilow's measurements available. The first of them is in accordance with the explanation offered for the kinetics of the reaction between bromic and hydrobromic acids, and at first sight seems to afford it independent support; but the second accounts for all that is known of the induction

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[1] Ostwald: Lehrbuch II, (2) 243 (1902).

[2] Zeit. phys. Chem., 46, 817 (1903).

[3] Ibid., 42, 670 (1903).

without the assumption of any hypothetical mechanism whatever.

In order to throw more light on the matter, I have studied the oxidation of arsenious acid in solutions containing bromic and hydriodic acids. In this case, the final product—iodine—does not react instantaneously with the arsenious acid, but slowly, according to known laws; so that if any arsenious acid were oxidized by the hypothetical intermediate acids, or in any other way than by the iodine formed in the reaction, the fact could be established, and the amount ascertained. My work has been much facilitated by the circumstance that the reaction between bromic and hydriodic acid and that between arsenious acid and iodine have already been studied in this laboratory by Mr. Clark[1] and Mr. Roebuck[2] respectively. This has enabled me to plan my experiments so that very little arsenious acid was oxidized by the iodine; any action of the hypothetical oxyacids would therefore readily be detected.

The reaction was carried out in a thermostat at 0° to 0.2°; the burettes and pipettes were calibrated by myself, and the solutions of arsenious acid, potassium iodide, potassium bromate, iodine and sodium thiosulphate were made from pure chemicals and standardized in the usual way. The iodide in the iodine solution was allowed for in calculating the concentration of the iodion.

In the tables and in the calculations, the amount of each reagent is expressed in cubic centimeters of hundredth-normal solution. Thus the number after $KBrO_3$ multiplied by $^1/_6 \times 167.1 \times 10^{-5}$ gives the number of grams of potassium bromate; the number after KI multiplied by $^3/_2 \times 166 \times 10^{-5}$ gives the number of grams of potassium iodide; the number after KBr multiplied by $^3/_2 \times 119.1 \times 10^{-5}$ gives the number of grams of potassium bromide; the number after H_2SO_4, multiplied by $^1/_2 \times 98.08 \times 10^{-5}$ gives the number of grams of sulphuric acid; the number after I multi-

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[1] Jour. Phys. Chem., 10, 679 (1906).

[2] Ibid., 6, 365 (1902); 9, 727 (1905).

plied by 126.85 × 10^{-5} gives the number of grams of free iodine, and that after As_2O_3 multiplied by $^1/_4$ × 198 × 10^{-5} the number of grams of arsenious acid. After *Vol.* is given the volume in liters in which these amounts of the reagents were dissolved.

The duration of the reaction, in minutes, is stated under t; the number of grams of bromate reduced may be found by multiplying the number under x by $^1/_6$ × 167.1 × 10^{-5}; and the number of grams of arsenious acid oxidized to arsenic acid, by multiplying the number under y by $^1/_4$ × 198 × 10^{-5}. In solutions containing both bromate and arsenious acid, therefore, the quantity of free iodine in the solution is represented by $x - y$.

The measurements fall naturally into three series.

Series I. The Effect of Arsenious Acid on the Reaction between Bromic and Hydriodic Acids

First of all it was necessary to know whether addition of arsenious acid affects the rate at which bromic acid is reduced by hydrogen iodide. For this purpose parallel sets of measurements were made, one in the presence of arsenious acid and one in its absence, all the other reagents being of the same concentrations in both.

The solutions of potassium bromate, potassium iodide and sulphuric acid were mixed in a large stoppered bottle, and at intervals samples were pipetted out, rendered alkaline with ammonium bicarbonate, and titrated with centinormal arsenious acid. The measurements are recorded in Tables I, II and III.

From each pair of numbers (x, t) so obtained, the value of the constant K_1 of the equation[1]

$$dx/dt = K_1(KBrO_3 - x)(KI - x)(H_2SO_4 - x)^2(Vol)^{-3} \qquad (5)$$

was calculated as follows. A curve was plotted on section paper with x and the right hand member of Equation 5 as coördinates, and the areas under the curve were measured. For each value of x the corresponding value of

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[1] Clark: loc. cit.

$$K_1(\mathrm{Vol})^{-3}\int dt/dx.dx = K_1 t(\mathrm{Vol})^{-3} \qquad (6)$$

was thus obtained; and from this the value of K_1 itself, by division by $(Vol)^{-3}\ t$. This method, which was suggested by Prof. Lash Miller, is perhaps the easiest way to determine K from a series of values of x and t, when the form of the differential equation is known.

Table I

$KBrO_3$, 199; KI, 1984; H_2SO_4, 2000; Vol., 0.600
(75 cc titrated)

t	x in 75 cc	$K_1 \times 10^{15}$
6	4.68	974
19	11.76	989
30	15.50	997
40	17.92	997
50	19.58	945
60	20.73	969
70	21.77	980
80	22.48	982
90	22.82	930
100	23.68	1041
	Average	980

Table II

$KBrO_3$, 199; KI, 1984; H_2SO_4, 4000; Vol., 0.600
(75 cc titrated)

t	x in 75 cc	$K_1 \times 10^{15}$
3	7.40	805
6	12.37	825
9	15.73	807
12	18.18	809
15	19.87	809
18	21.25	823
21	22.15	798
	Average	810

Table III

$KBrO_3$, 199; KI, 3968; H_2SO_4, 2000; Vol., 0.600
(75 cc titrated)

t	x in 75 cc	$K_1 \times 10^{15}$
5	6.95	928
10	11.52	905
15	14.84	903
20	17.28	901
25	19.17	909
30	20.42	909
	Average	909

Comparison of Tables I, II and III with Tables VIII, IX and X

t	x		$K_1 \times 10^{15}$		t	x		$K_1 \times 10^{15}$	
	I	VIII	I	VIII		II	IX	II	IX
6	4.68	4.82	974	—	3	7.40	7.45	805	828
12	(8.41)	8.34	—	—	6	12.37	12.07	825	797
18	(11.25)	11.13	—	—	9	15.73	15.44	807	789
24	(13.62)	13.59	—	—	12	18.18	17.99	809	793
30	15.50	15.31	997	977	15	19.87	19.81	809	796
36	(16.98)	16.88	—	—	18	21.25	21.05	823	783
42	18.28	18.38	—	—	21	22.15	22.63	798	—
		Average	980	984			Average	810	798

t	x		$K_1 \times 10^{15}$	
	III	X	III	X
5	6.95	7.08	928	—
10	11.52	11.75	905	935
15	14.84	14.90	903	909
20	17.28	17.43	901	917
25	19.17	19.15	909	901
30	20 42	20.55	909	911
		Average	909	911

When arsenious acid is present (Tables VIII, IX and X) the kinetic equation must be modified somewhat, because of the regeneration of acid and iodide by the action of iodine on arsenious acid:

$$HAsO_3 + I_2 + H_2O \rightleftharpoons HAsO_4 + 2HI \qquad (7)$$

The amount of iodide present at any moment is thus no longer represented by $KI—x$, as in Equation 5, but by $KI—x—y$, where y is the number of units of arsenious acid oxidized; similarly the acid present at any moment is given by $H_2SO_4—x—y$. Thus the kinetic equation becomes:

$$dx/dt = K_1(KBrO_3 - x)(KI - x - y)(H_2SO_4 - x - y)^2(Vol)^{-3} \qquad (8)$$

As in my experiments both KI and H_2SO_4 were large in comparison with x and y, the terms $KI—x—y$ and H_2SO_4—

$\overline{x-y}$ were nearly constant, and it was found convenient to replace them by their "effective averages" determined as follows at the suggestion of Mr. R. E. DeLury.[1] A curve was plotted with $x-y$ as ordinates and t as abscissae, using the values found by experiment. The area under this curve between $t = 0$ and $t = t'$, divided by t', is the "effective average" of $x-y$ from the beginning of the experiment to the moment t_1. This function may be written $X-Y$, and is defined by the relation:

$$X-Y = \frac{1}{t'}\int_0^{t'} \overline{x-y}\, dt \tag{9}$$

Introducing these "effective averages" into Equation 8, and integrating:

$$K_1 t'(KI-\overline{X-Y})(H_2SO_4-\overline{X-Y})^2\ (Vol)^{-3} = log\ nat\ \frac{KBrO_3}{KBrO_3-x} \tag{10}$$

The values of K_1 entered in Tables VIII, IX and X were calculated from x and t by means of this equation.

The values of K_1 so obtained from experiments in which arsenious acid was present and from others in which it was not, are collected after Table III; the comparison shows clearly that the rate at which bromic acid is reduced by hydriodic acid is not affected by the presence of arsenious acid, and that the slight apparent acceleration is due to the formation of acid and iodide which accompanied the oxidation of the arsenious acid.

Series II. The Oxidation of Arsenious Acid by Iodine and the Effect of Hydrobromic Acid on the Rate of this Reaction

The rate of the reaction between arsenious acid and iodine has been thoroughly studied by Roebuck; but as my experiments were made with concentrations outside the range of Roebuck's measurements, I thought it better to undertake a new series of my own, rather than rely on an extrapolation from his tables. New measurements were also needed to

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[1] See Jour. Phys. Chem., 10, 423 (1906).

ascertain what effect, if any, the presence of bromides might exert on the rate.

The solutions were mixed in a stoppered bottle, and at intervals a sample was pipetted out and analyzed. The method of analysis was that used by Roebuck, *viz.*, rapid titration with centi-normal thiosulphate without dilution or neutralization.

TABLE IV

As_2O_3, 200; KI, 2197; I, 198; H_2SO_4, 2000; Vol., 0.600
(50 cc titrated)

t	$I - y$ in 50 cc	$K_2 \times 10^{-4}$
2	15.68	169
7	14.88	154
12	14.08	159
17	13.44	155
22	13.03	140
27	12.67	133
32	12.27	130
37	11.56	142
42	11.06	145
52	10.41	143
72	9.27	140

TABLE V

As_2O_3, 200; KI, 2250; I, 247.3; H_2SO_4, 4002; Vol., 0.600
(50 cc titrated)

t	$I - y$ in 50 cc	$K_2 \times 10^{-4}$
16	18.75	177
30	17.51	166
45	16.65	159
60	15.70	156
75	14.95	156
90	14.25	152
105	13.68	151
120	13.15	150
135	12.64	150
150	12.17	150

TABLE VI

As_2O_3, 200; KI, 3968; I, 197; H_2SO_4, 2000; Vol., 0.600
(75 cc titrated)

t	$I - y$ in 75 cc	$K_2 \times 10^{-4}$
30	22.58	132
60	20.92	135
90	19.34	135
120	18.11	133
150	17.03	133
180	15.96	136
	Average	134

Table IV contains measurements with solutions of approximately the same concentrations as those of Table VIII in which bromic acid was used. Similarly Table V is parallel to Table IX and Table VI to Table X. The experiments of Table VI*A* were undertaken to find whether the decrease in the constant[1] K_2 of the kinetic equation[2]

$$dy/dt = \frac{K_2(I-y)(As_2O_3-y)(Vol)^2}{(KI-y)^2(H_2SO_4-y)} \qquad (11)$$

was due to the fall in the concentration of the iodine or to that of the arsenious acid.

TABLE VI*A*
As_2O_3, 100; I, 197; KI, 1984;
H_2SO_4, 4000; Vol., 0.600
(75 cc titrated)

t	I − y in 75 cc	$K_2 \times 10^{-4}$
20	23.31	—
40	22.03	—
60	20.92	155
80	20.17	142
100	19.29	145
120	18.61	143
140	18.11	143

TABLE VII
As_2O_3, 200; I, 247.5; KI, 2250;
H_2SO_4, 4002; KBr, 200;
Vol., 0.600
(50 cc titrated)

t	I − y in 50 cc	$K_2 \times 10^{-4}$
45	16.92	139
60	16.08	139
75	15.25	140
90	14.52	141
105	13.92	138
120	13.52	133
135	13.00	135
150	12.52	136

Table VII contains the results of measurements made in solutions containing six times as much bromide as was formed from the bromate in any of my experiments. The rate is noticeably (10-15 percent) less than in the experiments of Table V in which—apart from the bromide—the concentrations were the same; but it is evident that the retardation due to the bromide formed during an experiment may be neglected.

Further measurements of the rate of oxidation of arsenious acid by iodine are furnished by the latter part of Table IX; for although bromic acid was present initially, it was practically all reduced in the first half hour, and from then on the only

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[1] K_2 was computed in the same manner as K_1 of Tables I and II, by plotting a curve with y as abscissae and $K_2(Vol)^2dt/dy$ as ordinates.

[2] Roebuck: loc. cit.

reaction taking place in the solution was the oxidation of arsenious acid by iodine. The constant K_2 in Table IX was thus determined for the very solution in which the bromic acid had been reduced, $t = 70$ was taken as the initial point.

Series III. The Rate of the Reaction between Bromic, Hydriodic, and Arsenious Acids

For these experiments the reagents were mixed two by two—the arsenious acid and sulphuric acid solutions in one bottle and the potassium bromate and potassium iodide solutions in another. Both were kept in the thermostat, and for each experiment a certain amount of each was pipetted into a small stoppered bottle; the mixture was allowed to react for a measured time, and was then analyzed.

Before determining the iodine and arsenious acid in the product of the reaction, it is, of course, necessary to stop the reaction, or at least to slow it up so much that no appreciable change in the composition of the solution takes place during the progress of the analysis. In the present instance this is a difficult matter. Neutralization of the acid, or dilution of the solution, which stop or retard the liberation of iodine, accelerate its reaction with the arsenious acid; and it was only after many trials and calculations, based on the researches of Roebuck and of Clark, that the following method was perfected.

The mixture to be analyzed (75 cc in volume) was thrown into 450 cc of ice-cold water containing enough thiosulphate to remove all the iodine but one cubic centimeter (centinormal) or less. The remaining iodine was titrated in two minutes with centi-normal thiosulphate and starch by daylight or by the light of an Auer mantle, but not by gaslight. Enough ammonium bicarbonate was added to make the solution alkaline, and finally the arsenious acid was estimated with iodine.

Under these conditions, and when the diluted mixture contains before titration 1 cc $n/100$ iodine, 25 cc $n/100$ arsenious acid, 15 cc $n/1$ sulphuric acid and 4 cc of F/1 potassium iodide, a correction of about 0.03 cc $n/100$ must be added to the thiosulphate reading and to the iodine reading in the arsenite determination. This correction must be doubled if only half as much acid be present, and it varies roughly as the square of the excess of iodine not removed by the thiosulphate added to the water of dilution. If by mischance more thiosulphate has been added in dilution than is equivalent to the free iodine, this correction must not be applied.

If much bromic acid remains unreduced, iodine is liberated by it during the first titration. With the above mentioned concentrations of the various reagents, 25 cc *n*/100 bromic acid frees 0.02 cc *n*/100 iodine.

The error of the determinations is greater than the corrections, owing to the difficulty of making sure of the end-point with thiosulphate at such great dilution. This is the weakest point in the method of analysis adopted.

The results of three sets of experiments, with different concentrations of acid and iodide, are given in Tables VIII IX and X.

TABLE VIII

$KBrO_3$, 199; KI, 1984; H_2SO_4, 2000; As_2O_3, 200; Vol., 0.600
(75 cc titrated)

t	$x-y$ in 75 cc	As_2O_3-y in 75 cc	x	x calc.[1]	y	y calc.[2]	$K_1 \times 10^{15}$
6	4.60	24.78	4.82	4.63	0.22	0.23	1020
12	7.56	24.22	8.34	8.30	0.78	0.79	985
18	9.57	23.44	11.13	11.21	1.56	1.57	972
24	11.24	22.65	13.59	13.52	2.35	2.52	985
30	12.36	22.05	15.31	15.37	2.95	3.37	977
36	12.76	20.88	16.88	16.91	4.12	4.25	968
42	13.05	19.67	18.38	18.31	5.33	5.31	984

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[1] Calculated by use of $K_1 = 980 \times 10^{-15}$ from Table I.

[2] K_2 varies with the concentration of the arsenious acid. Hence for the calculation of each number of the column, a value of K_2 corresponding to the same concentration of arsenious acid was chosen from Table IV, viz: 158 for the first three, 150 for $t = 30$, and 145 for $t = 36$ and $t = 42$.

Table IX

$KBrO_3$, 199; KI, 1980; H_2SO_4, 4000; As_2O_3, 200; Vol., 0.600
(75 cc titrated)

t	$x-y$ in 75 cc	As_2O_3-y in 75 cc	x	x calc.[1]	y	y calc.[2]	$K_1 \times 10^{15}$	$K_2 \times 10^{-4}$
3	7.28	24.83	7.45	7.43	0.17	0.10	828	—
6	11.74	24.67	12.07	12.22	0.33	0.32	797	—
9	14.92	24.48	15.44	15.68	0.52	0.68	789	—
12	17.00	24.01	17.99	18.15	0.99	1.06	793	—
15	18.38	23.57	19.81	19.93	1.43	1.50	796	—
18	19.21	23.16	21.05	21.06	1.84	1.98	783	—
21	20.20	22.57	22.63	22.18	2.43	2.45	—	—
24	20.40	22.04	23.36	22.88	2.96	2.95	—	—
70	16.52	16.77	—	—	8.23	—	—	—
80	15.77	15.90	—	—	9.10	—	—	—
90	15.25	15.27	—	—	9.73	—	—	137[3]
100	14.73	14.73	—	—	10.27	—	—	129
110	13.79	14.04	—	—	10.96	—	—	135

Table X

$KBrO_3$, 199; KI, 3968; H_2SO_4, 2000; As_2O_3, 200; Vol., 0.600
(75 cc titrated)

t	$x-y$ in 75 cc	As_2O_3-y in 75 cc	x	x calc.[4]	y	y calc.[5]	$K_1 \times 10^{15}$
5	7.04	24.96	7.08	6.84	0.04	0.06	—
10	11.58	24.83	11.75	11.52	0.17	0.22	935
15	14.52	24.62	14.90	14.88	0.38	0.43	909
20	16.68	24.25	17.43	17.33	0.75	0.70	917
25	18.13	23.98	19.15	19.24	1.02	0.99	901
30	19.13	23.58	20.55	20.52	1.42	1.31	911
35	19.80	23.28	21.52	21.53	1.72	1.63	906
40	20.09	22.96	22.13	22.30	2.04	2.01	—
						Average	911

The constant K_1, referring to the rate of reduction of the bromic acid (Equation 8), was calculated as described on page 298.

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[1] $K_1 = 810 \times 10^{-15}$ (Table II).

[2] Values of K_2 from Table V.

[3] K_2 calculated from $t = 70$ as initial point; see page 300.

[4] $K_1 = 909 \times 10^{-15}$, for Table III.

[5] $K_2 = 134 \times 10^4$, from Table VI.

The rate of oxidation of the arsenious acid by the iodine liberated during the reaction may be expressed by the equation

$$dy/dt = \frac{K_2(x-y)(As_2O_3-y)(Vol)^2}{(KI-x-y)^2(H_2SO_4-x-y)} \qquad (12)$$

and values of K_2 might be computed by substituting for x and y their "effective averages" and integrating as explained on page 298; the terms involving x and y being almost constant, there is no *petitio principii* in this procedure. It was thought better, however, to calculate y for each measurement of the table, using Equation 12 and the values of K_2 from Tables IV, V and VI. Similarly, the values of "*x calc*" are obtained by the use of K_1 of Tables I, II and III.

The calculated and observed values of x and of y are entered in adjoining columns in Tables VIII to X; the differences are sometimes positive and sometimes negative but in no case exceed the error of analysis; that is, the arsenious acid actually oxidized is just what was acted on by the iodine liberated during the reaction, none has been oxidized by the hypothetical primary products of the reduction of the bromic acid. If these intermediate products had been quantitatively reduced by the arsenious acid (as has been assumed in the case of the analogous reaction with hydrogen bromide) the arsenious acid oxidized would have been from three times to seventy times as much as that actually observed, while the iodine liberated would have fallen to zero.

Conclusions

In solutions containing bromic hydriodic and arsenious acids, no arsenic is oxidized except by the action of the iodine liberated during the reaction; and the rate of reduction of the bromic acid, and the rate of liberation of iodine are unaffected by the presence of arsenious acid, except in so far as the oxidation of the latter by the iodine affects the concentrations of acid and iodide in the solution.

The action of hydrogen iodide on bromic acid, therefore, does not "induce" the oxidation of arsenious acid; and there is no ground for regarding the oxidation of arsenious acid in mixtures of bromic and hydrobromic acids as a case of chemical induction.

My thanks are due to Prof. W. Lash Miller at whose suggestion this investigation was undertaken and under whose direction it was carried out in the winter of 1905-6.

The University of Toronto,
February, 1907

THE PHYSICAL PROPERTIES OF LIQUID AND SOLID ACETYLENE

BY D. MCINTOSH

Since the development of a successful method of manufacturing calcium carbide in 1892, acetylene has been the subject of a great many investigations, most of which have dealt with the detonation of the gas under pressure, either alone or dissolved in liquids. But this interesting substance in its solid and liquid states has received little attention, and the physical constants obtained by observers such as Ansdell, Pictet, Cailletet and others, show so little uniformity that an examination of some of its more important properties which I have made, can hardly be valueless, particularly as liquid and solid acetylene have been prepared in large quantities and transported many miles for use as an illuminant. These measurements include:

(*a*) the vapor pressure curve of solid and liquid;
(*b*) the heats of vaporization;
(*c*) the specific heat of the liquid;
(*d*) the densities and atomic volume;
(*e*) the critical constants;

all of which are described in the following pages. At the same time some observations of solubilities and conductivities in liquid acetylene are given.

Preparation

The acetylene was prepared from calcium carbide by the action of water. Impurities were removed by washing with sodium hydrate and chromic acid, and drying was effected by concentrated sulphuric acid and phosphoric anhydride; it was then solidified in the apparatus shown in Fig. 1.

This consisted of a silvered vacuum vessel A, containing carbonic acid and ether. The vessel was closed by a rubber stopper, through which passed the condensation tube, and a tube connected with an[1] exhaust pump. Moisture was

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[1] With a good water-pump a temperature of —100° can be obtained.

prevented from entering the condensation chamber by connecting B with a tube kept underneath the surface of mercury. The acetylene was usually redistilled through B and condensed in a similar piece of apparatus, but this is of questionable advantage, as the vapor pressure curve of the redistilled substance was identical, within the limits of experimental error, with that of acetylene prepared by one condensation.

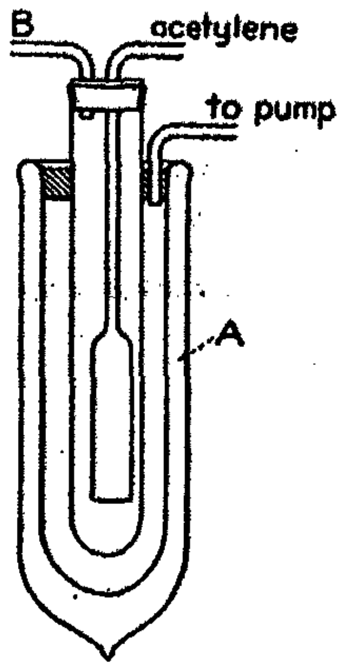

Fig. 1

The Constant Temperature Bath and the Vapor Pressure Curve

The vapor pressure of a body at low temperatures is often obtained by placing it in a tube surrounded by a liquid such as ether, cooled to a low temperature, and then noting the pressures as the temperature rises. Such measurements are usually affected by an error, as the temperature of the substance whose pressure is to be determined lags behind the outside temperature, and the values found are lower than the correct ones. This is particularly true of acetylene. As a solid, it conducts heat but slowly; and as a liquid, it easily superheats; so that one can keep liquid acetylene at —80° in an open vessel for some time, although its vapor pressure is much above an atmosphere. As it was necessary to maintain the substance at a constant temperature for some time the bath shown in Fig. 2 was used.

This bath consisted of a Dewar tube closed by a rubber stopper perforated with several holes, through which passed the capillary tube of a constant-volume hydrogen thermometer[1] and a tube for the acetylene attached to a mercury manometer and to a Toepler pump. One arm of the T tube is connected to a good exhaust pump, the other to a brass tap. A tube constricted at the upper end went to the bottom of the Dewar vessel, and through this bubbles of air continually passed, stirring the bath. When necessary, the tubes are protected by phosphorus pentoxide, and screw clamps are provided to regulate the exhaust. As the temperature falls the mercury rises in the thermometer until it touches the platinum point. Contact is thus made through a relay, which in its turn opens the brass stop-cock by means of a magnet. When the mercury drops below the platinum point the valve closes and exhaustion begins again. This arrange-

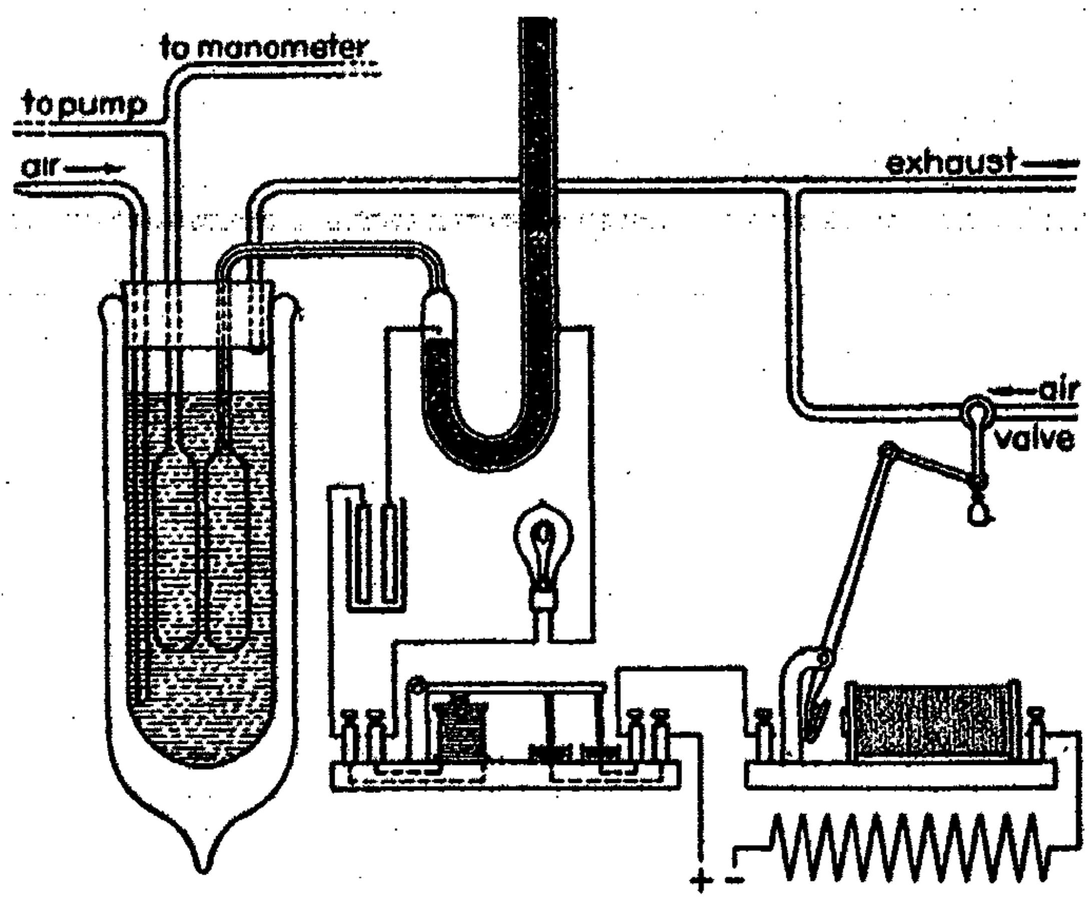

Fig. 2

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[1] Travers, Senter and Jaquerod: Phil. Trans. (A) 200, 105, (1900).

ment kept the temperature constant to between 0.3° and 0.4° as indicated by the hydrogen thermometer. The acetylene manometer never varied more than 10 mm. and this from the pressure curve represents only 0.15°. Temperatures higher than —78° were maintained by adding small quantities of cold ether to the bath.

The pressure below one atmosphere was measured by a closed mercury manometer; between one and two atmospheres by an open manometer; and for higher pressures a spring manometer, such as is used for critical pressure determinations, was available. Above two atmospheres the numbers can only be looked on as approximately correct.

The results are given in Table I, and the vapor pressure-temperature curves are shown in Fig. 3.

TABLE I

Temperature	Pressure (millimeters)	Temperature	Pressure (atmospheres)
—95.3	304	5.5	30.3
—92.5	383	—	—
—89.5	489	10.0	32.7
—86.9	592	—	—
—86.1	627	13.0	36.1
—84.3	726	—	—
—83.3	782	15.5	37.4
—82.1	863	20.0	40.8
—81.2	947	20.5	42.5
—78.4	1078	—	—
—77.6	1138	24.6	46.3
—75.3	1294	31.8	54.8
—74.0	1377	36.5	61.6
—72.2	1493	—	—

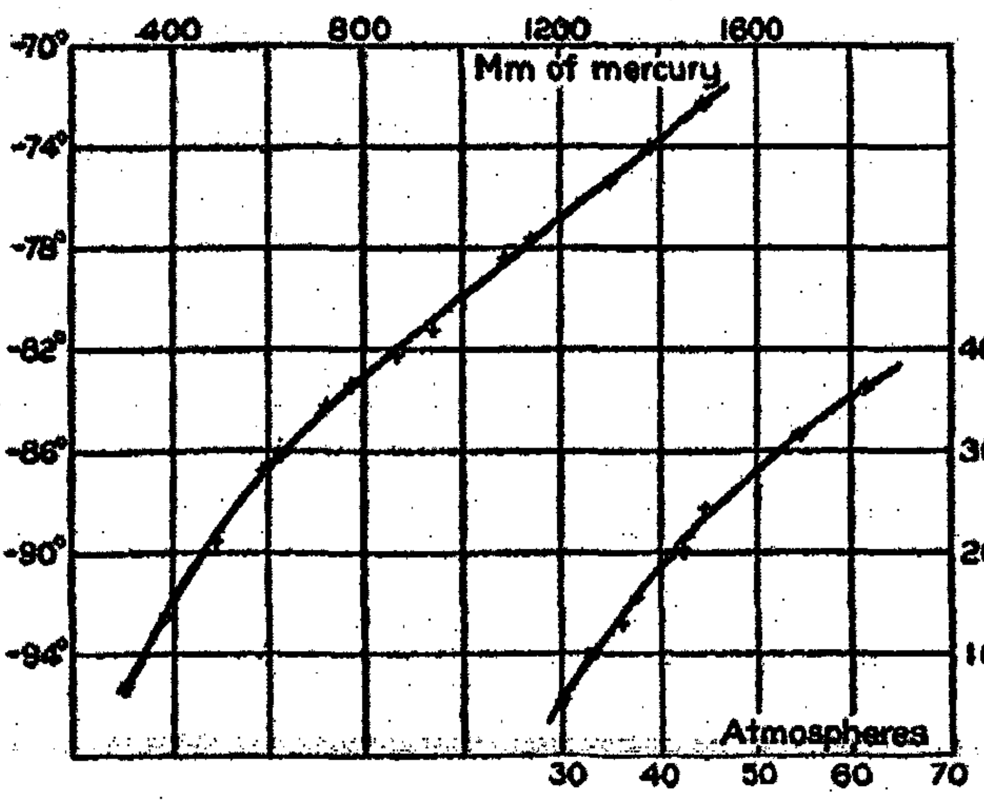

Fig. 3

In Table II the melting and subliming points of acetylene are given, the former from direct observation, the latter from the curve. The numbers observed by others are also recorded.

TABLE II

	Villard[1]	Willson and Suckert[2]	Ladenburg and Krügel[3]	Hunter[4]
M. P. —81.5 (895 mm.)	—81 (950 mm.)	—	—	—
S. P. —83.6 (760 mm.)	—85.	—82.2	—82.4	—74

Solid acetylene under atmospheric pressure evaporates without melting[5]. It may be liquefied by its own pressure

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[1] Comptes rendus, 120, 1262 (1895).

[2] Jour. Franklin Institute, 139, 327.

[3] Ber. chem. Ges., Berlin, 2, 1818 (1900).

[4] This Journal, 10, 330 (1906).

For pressures at higher temperatures in addition to above see Cailletet, Comptes rendus, 85, 85 (1877). Ansdell, Proc. Roy. Soc., 29, 209 (1879). Pictet, L'Acetylene Géuevè, 66 (1896). Lewis, Acetylene, p. 63.

[5] Crookes: Chem. News, 92, 148 (1905). "Carbon and arsenic are the only two elements that have melting-points above the boiling-points; and among compounds, carbonic acid and fluoride of silicium are the only other bodies with similar properties." Acetylene should be added to these.

in a test-tube closed by the finger. On opening the tube the acetylene at once solidifies, and this can be repeated many times with a small quantity of the liquid. This pretty experiment was shown me by Mr. E. LeSueur, of Ottawa, who has prepared solid acetylene in large amounts and has made a very complete study of its explosive qualities at low temperatures, covering the work lately done by Caro.[1]

Heats of Vaporization

Clausius has shown that the heat of vaporization can be calculated by the equation

$$\frac{1}{p}\frac{dp}{dt} = \frac{W}{RT^2},$$

where $\frac{dp}{dt}$ is the change of vapor pressure with temperature, p the pressure, T the absolute temperature, R the gas constant and W the latent heat of evaporation of 1 gram-molecule of the substance.

This value from the vapor pressure curve is:

For liquid acetylene at 950 mm. 21.3×10^{10} ergs
For solid acetylene at 760 mm. 23.0×10^{10} ergs.

These heats were directly determined in the apparatus shown in Fig. 4.

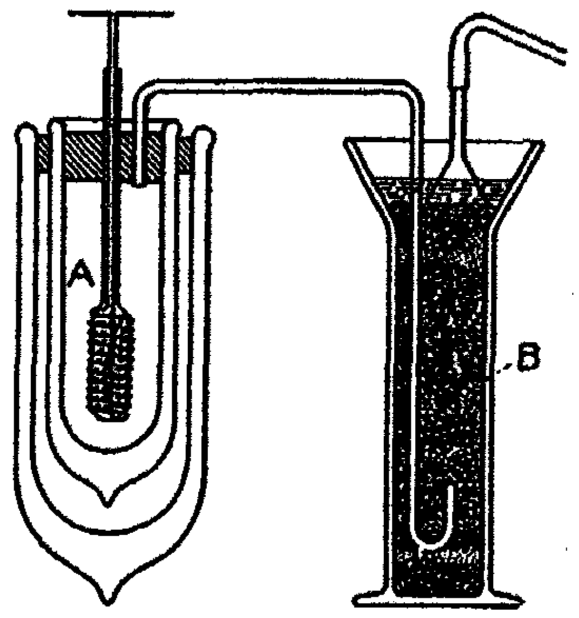

Fig. 4

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[1] Science Abstracts, 9A, 523 (1906).

The acetylene was placed in a small vacuum tube, A, closed by a rubber stopper through which passed a delivery tube, and the leads from a small platinum spiral used as a heating coil. The calorimeter was surrounded by solid carbon dioxide. The energy supplied was measured by calibrated Weston instruments. The delivery tube could be dipped into mercury, B, and thus a pressure sufficient to liquefy the gas obtained. The rate of evaporation due to external heat was measured before and after each experiment, and the gas was collected over water saturated with acetylene. The result for liquid, 21.4 and 20.6; mean 21.0×10^{10} ergs agrees with the calculated number.

The values for the heat of sublimation at atmospheric pressure were conflicting. With a small heating coil these were: 30.4, 31.0, 32.1, 31.7×10^{10} ergs; and with a larger coil: 35.7, 35.6, 35.7, 35.8×10^{10}. Neither set agreed even approximately with the calculated result, and this pointed to an error in the method. Apparently the heat from the coil was only partly used in vaporizing the solid. The heating spiral was then placed in a saturated solution of acetylene in toluene, and covered with the solid to the height of an inch. This reduced the heat of sublimation to 20.4, 21.8, 22.8, 21.1; mean 21.5×10^{10} ergs, a result agreeing much better with the theoretical.

The Latent Heat of Fusion

A measured amount of acetylene in a small Dewar vessel, fitted with a delivery tube closed by a stop-cock, was kept at a temperature just above its freezing-point in the constant temperature bath previously described. When the stop-cock was opened part of the liquid evaporated very quickly, leaving only solid in the tube. From the heat of evaporation at that temperature, and the amount of liquid evaporated, the heat of fusion was calculated, a small correction being made for "natural" evaporation. The results for a gram-molecule were: 4.2, 3.4, 4.2, 3.4, 4.0; mean 3.8×10^{10} ergs, so that we may write

$C_2H_2 - [C_2H_2] = 3.8J.$[1]

The Specific Heat of the Liquid

The calorimeter was a small vacuum tube containing a heating coil, and was closed by a rubber stopper through which passed a tube connected to a mercury manometer. A known volume of acetylene was placed in the calorimeter which was surrounded with solid carbon dioxide. The acetylene soon liquefied, and when at a steady temperature the pressure (and therefore, the temperature) was noted. From 50 to 100 volt-coulombs were used in heating the liquid and in evaporating the small volume that passed into the manometer (which could be corrected for) and the maximum pressure was recorded. Between —78.5 and —73 the values found per gram of acetylene were: 4.33, 4.40, 4.58, 4.38; mean 4.4×10^7 ergs. The specific heat is then a little higher than that of water.

The Densities of the Solid and Liquid

Acetylene was introduced into a tube consisting of a bulb and a graduated capillary tube, frozen in liquid air, exhausted and sealed. There was naturally no deposition of carbon such as Ansdell[2] experienced. The volume of liquid at a known temperature was noted, and a deep file mark was made on the tube, which was then brought to room temperature and weighed. The tube was cooled, broken, again weighed and calibrated, and from the data thus obtained the density was calculated. The change of volume with temperature was determined in a bulb with capillary shown in Fig. 5, kept at various temperatures in the constant temperature bath. The volume at —78.4 was taken as the standard since the density at this temperature was determined directly. The densities above —60° C can not be looked on as very accurate, since a large correction for the volume of gas over the liquid must be applied.

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[1] A correction for the expansion of the gas ought to be applied, but the results are very uncertain. The heat of fusion should approximate the difference between the heats of evaporation of liquid and solid.

[2] loc. cit.

The direct determinations were: At —78.4°, 0.6105 and 0.6101; at —15°, 0.517; at 14.7, 0.443; at 14.8, 0.440. The variation of density with temperature between —80° and —60° is given by the equation, $D_t = 0.613 - (80 + t)0.00234$. The complete results are given in Table III. There T is the temperature on the centigrade scale, D the density actually found, and D_1 the value from the curve.

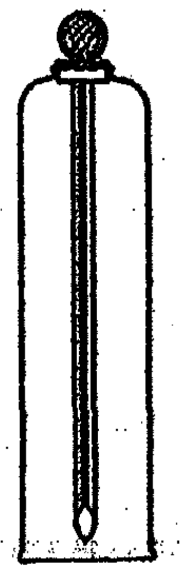

Fig. 5

TABLE III

T	D	D_1
—80	—	0.613
—79	0.611	—
—77.5	—	0.608
—75.7	0.605	—
—75.0	—	0.602
—74.4	0.601	—
—72.5	0.595	0.596
—71.6	0.593	—
—70.0	—	0.590
—68.7	0.587	—
—67.5	0.584	0.584
—65.9	0.581	—
—65.0	—	0.578
—64.8	0.577	—
—62.5	—	0.572

The density of the solid was approximated by freezing the liquid acetylene in the bulb of the tube shown in Fig. 5. The stem was jacketed with ether kept at —78.4°, so that the solid froze under considerable pressure. Its density at —85° was from 1.19 to 1.21 times that of the liquid at —78.4°, or about 0.73.

The Constitution of Acetylene

At atmospheric pressure, acetylene, were it a liquid, would have the density 0.618, and its molecular volume would be 42.1. Taking Kopp's values for the atomic volumes of hydrogen and carbon as 5.5 and 11, we get 33 as the molecular volume of acetylene. Poor agreement between calculated and observed results for the unsaturated hydrocarbons was noticed long ago by Buff[1]; the saturated hydrocarbons[2] give uniformly good agreement.

Guldberg[3] has pointed out that such want of agreement usually occurs in bodies, the ratios of whose boiling-points to critical temperatures vary widely from 0.667; and if the density of acetylene be chosen at the temperature that gives this ratio, the value of the molecular volume is 45.1—a result less satisfactory than before.

Now, in the case of oxygen, we have two values for the atomic volume: 7.8 for the hydroxyl and 12.2 for the carbonyl oxygen. The question then arises: Can we have two forms of carbon with different atomic volumes?

Nef[4] has shown that various bodies such as C_2I_2, which might be looked upon as substitution products of $H-C\equiv C-H$, are really acetylidene compounds. Now acetylene may have the acetylidene structure, and if so the divalent carbon has an atomic volume between 20 and 23.

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[1] Ann. der Chem., Supplement 4, 129 (1865).

[2] Ostwald: Lehrbuch I., 362, 376.

[3] Zeit. phys. Chem., 5, 374 (1890).

[4] Ann. der Chem., 270, 267 (1892); 280, 291 (1893); 287, 265 (1895); 298, 202 (1897); 309, 126 (1899). Jour. Am. Chem. Soc., 26, 1549 (1904). Lawrie: Am. Chem. Jour., 36, 487 (1906).

But there is a body, carbonic oxide, in which the carbon is undoubtedly divalent. Its density[1] at its boiling-point, 81.9 (abs.), is 0.797 and its molecular volume is, therefore, 35.1. The oxygen is carbonyl oxygen with an atomic volume of 12.2; or, taking the value from liquid[2] oxygen, 13.1. Deducting these values from the molecular volume of carbonic oxide we get 23 and 22 for the atomic volume of divalent carbon, numbers in good agreement with those obtained from acetylene. From the physical properties then we can write the acetylidene formula, $H_2C:C$ for acetylene. The addition compounds, to be spoken of later, are easier to understand if a carbon atom is looked on as divalent.

The Critical Constants

The critical temperature was measured in the ordinary way, the tube containing the liquid being immersed in a well stirred water-bath. The meniscus flattened and disappeared or reappeared between 36.4° and 36.5°. The thermometer used was compared with a standard, and also calibrated by means of hydrated sodium sulphate, whose melting-point, 32.38, is conveniently near the critical temperature of acetylene. Ansdell[2] gives 37.05°.

The opalescence in the neighborhood of the critical temperature, studied lately by Travers and Usher,[3] was always noticed but only with falling temperature. This appeared about 0.1° below the critical temperature, remained during a change of temperature of 0.3°, and then disappeared.

The critical pressure was found by means of a calibrated[4] manometer, using Altschul's method[5] to be 61.6 atmospheres. Ansdell's value is 68 atmospheres.

The determination of the density at the critical temperature called for patience and the method can hardly be recommended. A stout tube was two-thirds filled with acetylene,

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[1] Baly and Donnan: Trans. Chem. Soc., London, 82, 907 (1902).

[2] loc. cit.

[3] Proc. Roy. Soc., 78, 247 (1906).

[4] The manometer was calibrated only to 40 atmospheres.

[5] Zeit. phys. Chem., 11, 577 (1893).

sealed and the volume at the critical temperature noted. The lower part of the tube was then cooled in liquid air, and the volume was decreased by drawing off the upper end with a small blowpipe flame. The volume at the critical temperature was again found. After a number of trials several tubes were obtained which were almost exactly filled with acetylene at its critical temperature. The mean of these critical densities is 0.314, and the critical volume is 83 cc. From these values *a* and *b* in the Van der Waals' equation are 0.0880 and 0.00230, respectively.

Acetylene forms molecular combinations with ether, alcohol, acetone and perhaps with the halogen hydrides at low temperatures. These bodies crystallize and have sharp melting-points. They are probably analogous to the compound $C_2H_2,6H_2O$ described by Villard.[1] The great solubility of acetylene in organic liquids and the power to form compounds are doubtless cognate phenomena.

Liquid acetylene has, as would be expected, an exceedingly high electrical resistance; and this resistance is not markedly lessened by the addition of alcohol, ether, halogen acids, etc., etc.; it is, therefore, a non-conducting and non-ionizing solvent.

The measurements given in this paper are summarized in Table IV.

TABLE IV

M. P. (895 mm.)	—81.5
S. P.	—83.6
Heat of vaporization (liquid)	21.3*J*
" " " (solid)	23.0*J*
" " fusion	1.7*J* (?)
Specific heat	4.4*j*
Density (liquid —80°)	0.613
" (solid)	0.72
Molecular volume	43.1
Atomic volume of divalent carbon	20–23
Critical temperature	36.5°
" pressure	61.6
" volume	83 cc.
a	0.0880
b	0.00230

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[1] Ann. Chim. Phys., (7) II, 280 (1897).

McGill University, Montreal,
January, 1907

THE VAPOR PRESSURE OF AQUEOUS NITRATE SOLUTIONS

BY AZARIAH T. LINCOLN AND DAVID KLEIN

From both the practical and theoretical point of view the study of the vapor pressure of solutions is of great importance, and it would be very desirable to have much more information concerning the vapor pressures of aqueous as well as non-aqueous solutions. Most of the experimental data on vapor tensions were collected about twenty years ago, and fifteen years have elapsed since the comparatively recent work of Ramsay and Young was done. Many efforts have been made to devise new methods for the direct measurement of vapor pressures, but owing perhaps to the great experimental difficulties encountered in such determinations, rather indifferent success has been achieved, as will appear from the consideration of the various methods hitherto employed, which is given below.

Professor L. Kahlenberg[1], of the University of Wisconsin, devised a new, simple method for measuring vapor pressures based upon the principle of saturating a current of air with the vapor of the liquid whose vapor pressure is to be determined, by shaking the liquid thoroughly with the air as the latter passes over it. Some time ago the former of us visited his laboratory, and he exhibited his apparatus for measuring vapor pressures, explaining its various parts and the mode of operation. Owing to the large number of solutions that ought to be investigated, Professor Kahlenberg urged that we take up the measurements of aqueous solutions of nitrates by means of his method. This we have accordingly done. Although we have introduced some modifications, the apparatus employed by us, in its essential features, was originated by Professor Kahlenberg, and we desire to give him full credit for his work. Though he has not as yet presented in print, the

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[1] Science, N. S., 22, 74 (1905).

results of his own investigations with this apparatus, it should be definitely stated that we are publishing the present paper with his full knowledge and approval.

We have fully tested the efficiency of this method, which is like that of Regnault except that the very important feature of shaking the air and liquid together is introduced, and find that it yields very satisfactory results, which the experimental data presented herein show beyond question. We shall first discuss the principal methods hitherto used in the determination of vapor pressures, and then describe in detail the method as employed by us, and this will be followed by a discussion of the results obtained.

The "static" method consists in introducing the substance into a Torricellian vacuum and observing the depression of the mercury due to the vapor pressure of the substance (or solution). The barometric tube in which the vacuum is produced is kept at a constant temperature and is compared with another tube at the same temperature; thus the depression can be observed and the vapor pressure at that particular temperature can be obtained directly. Employing this method, numerous measurements have been made by Moser,[1] Magnus,[2] Wüllner,[3] Raoult[4] and very many others. Tammann[5] has shown that this method is liable to very great error, owing partly to small amounts of air remaining on the sides of the glass tube and particularly to the great influence on the vapor pressure of small quantities of impurities. Then, too, there is no assurance that the concentration of the solution is uniform, which in all vapor pressure work is one of the essential points, and further small drops of the solution adhering to the inner surface of the tube will introduce a very appreciable error.

The "indirect" method was perfected by Ramsay and

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[1] Wied. Ann., 14, 72 (1881).

[2] Pogg. Ann., 38, 93 (1836).

[3] Ibid., 103, 529 (1856); 110, 564 (1860).

[4] Zeit. phys. Chem., 2, 353 (1888).

[5] Wied. Ann., 32, 683 (1887).

Young[1] and consists in boiling the solution under various pressures and recording the corresponding temperatures. This method seems to yield very good results and Emden[2] has used it to measure the vapor pressure of many aqueous solutions of different concentrations. The originators of the method have used it extensively and their results are regarded as among the best measurements of vapor pressure; yet it is very singular that they did not determine the vapor pressure of water below 100° C, as above that temperature their values are accepted generally as standard determinations. It is desirable that we have a very accurate redetermination of the values for the vapor pressure of water below 100° C, for, as will appear in what follows, the accepted values are somewhat in question, and if the indirect method is applicable at these lower temperatures and it is a good method, it would be very desirable to have it applied to water. A few serious objections, however, have been raised against this method. It is pointed out that the liquid and vapor are both very liable to become superheated; then in the case of solutions vaporization of the solvent changes the concentration of the boiling solution and therefore the concentration is not known accurately; a very small change in the pressure causes a very marked change in the boiling-point; and what is perhaps one of the greatest objections to the method, is that it can be applied only to boiling solutions, which fact prevents its application to many solutions which are readily decomposed by heat.

Dieterici[3] has devised a differential method and many other workers have employed various methods, all of which as well as the methods mentioned above are too inflexible and not sufficiently variable so as to make them generally applicable and practicable.

Regnault[4] in 1845 employed a method for the determination of the vapor pressure of water which seems to yield

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[1] Phil. Trans., A 183, 107 (1892).
[2] Wied. Ann., 31, 145 (1887).
[3] Ibid., 62, 616 (1897).
[4] Ann. Chim. Phys., [3] 15, 129 (1845).

very good results and has but few of the objections that are raised against many of the other methods. The principle of the method is Dalton's law wherein the total pressure is the sum of the partial pressures of the components in the volume, *i. e.*, in a gaseous mixture the total pressure is equal to the sum of the partial pressures of the gaseous constituents. For example, in a given volume of air saturated with aqueous vapor the total pressure is the sum of the pressures of the air and of the aqueous vapor, from which the following relation is obtained:

$$\frac{\text{the total volume}}{\text{the volume of the aqueous vapor}} = \frac{\text{the total pressure}}{\text{the pressure of the aqueous vapor}}$$

Hence, in order to determine the vapor pressure at any given temperature it is necessary to know the total volume, the total pressure, and the amount (volume) of the aqueous vapor, and it follows that from these values the molecular weight can be calculated.

Regnault's method consisted in passing air through a flask containing a sponge moistened with water, and then through screens of moist silk, which were made by fastening the wetted silk to frames. From these the air passed through the absorption bulbs and then into an aspirator of known volume. There were a number of experimental difficulties which became manifest, but by overcoming these as much as possible Regnault found that there was a very satisfactory agreement between the results he obtained by this method and those obtained by the static method.

Tammann[1] in 1888 recalculated Regnault's results and showed that there was some considerable discrepancy between the experimental results of Regnault and the latter's calculated results. He likewise applied the method to the determination of the vapor pressure of hydrates and aqueous solutions, the values he obtained for the latter agreeing fairly well with the results obtained by other workers who used other methods. The method was modified by Ostwald and described by him[2]

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[1] Wied. Ann., 35, 322 (1888).

[2] Physical Chemical Measurements, p. 188, Walker's translation.

as follows: "Two Liebig's potash bulbs containing the solution, and one containing the water, are connected with each other. The last is weighed, and in its turn connected with a U-tube containing pumice soaked in sulphuric acid. A current of air is drawn through the apparatus. The air first saturates itself up to the vapor pressure of the solution, then takes up from the water the quantity of vapor necessary for complete saturation, all of which it finally gives up to the sulphuric acid. The loss of weight of the water vessel is to the increase of weight of the sulphuric acid as the difference between the vapor pressures of the solution and of pure water is to the vapor pressure of pure water." It was this modification of the method that Walker[1] used in the determination of molecular weights of substances in dilute solutions. Shaw[2] investigated this modification of the method of Regnault very carefully and in his experiments on hygrometric methods subjected it to a very thorough examination and indicated a number of sources of error. By the introduction of a nine-bulb Liebig's bulb, Will and Bredig[3] modified the method and applied it to the determination of the vapor pressures of alcoholic and ethereal solutions. Orndorff and Carrell[4] aimed to simplify the method by dispensing with the thermostat, so that it could be used as a general laboratory method for molecular weight determinations. They used alcohol as the solvent, and the solutes were urethane, diphenylamine, nitrobenzene, phenol, urea, etc. While the results for urethane and nitrobenzene might be said to be fair, in general the method did not give satisfactory results. Perman[5] has apparently used this method with a great deal of success in the determination of the vapor pressure of water. He employed in place of the usual Liebig's bulbs four egg-shaped wash-bottles of about 100 cc capacity, which were sealed to-

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[1] Zeit. phys. Chem., 2, 602 (1888).
[2] Phil. Trans. A., 179, 73 (1888).
[3] Ber. Chem. Ges., Berlin, 22, 1084 (1889).
[4] Jour. Phys. Chem., 1, 753 (1897).
[5] Proc. Roy. Soc., 72, 72 (1903).

gether and immersed in the thermostat. The last bottle was connected with a manometer and in turn with the absorption wash bottles and these with the aspirator which was placed in a large vessel of water. Air was drawn through the apparatus by siphoning the water from the aspirator into graduated flasks, and thus measuring the volume of air aspirated. The tube connecting the bottles in the thermostat and the absorption bottles was exposed to the air, and in order to prevent condensation was heated by small gas flames. Mr. Perman has succeeded in eliminating many of the objectional features of the air-bubbling method as previously employed.

Carveth and Fowler[1] substituted U-tubes for Liebig's bulbs and an air-bath thermostat for the water thermostat. They experienced great difficulty in starting and stopping the air current, to prevent the liquid being sucked back. To prevent this the air was drawn through the apparatus instead of being forced through. It is very evident that the pressure in the various parts of the apparatus was not the same and also different from the recorded atmospheric pressure, for it is very difficult to aspirate air through a long train without a very marked difference in pressure within the apparatus and the atmospheric pressure. They conclude "that the frequent failures in the application of the air-bubbling method require that the whole method be carefully examined before new results obtained by its use are accepted."

After the completion of the work herein described there came to our notice the recent work of the Earl of Berkeley and Mr. E. G. J. Hartley[2], wherein they used the general method of Ostwald and Walker, but modified the form of the bulbs and also employed a device for shaking the solutions. The four tubes which were substituted for Liebig's bulbs, were placed on a platform which was caused to oscillate so as to raise and lower the ends of the tubes, and thus caused the liquid to flow from one end of the tubes to the other and kept the solution stirred. The air was bubbled through, in the later

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[1] Jour. Phys. Chem., 8, 313 (1904).

[2] Proc. Roy. Soc., 77, 156 (1906).

experiments, at the rate of fifty bubbles in twenty-eight seconds, and days were required to complete one determination (ninety-six hours with a dilute sugar solution). Among the sources of experimental error with which the authors had to contend may be mentioned: carrying over the liquid from one vessel into another by too rapid bubbling and by the formation of septa of liquid, which were carried some distance by the air current before breaking; "the slight change of pressure resulting on the increase of work to be done by the air in moving the septa in the first vessel" (Mr. Whetham); the changes of pressure caused by the air bubbling through water in a vessel which was employed to "damp down" these changes; the duration of the experiments; the small loss in weight of the vessel containing the pure water; etc. The authors claim to have reduced the experimental errors so as to enable them to attain an order of accuracy of 5 percent.

Notwithstanding all of these objections stated above and many others, such as the difficulty of obtaining the air saturated with aqueous vapor, the condensation of the vapor on glass surfaces, etc., which have been examined by the authorities quoted above, the air saturation method has many advantages over other methods. A few of these are: (1) measurements may be made at ordinary temperatures and pressures in a comparatively short time; (2) no chemical decompositions occur in solution such as are known to take place in boiling liquids; (3) no costly apparatus is employed. But to the usual form of apparatus, such as has been employed by the experimenters mentioned above, the following objections have been raised: (1) The pressure is not the same in all of the bulbs containing the solvent and the solutions, and as the difference may be very considerable, the error introduced is not negligible; (2) it is well known that the concentration of the surface layers of the solution differs from that of the rest of the liquid, and as these surface layers are the last ones with which the air comes in contact, the true vapor pressure of the solutions is not being measured.

In our work this latter source of error was eliminated by shaking laterally the simple horizontal tube which we term the "saturator" containing the solutions, the vapor pressures of which were to be determined. By employing these unique features invented by Professor Kahlenberg, for agitating the contents violently while the air is drawn through the tube, it was thought advisable to study the limitations of this saturation method and to perfect the apparatus in order to obviate some of the difficulties encountered by previous investigators.

We shall, therefore, in the presentation of the experimental work, give a somewhat detailed description of the apparatus, the experimental data obtained in testing its efficiency, and finally the values for the vapor pressure of water, and of solutions of potassium nitrate, lithium nitrate and sodium nitrate. Then we shall discuss in a general way the data herein presented.

Experimental Part

The arrangement of the apparatus employed is shown in a general view in Fig. 1. Besides the aspirator which is shown in Fig. 2, the train consists of (1) the drying vessels, J′, J, for purifying the air employed; (2) the system for insuring saturation of the air consisting of I, H, G and F; (3) the saturator E, E, F, G and H being placed in the thermostat; (4) the absorption bulbs C and D, and the Drechsel bottle, B. The air was brought in from outside the building, passed through J′, which contained pumice stone moistened with sulphuric acid to remove ammonia and then through J, which con-

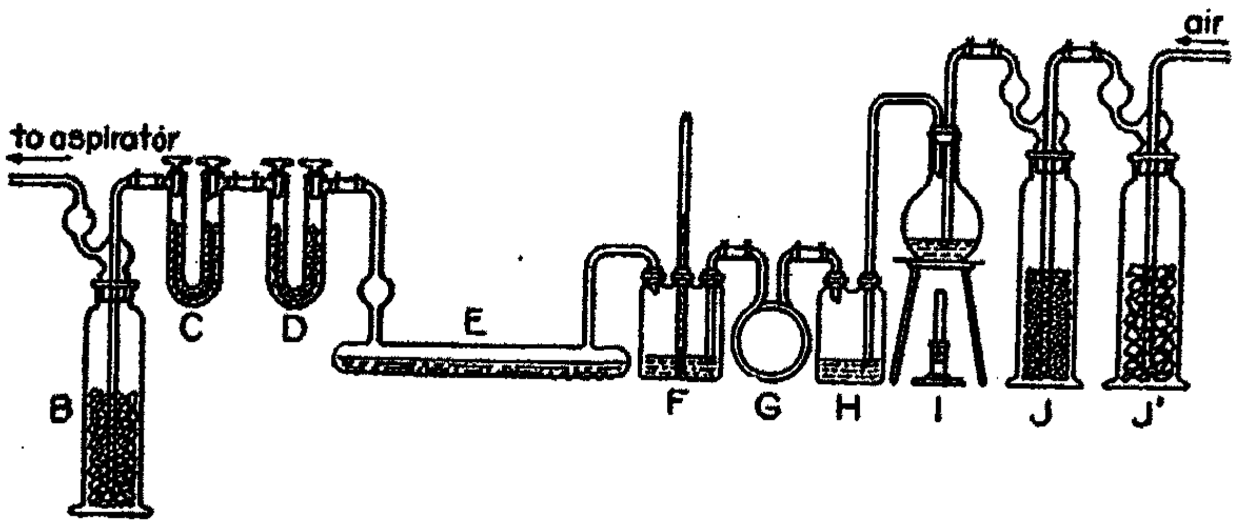

Fig. 1

tained soda lime, to remove carbon dioxide. The air thus purified was bubbled through I, which, in most of the experiments, was maintained at a high temperature; this we shall designate as the "supersaturation" device, where the air becomes saturated with water vapor at a temperature higher than that of the experiment, 25°; *i. e.*, it is supersaturated with respect to the temperature of the experiment. The air now enters the thermostat that contains the Woulff bottle, H, which contains pure water to bring the air to saturation at 25° C; then it passes through the lead coil, G, five feet long, to insure that the air is cooled to the temperature of the experiment, then it passes through another Woulff bottle containing a solution of the same strength as that in the saturator, the vapor pressure of which is to be determined. The object of this is, of course, to bring the aqueous content of the air down to the point of equilibrium with the solution, so that there would be little change in the concentration of the solution in the saturator. While the air is passing through the saturator E, the liquid in it is violently agitated in order to be sure that the air becomes saturated with aqueous vapor, and that it is in equilibrium with the liquid phase. The air now leaves the saturator passing through the absorption tubes D and C which contain pumice moistened with concentrated sulphuric acid, and phosphorus pentoxide, respectively, through the wash bottle, B, containing pumice and sulphuric acid, thus preventing any moisture from the aspirator passing to the absorption tubes, and finally the air is collected in the aspirator where it is measured.

It will be necessary to describe some parts of the apparatus more in detail.

Thermostat and Shaking Apparatus

The thermostat consisted of a large square galvanized iron tank, 30 by 30 by 25 inches. The thermo-regulator was of the ordinary toluene-mercury type, and it was very easy to maintain the temperature within ±0.02° C as read on a Beckmann thermometer, for a day at a time, or during the duration of an experiment. After many unsuccessful trials with various kinds of shaking apparatus the following was constructed and gave complete satisfaction. Along the upper edge of one side of the thermostat was fastened an axle carrying at each end a heavy cast-iron pulley 6 inches in diameter, and on the center was a cone pulley of three steps, 2 inches, 3 inches and 4 inches. Directly beneath this pulley was another cone pulley made of brass and with steps of the same size. This was fastened to a heavy cast-iron block which was held in position in the tank by a clamp. On this lower pulley was an eccentric to which was attached a shaft forked at the free end and terminating in two brass collars, so arranged as to fit the glass saturator and provided with a bolt and nut arrangement by means of which the saturator could be securely fastened. Directly above the saturator across the top of the tank $9^1/_2$ inches from the side bearing the shaft and pulleys was placed a wooden strip from which the saturator was suspended by means of two heavy copper wires terminating in two brass collars similar to those attached to the eccentric shaft. These collars were fastened around the saturator and served to keep it at the proper depth in the bath. The tubes A and B of the saturator were fastened by means of copper wire to this wooden strip in such a way as to permit of a little free play. The stirring device consisted of a pulley and axle carrying a large brass paddle. The shaking and stirring devices were both run by a one-sixth horse-power 100-volt direct current motor of 1600 R. P. M., which was belted to one of the end pulleys on the main axle. By this means the saturator was given a speed of about 200 strokes, one inch in length per minute.

The Saturator

The saturator represented by E in Fig. 1, was made entirely of glass 20.5 inches long and 1.5 inches in diameter with arms 5.5 inches long. The small bulb 2.5 inches in diameter prevented liquid particles from being carried over mechanically. The main tube was filled half full of the solution, the vapor pressure of which was to be determined. This required about 150 cc. The saturator was then placed in the thermostat and connected with the shaking device by means of which its contents were kept in motion.

The Aspirators

The aspirators employed were two large glass vessels of about 32 liters capacity, and were each provided with a tubulus at the bottom (Fig. 2). These vessels were used alternately as aspirator and receiver. The one employed as an aspirator was placed on the table and the water was permitted to flow from it through a tube in the tubulus into the other vessel, which served as a receiver and was placed on the floor. When the required amount of air had been aspirated through the apparatus the flow of water was stopped and the vessels interchanged, when they were again ready for another experiment. In this way the same quantity of water could be used over and over again. The mouth of each of the vessels was closed by a large rubber stopper which was perforated with five holes to admit the following; an accurately calibrated thermometer reading to tenths of a degree and estimated to hundredths; an oil manometer, which carried a millimeter scale; a bent tube to connect the aspirator with

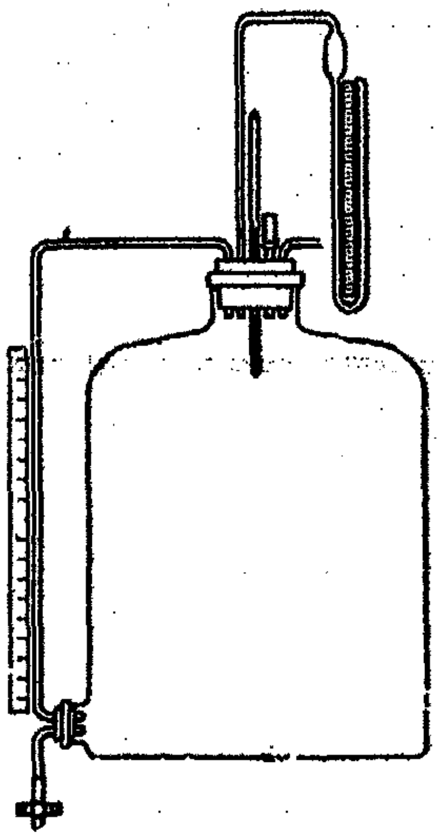

Fig. 2

the apparatus and through which the air escaped when this vessel was being used as a receiver; a small tube which was securely closed by a rubber tube and a screw clamp when the vessel was employed as an aspirator, but when it was used as a receiver this tube was connected with the tube in the tubulus of the aspirator, and water was thus permitted to flow from the aspirator into the receiver. The stopper carried another tube which also passed through the rubber stopper in the tubulus, forming a glass water-level. This was an indicator by means of which the amount of water that was removed from the aspirator could be easily and accurately determined. It was, of course, necessary to calibrate the aspirator very carefully and the calibration was put upon this water-level tube as the position of the meniscus could be much more accurately located in the small tube than in the large vessel. The aspirators were calibrated by filling the vessel to a definite mark and then allowing the contents to run into carefully graduated two-liter flasks and marking the position of the meniscus in the water-level tube after each two liters had been removed. This operation was repeated several times and finally verified by weighing the aspirator and its contents, then running out the water down to the thirty-two liter mark and weighing again. The loss in weight represented the water removed and its volume at that particular temperature was then calculated. A Fairbanks platform scale accurate to 0.002 pounds was used in weighing the aspirators. A comparison of the following data shows that the volume of the aspirators was known quite accurately.

Aspirators	A		B	
Volume by direct calibration	24.00	l	32.00	l
Volume by weighing	23.98	l	31.96	l

The absorption vessels comprised two tubes with ground glass perforated stoppers of the Schwartz type; one contained pumice stone moistened with concentrated sulphuric acid; the other was filled with alternate layers of glass-wool and phosphorus pentoxide. After each experiment the sulphuric acid was drained from the pumice, the tube rinsed out with fresh sulphuric acid and then a very small quantity of fresh concentrated acid was poured in, but not enough to fill the lower bent part of the U-tube. The phosphorus pentoxide served for a number of experiments without refilling.

As the vapor pressure of water and of solutions is greatly affected by any fatty or oily matter the greatest care was taken throughout this work to have all the apparatus and water free from this matter. All of the glass parts were cleaned with potassium dichromate and sulphuric acid and then steamed with fat-free water. This water was also used in the preparation of the solutions and was obtained by treating ordinary distilled water with potassium permanganate and sulphuric acid and distilling into barium hydrate from which the water was again slowly distilled and collected out of contact with the air.

The horizontal outlet tube connecting the saturator with the absorption tubes was outside the thermostat, and as the room temperature was usually different (lower) from the temperature in the thermostat it was necessary to heat this tube above the temperature of the bath to prevent condensation. This was necessary only in the case of pure water and dilute solutions as the amount of water in the air from concentrated solutions was below the quantity required to saturate the air at that temperature. However, the tube was heated when necessary by passing an electric current through a platinum wire coiled around it. Further, it was necessary to have this horizontal tube perfectly clean and dry for if any salt should remain in it a slight amount of it would dissolve in the aqueous vapor and be carried over into the absorption tubes and thus vitiate the results. In the case of salts forming hydrates they would abstract water from the vapor in the air, and too little water would be absorbed by the drying materials, and the values would be too low.

The calculations in all of the following work have been made by means of the formula given by Tammann:

$$f = \frac{H}{1 + \frac{V(1 + Kt')Wd(H - f')}{P(1 + K't')760}} \text{ where}$$

t = temperature of the saturated air
f = vapor pressure of water vapor at t
t' = temperature of aspirator at the end of the experiment
f' = vapor pressure of water at t' (found in L B tables)
H = barometric reading corrected to 0°
K' = coefficient of expansion of air, 0.003671
K = coefficient of expansion of water (negligible)
V = volume of aspirator at 0°
W = absolute weight of one liter of air at 0°
d = theoretical density of water vapor
Wd = 0.8082 gram
P = weight of water absorbed by the absorption tubes

It was first necessary to test the method thoroughly to determine its limitations and efficiency. One of the great objections made to the air-bubbling method is that the air has to be aspirated very slowly to insure saturation. It was nevertheless found by Regnault that the rate of aspiration had no effect on the vapor pressure of water even when the rate was as high as 25 liters per hour. Tammann came to the same conclusion although his speed did not exceed 6 to 10 liters per hour. The tendency of the more recent workers who employed this method seems to be to use a much slower rate of aspiration to be sure that equilibrium exists, between the vapor and the liquid phases. Ostwald aspirated 3 to 4 liters per hour while Carveth and Fowler passed the air at the "rather rapid rate of $\frac{3}{4}$ liters per hour." The Earl of Berkeley and Mr. E. G. J. Hartley passed the air at the rate of 50 bubbles in 28 seconds, thus employing several days for one determination. If the air has to be aspirated at the rate employed by these recent workers the great length of time required to make a determination would certainly be a great objection to the method. But fortunately it is not true as the results given in Table I prove conclusively. In this table are given our experimental data collected on the effect of the rate of aspiration on the vapor pressure of water. The headings of the columns have the same significance as the symbols given in the formula used by Tammann:

H	barometric reading corrected to 0° C.
V	volume of the aspirator at 0° C.
t'	temperature of aspirator at end of experiment
Rate	is expressed in liters per hour
$H-f'$	the difference between the barometer readings corrected at 0° and the vapor pressure of water at t', found in Landolt and Börnstein's tables
P	weight of water absorbed by the absorption tubes
f	vapor pressure of water at the temperature t

TABLE I

The influence of the rate of aspiration on the vapor pressure of water

H	V	t'	Rate	$H-f'$	P	f
733.70	28	21.00	5	715.20	0.6608	23.84
734.48	32	23.05	5	713.58	0.7434	23.72
741.60	32	22.20	8	721.70	0.7506	23.84
748.94	32	20.85	10	730.61	0.7549	23.78
753.25	32	23.98	16	731.10	0.7411	23.76
					Mean	23.788

The values of f given in the last column show beyond a doubt that the rate of aspiration does not affect the value of the vapor pressure of water, as the value is almost identically the same when the rate is 5 liters per hour as when it is 16, or three times as fast. It therefore follows that the vapor is in equilibrium with the liquid phase and that there is no necessity for consuming days, as some workers have done, in order to make one determination when a few hours answer much better, since it is easier to keep the conditions constant for a short period than for a long one. Furthermore, the slight changes in the temperature and pressure are much more important than the rate of aspiration, and it is not always an easy matter to keep them constant over a long period of time.

Shaw called attention to the difficulty experienced in saturating air with aqueous vapor and concluded that possibly Dalton's Law does not hold as the presence of air and even of nitrogen retards the development of a maximum vapor pressure and it is very much slower than when a vacuum is employed and the value obtained for the vapor pressure of water in vacuum is slightly greater than that obtained for saturated air. Carveth and Fowler seem to think that one of the most vital points in the air-bubbling or chemical method, as it is sometimes called, is the difficulty experienced in saturating the air aspirated through the apparatus, that is, in establishing equilibrium between the liquid and the vapor phases. From their own experimental difficulties they seem to think that "it is probably doubtful in all previous work, whether the results were not obtained with non-saturated air, and that if the air could be thoroughly saturated, very different results would be obtained." They reason that since a salt in solution dissolves and reaches the point of saturation only after long contact with the solvent and after vigorous shaking, it is very probable that air would not become readily saturated with water vapor. They proposed that in order to insure perfect equilibrium between the liquid and vapor phases it would be well to do as is done in the case of solutions of salts, to saturate at a higher temperature and then bring to a lower temperature and thus establish the equilibrium from a condition of super-saturation. Experiments were devised by them to test this point and they conclude that "sufficient results have been obtained in the comparative study of the saturation and super-saturation of air by water at a temperature of 62° to suggest that the ordinary method of bubbling air through a solvent or solution to produce complete saturation of the air may be very inaccurate in practice; only with very special precautions, indeed, can such absolute saturation be obtained." The authors should have carried their analogy between the saturation of solvents with salt, and of air with water vapor a little farther. They pointed out very clearly that in order to insure a saturated solution it is usually well to *shake* the solution thoroughly as well as saturate it at a higher temperature and then bring it down to the desired temperature when some of the solid phase is present. In our experiments we *agitated* the solution very vigorously and at the same time brought the air from a state of super-saturation to that of saturation, or from a state of non-saturation to a condition of saturation. It appears as though a condition of saturation, *i. e.*, a condition of equilibrium, should be reached from either direction, and that the results should be the same. In order to test this, a large number of determinations were made and the results are recorded in Table II and Table III. They were made when unsaturated air was employed by removing the wash bottles, H and I, and passing the air directly into the lead coil where it became warmed and then passed on into F containing water and then into the saturator E. These results are given in Table II and the columns have the same significance as in Table I.

TABLE II

Vapor pressure of water *without* "super-saturation"

H	V	t'	$H - f'$	P	f
740.53	26	23.30	719.27	0.6060	23.83
749.61	32	22.50	729.47	0.7456	23.71
733.70	28	21.10	7[illegible]0	0.6608	23.84
728.21	32	22.80	707.58	0.7451	23.75
752.36	32	20.60	734.30	0.7506	23.67
747.92	32	21.70	728.61	0.7467	23.67
734.48	32	23.05	713.58	0.7434	23.72
743.40	32	20.60	725.34	0.7504	23.65
741.81	32	23.90	719.76	0.7420	23.74
750.51	32	19.75	733.32	0.7580	23.80
741.60	32	22.20	721.70	0.7606	23.84
739.72	32	17.30	725.00	0.7690	23.84
				Mean	23.755

The wash bottles H and I were now replaced and the temperature of the water in I raised to 50°–60°, and the experiments conducted similarly to those recorded in Table II. The results of these are given in Table III where the columns have the same significance as in Table II.

It is very apparent that the results for the vapor pressure of water are identical in the two cases of "super-saturation"

TABLE III

Vapor pressure of water *with* "super-saturation"

H	V	t'	$H - f'$	P	f
748.94	32	20.85	730.61	0.7549	23.78
754.16	32	21.88	734.64	0.7493	23.76
753.25	32	23.98	731.10	0.7411	23.76
				Mean	23.766

and "under-saturation," and that equilibrium has been approached from both sides. This indicates that the air is saturated with water vapor and also is in accord with the statement of Perman that "when air is aspirated through water, it becomes saturated with aqueous vapor with great rapidity."

The air as it entered the aspirator was free from moisture, and we assumed that during the course of the experiment it became saturated with water vapor. In our calculation we had, of course, to correct for this, and the values we used for the observed temperatures were those given in Regnault's table. In the very careful work by Shaw on the hygrometric methods he states "that we may assume that the air in the saturator is saturated."

In order to verify our assumption the pressure and temperature of the air in the aspirator were observed after a determination of the vapor pressure of water. The aspirator was then tightly closed to insure against leakage and was permitted to remain in this condition until the next morning when the temperature and pressure were again observed. The readings of the temperature and pressure were again taken a few hours later, and assuming the air saturated, the true volume of air in the aspirator was calculated from the data collected. The following results were obtained:

	Volume	Time Hours
1	21.15 liters	0
2	21.14 "	12
3	21.18 "	15

It therefore appears that the assumption that the air was saturated when the measurement of the volume was taken was valid, and this assumption was used throughout the experiments.

One other point concerning the efficiency of the apparatus was considered: Was the bulb on the saturator sufficient to break all bubbles and prevent any of the particles of the solution being carried over mechanically? In order to test this the absorption tubes were removed and replaced by an empty U-tube which was placed in ice-water. A solution of lithium nitrate was used in the saturator and the experiment conducted as in all other cases with the exception mentioned. The liquid collected in the U-tube gave no test for lithium or for nitrates, which proved conclusively that not any of the solution in the saturator was carried over into the absorption tubes.

Having fully convinced ourselves that the method is perfectly reliable, our attention was turned to the application of it to the study of solutions. The general method of carrying out the experiment was the same as in the case of water except that we began with a very concentrated solution of the salt in the saturator E and in the Woulff bottle F, see Fig. 1. H contained pure water to produce equilibrium from the super-saturator I. In most cases it was not necessary to raise I above the room temperature as the vapor pressure of the solution was very much less than that of pure water. After the vapor pressure of the solution had been determined, the solution was removed and diluted, returned to the saturator and Woulff bottle and the vapor pressure of this new solution determined. This method was employed for the whole series of concentrations.

Potassium nitrate solutions were the first employed. These were prepared from a recrystallized sample of Kahlbaum's potassium nitrate which was dissolved in pure water. These solutions were analyzed by drawing a portion of the solution into a 10 cc pipette, the upper end of which was cut off close to the bulb and closed by means of a rubber tube and a screw clamp. The contents of the pipette, the weight of which was obtained by difference, was introduced into a weighed platinum dish and evaporated to dryness. The residue was heated in an air-bath at 110° to constant weight. Duplicate determinations gave very concordant results. A sufficient number of determinations were made in order to be certain that the vapor pressure of the solution was accurately known. The solution was then diluted and the procedure was as just described for the determination of each concentration. The results for solutions of potassium nitrate are given in Table IV. The significance of the letters at the head of the columns is the same as in preceding tables, while C represents the concentration expressed in the number of grams of solute in 100 grams of water, $\mu = \frac{f-f''}{fC} 1000$, where μ represents 1000 times the relative lowering which 1 gram of substance would produce at the particular concentration, f'' the vapor pressure of the solution, and M the molecular weight as calculated from the lowering of the vapor pressure.

TABLE IV

Vapor pressure of potassium nitrate solutions

C	H	V	t'	$H-f'$	P	f''	μ	M
21.77	738.45	32	20.75	720.22	0.7063	22.33		
21.77	752.09	32	24.50	729.24	0.6977	22.47		
21.77	753.44	32	24.30	730.86	0.7006	22.53		
21.77	752.05	32	24.60	729.06	0.6976	22.47		
21.77	744.08	32	24.50	721.33	0.6947	22.57		
					Mean	22.49	2.46	69.39
10.45	746.26	32	24.00	724.08	0.7196	23.09		
10.45	743.04	30	22.00	723.38	0.6843	23.19		
10.45	745.17	28	21.30	726.33	0.6361	23.01		
10.45	750.38	32	22.10	730.60	0.7237	23.00		
10.45	750.89	32	21.90	731.35	0.7271	23.08		
10.45	745.28	32	22.90	724.52	0.7267	23.18		
					Mean	23.09	2.70	64.83

It is perhaps well to ask whether there was any change in the concentration of the solution in the saturator due to the passage of so much air over the solution. In order to determine whether there was any change whatever, the solution was analyzed before conducting the experiment, and then it was removed from the saturator and analyzed again. It was found that the solution contained the same

	I	II
Before experiments were made	9.45	9.46
After experiments were made	9.46	9.46

percent of potassium nitrate. Hence it is possible to avoid concentration changes in the saturator by passing air through a sufficient number of Woulff bottles containing the solution before it reached the saturator and that we had succeeded in preventing any change.

Lithium nitrate was next selected for determinations of the vapor pressure of its solutions, owing to its great solubility. The salt was recrystallized several times and the concentrated solution obtained by dissolving in pure water. Samples of the solutions were analyzed by weighing by difference as in the case of potassium nitrate, evaporating to dryness in a platinum dish, moistening with sulphuric acid, carefully driving off the excess of acid, and weighing the residue as lithium sulphate from which the lithium nitrate content was calculated. This gave very satisfactory results. Then after the vapor pressure of the solution had been determined it was diluted, and the measurements of the vapor pressure of this solution made. This process was continued until the requisite dilutions were obtained. The results are given in Table V, the letters at the head of the columns having the same significance as in Table IV.

TABLE V
Vapor pressure of lithium nitrate solutions

C	H	V	t'	$H-t'$	P	f''	μ	M
57.18	747.06	32	22.90	726.30	0.4649	15.00		
57.18	746.26	32	21.40	727.30	0.4662	14.93		
57.18	744.02	32	22.60	723.66	0.4645	14.97		
					Mean	14.97	6.47	17.53
47.86	734.44	32	22.60	714.05	0.5216	16.76		
47.86	741.37	24	23.30	720.11	0.3858	16.64		
47.86	739.86	32	27.00	713.28	0.4995	16.83		
					Mean	16.74	6.18	2054
40.21	749.82	32	22.60	729.43	0.5509	17.69		
40.21	748.12	32	24.45	725.33	0.5464	17.71		
40.21	748.00	32	24.68	725.90	0.5451	17.67		
					Mean	17.69	6.36	21.09
31.82	741.53	32	26.10	716.39	0.5823	19.01		
31.82	738.57	32	25.55	714.24	0.5852	19.05		
					Mean	19.03	6.25	2304
23.08	742.34	32	22.95	721.52	0.6397	20.49		
23.08	741.98	32	22.40	721.84	0.6410	20.45		
23.08	734.41	32	23.05	713.47	0.6391	20.48		
					Mean	20.47	6.01	25.85
16.82	748.36	30	24.80	719.09	0.6216	21.42		
16.82	741.09	32	24.70	717.96	0.6653	21.48		
16.82	734.86	32	26.00	709.87	0.6613	21.49		
					Mean	21.46	5.73	28.25
11.61	730.29	32	23.05	709.34	0.6931	22.17		
11.61	728.43	32	23.18	707.35	0.6923	22.16		
					Mean	22.17	5.79	28.94
8.41	740.52	32	24.25	718.10	0.7068	22.72		
8.41	740.92	32	23.30	719.66	0.7078	22.65		
8.41	740.55	32	21.10	721.93	0.7170	22.69		
					Mean	22.69	5.35	32.40
5.14	745.26	32	22.05	725.54	0.7298	23.19		
5.14	742.65	32	22.95	721.77	0.7268	23.19		
5.14	742.65	32	22.00	723.02	0.7286	23.15		
					Mean	23.18	4.75	36.98

The vapor pressure of solutions of sodium nitrate was next determined. We desire to thank Professor Kahlenberg of the University of Wisconsin for the very pure sample of sodium nitrate prepared by Kahlbaum, which he was kind enough to send us. The solutions were analyzed by evaporating a weighed portion to dryness and after drying at 110° weighing as sodium nitrate. The data are presented in Table VI in which the heading of the columns has the same significance as in the preceding tables.

TABLE VI

Vapor pressure of sodium nitrate solutions

C	H	V	f'	$H-f'$	P	f''	μ	M
75.65	740.75	32	29.50	710.09	0.5572	18.55		
75.65	741.46	32	27.60	714.01	0.5633	18.55		
75.65	740.82	32	28.75	711.47	0.5613	18.51		
					Mean	18.54	2.92	48.13
49.53	739.09	32	28.55	710.08	0.6060	20.02		
49.53	740.04	32	27.85	712.19	0.6103	20.08		
					Mean	20.05	3.15	48.18
32.48	741.08	32	23.90	719.03	0.6601	21.22		
32.48	740.18	32	24.02	718.00	0.6588	21.20		
					Mean	21.21	3.31	48.63
11.69	736.41	32	24.95	712.93	0.7052	22.76		
11.69	735.67	32	24.75	712.48	0.7074	22.80		
					Mean	22.78	3.53	48.91

Discussion of Results

The value given by Landolt and Börnstein for the vapor pressure of water at 25° C that is generally accepted as the best is 23.55. This value was obtained from a recalculation of Regnault's experimental data. It is about 1 percent higher than the value obtained by other experimenters who employed the air-bubbling method, except Perman whose results at 20° and 30° are about 1 percent higher than the values given by the recalculation of Regnault's data. The interpolated value from Perman's results for 25° agrees very well with our value of 23.76. Tammann[1] has shown that the values of the vapor pressure of water given by Regnault in his paper are wrong, and points out that a greater divergence exists between values obtained by the air-bubbling method and the static method than appears from the results reported by Regnault. The question naturally arises, Are we justified in making all of these elaborate recalculations that have been made by Tammann and others, of the experimental data of Regnault? It is very apparent that new determinations of the vapor pressure of water would be of much value, and from the work of other experimenters with the air-saturation method and from the data herein presented it seems as though this method is quite suitable for such determinations. If this method were to be used the experimental errors could be greatly reduced by aspirating much larger quantities of air. The air would, however, have to be collected over some liquid other than water, and one whose vapor pressure was accurately known.

There are a few theoretical considerations which we wish to take up in connection with the data presented herein. The vapor pressure of solutions is used very much as a basis for calculations of the molecular weights in solution. Wüllner's Law states that the lowering of the vapor pressure is approximately proportional to the quantity of the substance dissolved in a given amount of liquid. In Tables IV to VI the columns headed μ represent 1000 times the relative lowering of the vapor pressure which 1 gram of the substance would produce at that particular concentration. This, of course, according to the law just referred to, should be constant, providing no electrolytic dissociation took place, and μ should decrease with an increase in concentration for dissociated substances. In Table VII are collected various values for potassium nitrate showing the relation between μ and the concentration.

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[1] Wied. Ann., 35, 322 (1888).

TABLE VII

Concentration	μ	Temperature	Determined by
25.04	2.52	100° C	Tammann
11.76	2.75		
11.222	2.87	18°–20°	Walker
20.071	2.38	25.86°	Emden
10.036	3.00		
21.77	2.46	25°	Lincoln and Klein
10.45	2.70		

It is very apparent that the values of μ decrease with the increase in concentration and our results are in accord with those of the other workers.

In Table VIII are given the values for lithium nitrate.

TABLE VIII

$LiNO_3$ (Tammann) Concentration

	15.92	35.01	59.06
Temperature	μ	μ	μ
30.9° C	7.57	7.40	6.63
38.2	6.56	7.11	6.87
46.7	5.71	6.29	6.46
50.4	5.61	6.25	6.44

$LiNO_3$ (Lincoln and Klein) at 25° C.

Concentration	μ
57.18	6.47
47.86	6.18
40.21	6.36
31.82	6.25
23.08	6.01
16.82	5.73
11.61	5.79
8.41	5.35
5.14	4.75

In both series of results, Tammann's and our own, the values of μ increase with an increase in the concentration, except at 30.9° and possibly at 38.2°, just the reverse of what they do in the case of potassium nitrate. That is, in the case of potassium nitrate the dissociation increases with the dilution, while for the lithium nitrate solution the above facts indicate that the dissociation increases with an increase in the concentration, or in other words, more parts are dissociated, relatively, in strong lithium nitrate solutions than in dilute solutions.

In the case of sodium nitrate, however, we have the same general relation as for potassium nitrate, the values of μ increase with a decrease in the concentration.

In the determination of molecular weights of substances in solution we make use of the lowering of the freezing-point, the rise of the boiling-point, and the lowering of the vapor pressure. All of these methods depend upon the *colligative* properties of the solutes, *i. e.*, upon the number of molecules concerned, and not upon the nature or magnitude of the molecules. In the case of the vapor pressure of solutions, for instance, the lowering is proportional to the number of molecules present, or if the substance is dissociated, the change in the vapor pressure will be due to the total number of molecules and part molecules present resulting from the electrolytic dissociation. Then such substances as potassium nitrate, sodium nitrate, and lithium nitrate should give us a vapor pressure which is proportional to the number of parts which are in solution. At the concentrations which are practically the same, expressed in parts per hundred parts of solution, *i. e.*, for potassium nitrate, 10.45; for sodium nitrate, 11.69; for lithium nitrate, 11.61; the values for μ are 2.70, 2.53 and 5.79 respectively. Now if we express the concentrations in terms of the number of gram-molecules present, we would have approximately for potassium nitrate, 0.103; for sodium nitrate, 0.138; and for lithium nitrate, 0.163 gram-molecules, which would correspond to lowerings of 2.70, 3.59 and 4.40 respectively. It is apparent that assuming the same degree of dissociation at these concentrations the values for potassium nitrate and sodium nitrate are practically what they should be, while lithium nitrate gives 5.79 as against the required value of about 4.4. From this it should follow that since the lowering of the vapor pressure of the lithium nitrate solution is greater than it should be, it is more highly dissociated than either potassium nitrate or sodium nitrate.

From the work of Raoult and Van't Hoff it has been made clear how the molecular weight can be calculated from vapor pressure measurements by the following formula, $M = \frac{18Cf''}{f - f''}$, where 18 is the molecular weight of water, and C, *f* and *f''* have the same significance as in the preceding tables. These values have been calculated and incorporated in the last column in Tables IV to VI. For example, the value of M for lithium nitrate in the most concentrated solution employed is 17.53, while in the most dilute it is 36.09, whereas the theoretical value is 69.07. In the most dilute solution we get a value that approximates one-half (34.5) of the molecular weight, showing a dissociation of nearly 100 percent, while in the most concentrated solutions employed, the value 17.53 is about one-fourth of the theoretical molecular weight which would correspond to a dissociation of about 200 percent, or, we would conclude that lithium nitrate, in most concentrated solutions is dissociated into more than two ions, which is apparently untenable. The calculated molecular weight decreases with the concentration, whereas, according to the theory, we should expect an increase. It might be suggested that our determinations of the vapor pressure of lithium nitrate solutions are "experimentally wrong;" then this, too, would have to be stated of Biltz's[1] freezing-point determinations, since he found that the molecular weight of lithium nitrate in a solution of 7.02 grams per 100 grams of water is 36.8, and in a solution of 1.154 grams per 100 grams of water it is 38.4.

In the case of potassium nitrate our values for the molecular weight by the vapor pressure method are very similar to those obtained by Kahlenberg[2] by the boiling-point method. At a concentration of 21.333 grams he obtained for the molecular weight 65.0, and at a concentration of 9.727 grams a value of 61.5, while Jones-Barnes-Hyde[3] give the value 70.9 for the molecular weight of potassium nitrate at a concentration of 10.119 grams by the freezing-point method. Hence, the values obtained by the vapor pressure method agree equally well with those values obtained by the "standard methods." In the case of sodium nitrate we have a value for

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[1] Zeit. phys. Chem., 40, 202 (1902).

[2] Jour. Phys. Chem., 5, 339 (1901).

[3] Am. Chem. Jour., 27, 29 (1902).

the molecular weight which is practically constant over a wide range of concentration. This value (48.13 to 48.91) is nearly one-half of the theoretical molecular weight (85.1). An explanation of this is not apparent at present.

This relation which exists between the concentration and the relative lowering of the vapor pressure can perhaps be shown best by the accompanying curves Fig. 3 which are, in a way, self-explanatory. The points lie upon well-defined, straight lines, although there is a sharp break in the lithium nitrate curve and also in the sodium nitrate curve. It appears as though the vapor pressure lowering increased too rapidly with the concentration in the case of lithium nitrate, and the reverse for sodium nitrate. These curves represent in a marked degree what we may call the "individuality" of the salt. This is further emphasized in the following table compiled from Tammann's work as given in Landolt and Börnstein's "Tabellen" (1905). The table gives the lowering of the vapor pressure of water at 760 mm caused by approximately the same concentration of various salts of sodium, potassium and lithium. The heading of the columns is self-explanatory.

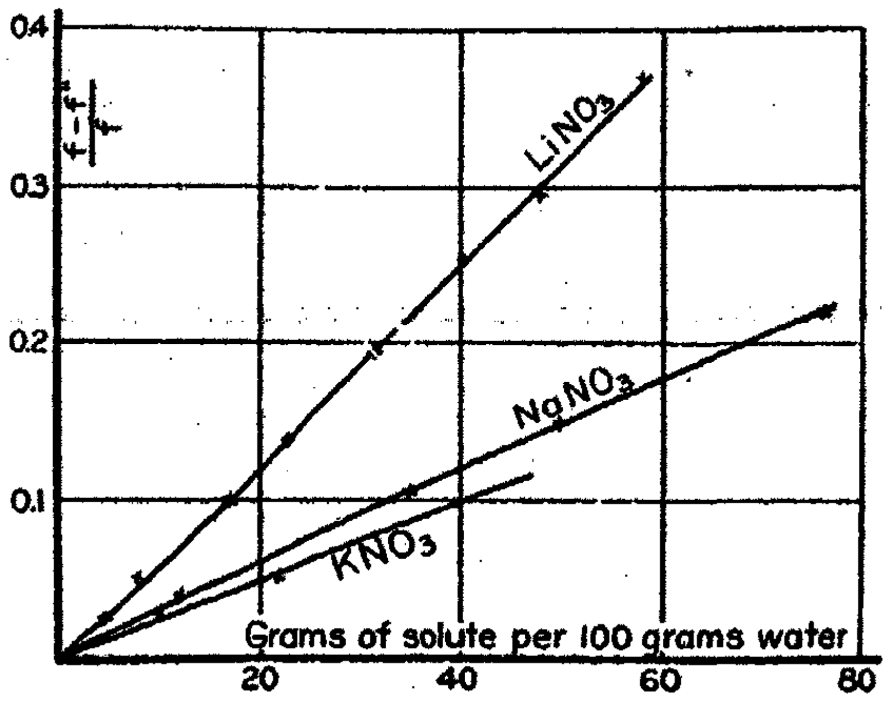

Fig. 3

The lowering decreases for the three metals in the order of arrangement of the acid radicals given in the table, except that lithium bromide gives a smaller value than lithium nitrate. For any salt the lowering is a function of the combining weight of the metal, the smaller the combining weight, the greater the lowering of the vapor pressure.

TABLE IX

	Potassium		Sodium		Lithium	
	Conc.	Lowering	Conc.	Lowering	Conc.	Lowering
Cl	31.68	108.0	36.91	187.5	36.6	341.8
Br	32.70	69.8	38.98	117.3	31.6	124.1
NO_3	33.90	64.2	37.00	98.4	32.5	145.9
I	30.70	47.6	36.00	77.0	34.9	88.5
SO_4	21.22	32.1	32.89	56.5	30.2	81.1

Raoult's formula does not apply to very concentrated solutions since it was originally promulgated only as an approximate formula for dilute solutions, and it might be worth while to inquire where the dividing line between dilute and concentrated solutions is located. Or, are factors other than the mere number of particles in the solution to be taken into consideration as influencing the vapor pressure of solutions, the freezing-point and the rise of the boiling-point? From the revival of the "hydrate theory" to explain some of these irregularities it would seem as though there was also a leaning toward the old "chemical affinity" idea of some kind of reaction between the solvent and the dissolved substance. In this connection it is interesting to see that Dr. Nicol[1] held a similar view in 1886 when he said: "It may be noted in passing, that unless a salt molecule were capable of disturbing the equilibrium of the whole of the water molecules present, it could have no effect on the vapor pressure of water." Dr. Kahlenberg[2] says: "We have seen above (and the literature is replete with records of facts illustrating this same point) that substances of similar chemical composition, when dis-

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[1] Phil. Mag., 22, 502 (1886).

[2] Jour. Phys. Chem., 5, 339 (1901).

solved in the same solvents, behave similarly, as far as the changes of the boiling and freezing-points are concerned; this clearly shows that the influence of the chemical nature of the dissolved substance enters into the determination of the molecular rise of the boiling-point and the molecular lowering of the freezing-point." He might equally well have made his remarks apply to vapor pressure determinations.[1] In the theoretical discussion relating to concentrated solutions there are many other important phases of the subject which it is necessary to consider, but owing to the meager data we have collected so far, we shall defer a detailed discussion of them. It is our purpose, however, to continue this work on the vapor pressure of nitrate solutions.

Summary

We have shown that:

1. By agitating the solution the vapor pressure of which is to be determined, the air saturation method yields very accurate results.

2. The air aspirated through the solutions *is* saturated with aqueous vapor, *i. e.*, is in equilibrium with the liquid phase.

3. The statement of Regnault and of Tammann that the rate of aspiration has no effect on the vapor pressure has been confirmed.

4. Vapor pressure determinations of solutions of potassium nitrate, sodium nitrate and lithium nitrate have been made.

5. The values for the vapor pressure lowerings give values for the molecular weight of potassium nitrate that are, as far as general trend is concerned, in accord with what we should expect upon the basis of the electrolytic theory of dissociation, while sodium nitrate and lithium nitrate do not.

6. If Raoult's formula is applicable to concentrated solutions, the molecular weight of lithium nitrate is far below

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[1] Compare Phil. Mag., Feb., 1905; also Trans. Faraday Soc., 1, 9 (1904); and Chemiker Zeitung, 29, No. 81 (1905).

the value required by the dissociation theory at complete dissociation. These values decrease with increasing concentration.

7. The lowering of the vapor pressure is apparently not solely a function of the number of parts in solution, but the individuality of the particular salt manifests itself and must be taken into consideration.

The University of Illinois,
Urbana, Illinois,
December, 1906

NEW BOOKS

Die chemische Energie der lebenden Zellen. *By Oscar Loew. Zweite Auflage. 17 × 24 cm: pp. iv + 133. Stuttgart: Fr. Grub, 1906. Price: paper, 3 marks; bound, 4 marks.*—The first edition of this work was condensed and translated into English and published in 1896 under the title, "The Energy of Living Protoplasm." In the present edition the author has aimed to omit everything of secondary importance, which has resulted in a reduction of the number of chapters. Some idea of the contents of the book may be obtained from the headings of the ten chapters it contains. These are as follows: essential properties of living cells, chemical characteristics of living substance, the character of biochemical work, formation of albumin in lower fungi, formation of albumin in phanerogams, theory of the formation of albumin, a labile proteine substance as the reserve material in plants, chemical characteristics of the labile proteine substance, lability and activity in protoplasm, theory of cellular respiration.

According to the author, protoplasm is a labile structure built up of labile chemical material. From studies in plant physiology the conclusion is drawn that the labile condition of the plasma proteines, to which paramount importance is attached, is due to the coexistence of aldehyde and amido groups. From extensive toxicological experiments it is concluded that substances which attack amido groups or react with aldehyde groups in neutral solutions at high dilution, also kill living matter at high dilution.

It is considered that kinetically labile substances can transform heat into chemical energy and thus produce catalytic effects, and that this chemical energy can be carried over to sugars, fats, lecithin, and amido acids, whereby these are modified by induced autoxidation. Nothing is said of the second law of thermodynamics in this connection, and to be sure data are not at hand whereby to test the validity of this law in the realm of biology. It will be recalled that Helmholtz himself doubted whether the law holds good in the case of living beings.

Ostwald's views of catalysis are combated and shown to be inadequate; and enzymes are considered to be labile proteine bodies. The polypeptide theory is pronounced plausible from the chemical point of view, but improbable in the light of physiological facts.

As is well known, the author has done much excellent work in chemical plant physiology, and it is consequently particularly gratifying that he presents in this monograph in condensed form some of the most important results of his labors together with the work of others. Throughout the book a most admirable scientific spirit is manifest, in that the author seeks to base all his conclusions and opinions upon carefully established experimental facts. To all who are seeking to gain a better insight into the physical and chemical problems that confront us in living matter, a careful reading of this volume can be highly recommended. *L. Kahlenberg*

Physikalische Chemie der Zelle und der Gewebe. *By Rudolf Höber. Zweite, neubearbeitete Auflage. 16 × 23 cm; pp. viii + 460. Leipzig: Wilhelm Engelmann, 1906. Price: bound, 14 marks.*—In this new edition there is much that is new. Our knowledge of colloids has increased; and we know more about the physiological effects of salts and mixtures of salts. The book was apparently just too soon to contain a reference to Kahlenberg's work on the permeability of membranes but, in the next edition, this will afford a welcome confirmation of Overton's views, p. 169.

Among the most interesting things in the book are: the evidence in favor of a variable permeability, 180; the continuous flow of water through a frog's skin, p. 338; the regulating power exerted by protoplasm, p. 420; the weakness of the crusade against salt, p. 300; the resorption in the intestinal tract, p. 319; the difference between the colors that stain the living cell and those that stain the dead cell, p. 172; the different effects due to mixing toxine and antitoxine in successive portions, p. 237; the osmotic pressure in the different organs, p. 345.

Wilder D. Bancroft

The Chemistry and Physics of Dyeing. *Being an Account of the Relations between Fibres and Dyes, the Formation of Lakes, and the General Reactions of Colloids, and Their Solution State. By W. P. Dreaper. 15 × 23 cm; pp. viii + 315. Philadelphia: P. Blakiston's Son & Co., 1906. Price: $3.00.*—"It is advisable that the modern dyer should have some knowledge of the general reactions, which give rise to the results obtained in the many processes, involved in the dyeing and bleaching of textile fibres. Without some such knowledge it is difficult to appreciate their nature; or be in a position to control their working in a systematic manner."

"The dyer must watch other things besides his dye-pots and his tinted yarns. He must know something of the general reactions of colloids, as typical of those which may possibly take place in the substance of the materials he has to prepare, and dye. It is important, too, that he should have some knowledge of the general principles which seem to govern solution, and the action of temperature, etc., on the dye liquors, and fibres."

The subject is treated under the following headings: historical introduction; properties of fibres, and their reactions; dyes and lakes, and their properties; action and nature of mordants; state of fibres, and action of assistants; solution, and the properties of colloids; physical action, and solid solution; evidence of chemical action in dyeing; part played by colloids in dyeing, and lake formation; the action of light on dyeing operations, and dyed fabrics.

So little really careful work has been done along these lines that the author can do little more than to point out the problems which should be solved. This he has done very successfully and it is this which constitutes the merit of the book.

When dark shades of indigo extract on wool are treated with a sodium sulphate solution, pp. 153, 275, the color is removed to such an extent that the dye is precipitated.

The action of sulphuric acid on wool, p. 155, and the precipitation of the dyes by sulphuric acid, p. 191, is worthy of study.

The difference in fastness between colors dyed 'direct' and those dyed 'ingrain,' p. 195, reminds one of the difference between the carrying down of barium chloride by barium sulphate and the infinitesimal absorption of barium chloride by precipitated barium sulphate.

The effect of temperature on the formation of lakes, p. 157, and the action of salts on the dehydration of cupric hydroxide, p. 127, should be simple problems, and the behavior of sodium metatungstate, p. 286, could undoubtedly be studied as a problem in inorganic chemistry.

The red, and not bronze, color of magenta when ground up with powdered chalk, p. 170, is of distinct importance with reference to Witt's theory of dyeing as a case of solid solution. Incidentally it may be mentioned that the author falls into the error of taking the applicability of the distribution law as the criterion of the existence of a solid solution.

The relation between the hydrolysis of the sulphonated basic dyes in water or alcohol, p. 131, and the dyeing of wool should be looked into. If results obtained by dyeing amyl alcohol are really identical with those for silk and wool, p. 229, the theoretical side of the problem becomes simplified. The bearing of this on the behavior of silk, wool and cotton towards an emulsion of oil, water and potassium carbonate, p. 267, certainly should be studied.

The action of light and oxygen on dyes, p. 289, opens up an enormous field of fascinating research.

One might go on in this way for a long time citing passage after passage from the book. Whether the volume will be of value to dyers is a question which the reviewer is not qualified to answer. It is a treasure-house of problems for the physical chemist. *Wilder D. Bancroft*

Einführung in die Phasenlehre und ihre Anwendungen. *By Alex. Findlay. (Handbuch der angewandten physikalischen Chemie. Herausgegeben von Prof. Dr. G. Bredig). Band VI. 16 × 25 cm; pp. vii + 224. Leipzig: Johann Ambrosius Barth, 1907. Price: paper, 10 marks; bound, 11 marks.*—This is chiefly a translation of the English edition and is therefore a good book. Among the additions are: the equilibrium between iron, carbon and oxygen; an improved diagram for steel; the diagram for ferric chloride, hydrochloric acid and water; Fedotieff's work on the ammonia soda process; Meyerhoffer's work on barium nitrite and on the equilibrium between barium carbonate and potassium sulphate; Miller and Kenrick's work on basic salts; some methods of indirect analysis of solid phases; and a couple of paragraphs on the formation of minerals.

A few errors have passed into the translation, notably the impossible diagram for the different modifications of ice, p. 16, and the text referring to it, p. 20. *Wilder D. Bancroft.*

The Elements of Chemical Engineering. *By J. Grossmann, with a Preface by William Ramsay. 13 × 20 cm; pp. vi + 152. London: Charles Griffin and Company, 1906. Price: bound, $1.50 net.*—This little book is intended to bridge over the gulf between the laboratory, where one works with gram or even milligram lots, and the factory, where one works with ton lots or hundred-ton lots. The headings of the chapters bring this out: the beaker and its technical equivalents; distilling flasks, Liebig condensers, fractionating tubes, and their technical equivalents; the air-bath and its technical equivalents; the blow-pipe and the crucible, and their technical equivalents; the steam boiler and other sources of power; general remarks on the application of heat in chemical engineering; the funnel and its technical equivalents; the mortar and its technical equivalents; measuring instruments and their technical equivalents; materials used in chemical engineering, and their mode of application; technical research and the designing of plant.

The book can be finished in an evening and the time will not be wasted. The author does not pretend to do anything more than give a popular introduction to the elements of chemical engineering and he has been pretty successful in the task he has set himself. There may well be a difference of opinion as to the class of men for whom the book is intended. The book is written avowedly for students who are planning to go into technical work. To the reviewer it seems as though these students need stronger meat. A man who is nearly ready to start at technical work does not wish to be coddled. He wants a great deal more information than he can get out of this book and he will probably not begin with a primer. On the other hand, the book is an admirable one for people who are not going into technical work. The student who is going to teach is interested in knowing what are the technical equivalents of the beaker, the air-bath, the funnel, and the mortar. He will read carefully the chapter on technical research though he will not get much out of it. In this country the popular primer is for the man who is not going farther in the subject. To these men the book can be recommended unqualifiedly. The others would probably be better off if they should read the book also; but it is hardly to be expected that they will. *Wilder D. Bancroft*

Nouvelles Orientations scientifiques. *By Fernando Alsina. Ouvrage traduit du Catalan avec l'autorisation de l'auteur, par J. Pin Y Soler. 13 × 22 cm; pp. 164. Paris: Garnier Frères.*—The author of this speculative treatise holds that the particles of ponderable bodies can exert no influence beyond themselves; that it is false to attribute to such particles forces of affinity, cohesion, repulsion, and the like. His thesis is that physical and chemical phenomena are to be explained by a relation between movements of ponderable particles and movements of the ether. He maintains that in this way many of the more important outstanding problems of the physical sciences can easily be solved. The bearing of this contention on a variety of chemical phenomena is discussed in detail in the book. *J. E. Trevor.*

Die Formelzeichen. *Ein Beitrag zur Lösung der Frage der algebraischen Bezeichnung der physikalischen, technischen, und chemischen Grössen. By Olof Linders. 17 × 27 cm; pp. 96. Leipzig: Jäh und Schunke, 1905.*—In this pamphlet the author emphasizes the desirability of a uniform notation for the algebraic quantities employed in the exact sciences, and tabulates suggestions that have been offered for the notation of a large number of quantities, together with systematically constructed proposals of his own. Those who feel that the growth of an extensive and slowly developing system of notation can be furthered by concerted action will be interested by the earnest effort here made to that end. *J. E. Trevor*

A NEW TYPE OF CATALYSIS. THE ACCELERATION BY CHROMIC ACID OF THE REACTION BETWEEN BROMIC AND HYDRIODIC ACIDS

BY ROBERT H. CLARK

The catalytic action of chromic acid on the rate of oxidation of hydrogen iodide by bromic acid was discovered by Ostwald in the course of his "Studien zur chemischen Dynamik;"[1] and when my own work had cleared up the kinetics of the reaction in question,[2] I entered on a detailed investigation of this case of catalysis, which has yielded some very remarkable results.

The method of carrying out the measurements, the stock solutions, and the units employed in recording the results, are all as described in my previous paper, with the addition of a solution of potassium bichromate, 0.1667-F, and another 0.001251-F, which were standardized against the acid by means of a solution of caustic potash and phenolphthalein. In the tables the number of cubic centimeters of 0.00125-F bichromate[3] is given under *Cr*.

As in the reaction between bromic and hydriodic acids, the presence of air had no material effect on the results of the measurements; and small quantities of iodine, such as are liberated during the reaction, exerted little or no effect on the rates.

Effect of the Bichromate on the Rate

The fact that the increased liberation of iodine in presence of chromic acid is not accompanied by a proportional reduction of the latter was observed by Ostwald, who found also that the increase in rate is proportional to the concentration of the chromic acid. Both these conclusions are supported by the measurements of Table I. In the first place, the

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[1] Zeit. phys. Chem., 2, 138 (1888).

[2] Jour. Phys. Chem., 10, 679 (1906).

[3] 0.00125 gram-formula-weights $K_2Cr_2O_7$ per liter.

TABLE I

$KBrO_3$, 20.5; KI, 98.67; HCl, 95.15; Vol., 250 cc; Temp., 30° C.

t	Cr	x	x'	R_0	Ac/Cr	t	Cr	x	x'	R_0	Ac/Cr
5	0	0.19	0.19	0.038	—	10	0	0.38	0.385	0.038	—
5	2	0.35	0.354	0.071	0.017	10	2	0.70	0.71	0.071	0.016
5	4	0.50	0.505	0.10	0.015	10	4	0.95	0.97	0.097	0.015
5	6	0.65	0.659	0.13	0.015	10	6	1.25	1.28	0.13	0.015
5	10	0.97	0.98	0.20	0.016	10	10	1.92	1.99	0.20	0.016
5	12	1.17	1.20	0.24	0.017	10	12	2.30	2.40	0.24	0.017
5	14	1.29	1.33	0.27	0.016	10	14	2.55	2.67	0.27	0.018
5	16	1.48	1.52	0.30	0.016	10	16	2.90	3.14	0.31	0.017
5	18	1.64	1.70	0.34	0.017	10	18	3.22	3.39	0.34	0.016
5	20	1.83	1.89	0.38	0.017	10	20	3.55	3.77	0.38	0.017

values of x' for $t = 10$ are just double those for $t = 5$, therefore no perceptible diminution in the concentration of the bichromate (reduction) can have occurred in the interval. In the second, the rate of liberation of iodine (R_0) is not proportional to the concentration of the bichromate, but the acceleration:

$$Ac = R_0 - R_0(Cr = 0)$$

is; this is shown by the constancy of the quotient Ac/Cp, and graphically in Fig. 1. The experiments of Table II, more-

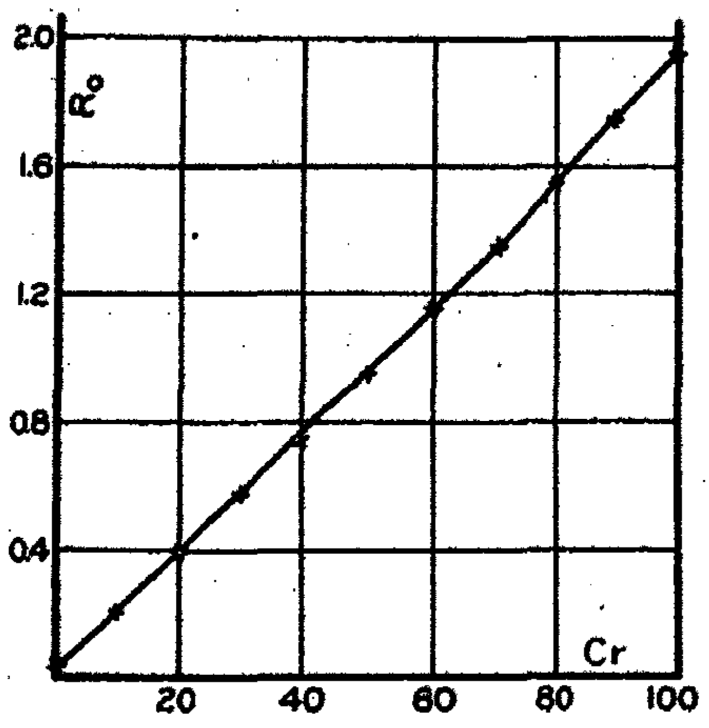

Fig. 1

TABLE II

$KBrO_3$, 20.5; KI, 98.67; HCl, 95.15; Cr, 2.0; Vol., 250 cc; Temp., 30° C.

t	x	x'	R_0
240	13.95, 14.07, average 14.01	19.83	0.083
300	16.33, 16.33, " 16.33	24.65	0.082

$$\frac{24.65 - 19.83}{300 - 240} = 0.080$$

over, show that even after the reaction had proceeded for four hours during which the additional iodine liberated because of the presence of the bichromate was oxidimetrically equivalent to 56 percent of the latter, there was no diminution in the rate of liberation of iodine except that due to the fall in the concentrations of the bromate, iodide and acid, which was allowed for in computing R_0.

EFFECT OF THE CONCENTRATIONS OF BROMATE, IODIDE AND ACID ON THE RATE

Systematic measurements were undertaken to ascertain the effect of changes in the concentration of each of the reagents in turn, on the rate of liberation of iodine. The results, which are contained in Tables III-VI, show that the rate is

TABLE III

$KBrO_3$, 20.5; KI, 98.67; HCl, 95.15; Vol., 250 cc; Temp., 30° C.; $t = 5$

Cr	x	x'	R_0	Cr	x	x'	R_0
0	0.19	0.19	0.038	18	1.64	1.70	0.34
1	0.25	0.253	0.05	20	1.83	1.89	0.38
2	0.35	0.354	0.07	30	2.70	2.83	0.57
3	0.40	0.404	0.08	40	3.50	3.71	0.74
4	0.50	0.505	0.10	50	4.35	4.69	0.94
6	0.65	0.659	0.13	60	5.25	5.74	1.15
8	0.81	0.82	0.16	70	6.07	6.73	1.35
10	0.97	0.98	0.20	80	6.95	7.82	1.56
12	1.17	1.20	0.24	90	7.65	8.71	1.74
14	1.29	1.33	0.27	100	8.35	9.73	1.95
16	1.48	1.52	0.30				

TABLE IV

$KBrO_3$, 20.5 × f; KI, 98.67; HCl, 95.15; Vol., 250 cc; Temp., 30°C

t	Cr	f	x	x'	R_0
5	10	2	2.00	2.07	0.41
5	12	2	2.33	2.42	0.48
5	14	2	2.60	2.71	0.54
5	16	2	2.95	3.10	0.62
5	18	2	3.27	3.45	0.69
5	20	2	3.57	3.78	0.76
5	6	3	2.01	2.02	0.40
5	10	3	2.87	3.01	0.60
5	14	3	3.82	4.06	0.81
10	18	2	6.30	7.01	0.70
10	20	2	6.80	7.61	0.76

TABLE V

$KBrO_3$, 20.5; KI, 98.67 × f; HCl, 95.15; Vol., 250 cc; Temp., 30° C

t	Cr	f	x	x'	R_0
5	10	2	2.00	2.07	0.41
5	12	2	2.32	2.41	0.48
5	14	2	2.58	2.68	0.54
5	16	2	2.94	3.06	0.61
5	18	2	3.24	3.40	0.68
5	20	2	3.58	3.77	0.76
5	6	3	2.00	2.01	0.40
5	10	3	2.87	2.99	0.60
5	14	3	3.80	4.00	0.80
10	16	2	5.70	6.23	0.62
10	18	2	6.30	6.93	0.69
10	20	2	6.79	7.52	0.75

TABLE VI

$KBrO_3$, 20.5; KI, 98.67; HCl, 95.15 × 2; Vol., 250 cc; Temp., 30° C; $t = 5$

Cr	x	x'	n, 1st appx.	n, 2nd appx.	R_0
0	0.90	0.91	2.00	2.00	0.18
2	1.17	1.19	1.72	1.73	0.24
4	1.48	1.51	1.58	1.58	0.30
6	1.86	1.91	1.52	1.53	0.38
8	2.22	2.30	1.45	1.49	0.46
10	2.58	2.68	1.41	1.44	0.54
12	2.97	3.10	1.35	1.37	0.62
14	3.27	3.42	1.34	1.36	0.68
16	3.61	3.83	1.29	1.32	0.77
18	3.96	4.21	1.27	1.30	0.84
20	4.30	4.60	1.23	1.28	0.92
30	6.05	6.63	1.16	1.22	1.33
40	7.44	8.32	1.09	1.13	1.66
50	9.00	10.30	1.03	1.12	2.06
60	10.30	12.04	0.97	1.07	2.41
70	11.50	14.17	0.93	1.05	2.83
80	12.95	15.71	0.90	1.01	3.14
90	14.19	17.63	0.89	1.01	3.53
100	15.22	19.24	0.87	0.96	3.85

proportional to the concentration of the bromate and to that of the iodide (the same as in absence of chromate); but that the effect produced by changing the concentration of the acid depends on the amount of bichromate present.

The experiments of Table III serve as standard for comparison, while in the other three the concentrations of bromate, iodide and acid respectively were multiplied by the variable factor f. Under R_0 in the last column is entered the "initial rate"

$$R_0 = dx/dt(x = o) = x'/t$$

that is, the number of cubic centimeters of hundredth-normal iodine liberated per minute in a solution of the composition indicated at the head of the table.

Method of computing x' and n

The general differential equation connecting the rate of liberation of iodine with the concentrations of the reagents may therefore be written:

$$dx/dt = K(A-x)(B-x)(C-x)^n(1 + M.Cr) \qquad (1)$$

where A, B and C are the concentrations of the bromate, iodide and acid respectively, and n depends on the concentration of the bichromate; K and M are constants.

By comparing the iodine readings (x) from Tables III and VI, in the latter of which the concentration of the acid was double that in the former, a first approximation to the values of n was obtained:

$$n\ first\ approx. = \frac{\log x\ (Table\ VI) - \log x\ (Table\ III)}{\log 2} \qquad (2)$$

The values so computed are entered in Table VI under "*n first approx.*" These approximate values were then introduced into Equation (1), which was integrated by series, and used to obtain a first approximation to the values of x' for Table VI.

$$x' = KABC^n t(1 + M\,Cr) = x + (1/2A + 1/2B + n/2C)x^2 +$$
$$1/3A^2 + 1/3B^2 + \overline{n^2 + n}/6C^2 + 1/3AB + n/3AC + n/3BC)x^3 \qquad (3)$$

A second approximation to the true value of n was then made, using x' (Equation 3) in place of x in Equation (2); the numbers so obtained are entered under "*n second approx*" in Table VI. Fig. 2 shows these values of n plotted as a

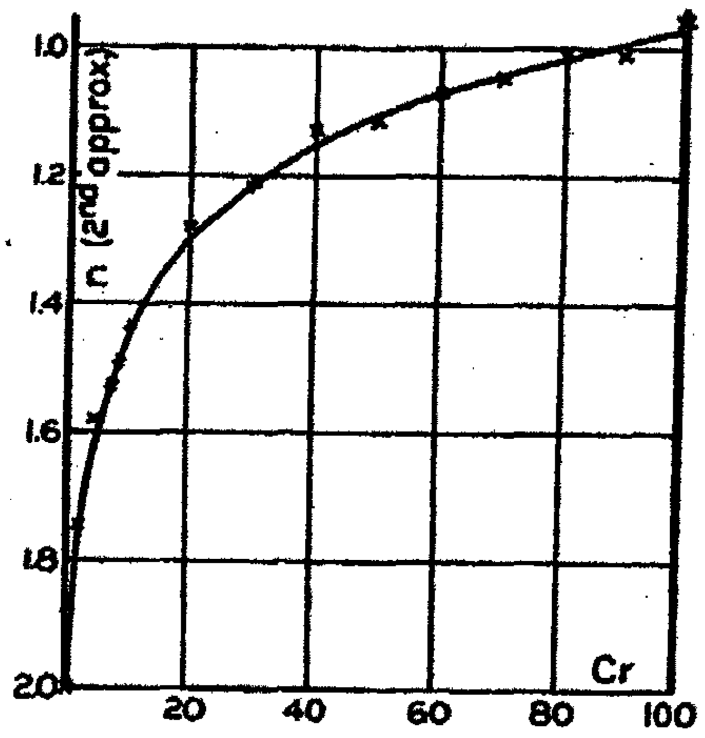

Fig. 2

function of Cr. When $Cr = 0$, the rate is proportional to the second power of the concentration of the acid; on addition of potassium bichromate the power diminishes until $Cr = 80$, when the rate is proportional to the first power of the concentration of the acid, and the curve (Fig. 2) becomes a straight line.

In Ostwald's "Lehrbuch der Allgemeinen Chemie" II (2), p 262, that author says: "So long as the catalyser is neither altered, formed, nor destroyed by the reagents or products of the reaction, its influence is exerted only on the value of the velocity constant, and not on the character of the kinetic equation." The present case is evidently an exception.

INTERPRETATION OF THE RESULTS

These results may be expressed by assuming that:

(*i*) In solutions containing bromate, bichromate acid and iodide, two reactions take place simultaneously, both resulting in the liberation of iodine.

(*ii*) The rate of the first reaction is proportional to the concentrations of the bromate, and iodide and to the square of that of the acid; while that of the second is proportional to the concentrations of bromate, iodide and acid, and slightly less than proportional to that of the bichromate.

(*iii*) The second reaction takes place without proportional reduction of the bichromate.

The corresponding kinetic differential equations are:

$$\partial x/dt = K_1(A-x)(B-x)(C-x)^2, \text{ and}$$
$$\partial x/dt = K_2(A-x)(B-x)(C-x)Cr$$

and the rate at which iodine is liberated in the solution:

$$dx/dt = (A-x)(B-x)(C-c)(K_1\overline{C-x} + K_2Cr) \qquad (4)$$

The values of the two constants in this equation were calculated from the two experiments of Table VI in which $Cr = 0$ and $Cr = 100$ respectively; they are, $K_1 = 645 \times 10^{-12}$ and $K_2 = 333 \times 10^{-10}$. The change of n with the concentration of the bichromate (Table VI and Fig. 2) is in quantitative accord with these assumptions, as may be seen by comparing the values of "*n second approx*" in Table VI with those calculated from the equation:[1]

$$n\ calc. = \frac{log(2K_1C + K_2Cr) - log(K_1C + K_2Cr)}{log\ 2} + 1 \qquad (5)$$

TEMPERATURE COEFFICIENT

In order to find the temperature coefficients of the rates involved, I repeated the experiments of Table IV at zero. (See Table VII.)

TABLE VII

Cr	*n*, 2d appx.	*n* calc.	Cr	*n*, 2d appx.	*n* calc.
0	2.00	2.00	20	1.28	1.26
2	1.73	1.75	30	1.22	1.19
4	1.58	1.62	40	1.13	1.12
6	1.53	1.53	50	1.12	1.11
8	1.49	1.47	60	1.07	1.10
10	1.44	1.41	70	1.05	1.09
12	1.37	1.37	80	1.01	1.07
14	1.36	1.34	90	1.01	1.06
16	1.32	1.30	100	0.96	1.04
18	1.30	1.28			

Under "coeff" is entered the temperature coefficient, that is the cube root of the ratio of the two rates R_0 at 30° and at 0°. The coefficient varies with the amount of bichromate present, as is shown graphically in Fig. 3; the similarity between this curve and that of Fig. 2 furnishes another argument in support of the assumption of two simultaneous reactions. The coefficient falls off gradually as the quantity of bichromate increases until $Cr = 60$, when it becomes constant at 1.19; this may be taken as the temperature coeffi-

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[1] In Table VI the concentration of the acid was twice that in Table III; hence, comparing values of R_0 from experiments in which the concentration of bichromate was the same,

by Equation (1) $\quad \frac{R_0\ (Table\ VI)}{R_0\ (Table\ III)} = 2^n$

by Equation (4) $\quad \frac{R_0\ (Table\ VI)}{R_0\ (Table\ III)} = \frac{2(2K_1C + K_2Cr)}{K_1C + K_2Cr}$

Equation 5 is obtained by equating these two expressions and taking the logarithms; C refers to the acid of Table III.

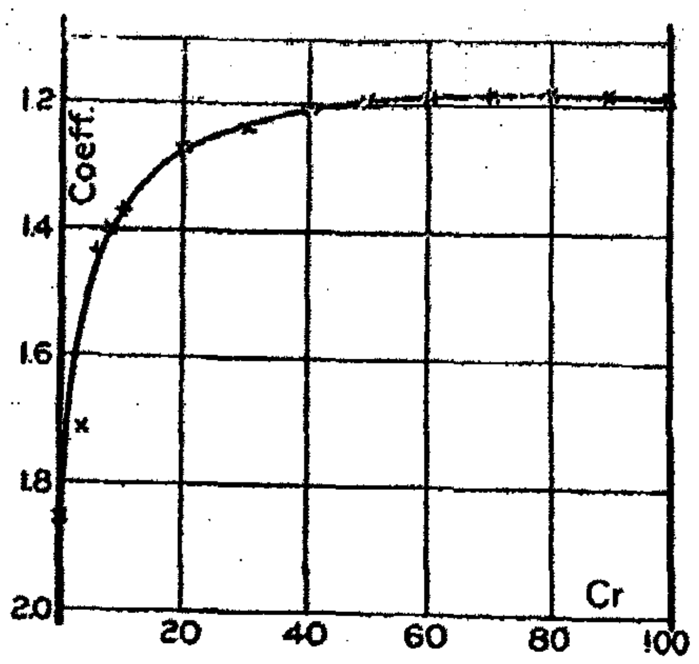

Fig. 3

cient of the second reaction of page 359, while that of the first is 1.85.

TABLE VIII

$KBrO_3$, 20.5; KI, 98.67; HCl, 190.3; Vol., 250 cc; Temp., 0° C; $t = 5$

Cr	x	x'	R_0	Coeff.
0	—	—	—	1.85[1]
4	0.30	0.30	0.06	1.71
6	0.63	0.63	0.13	1.43
8	0.85	0.87	0.17	1.40
10	1.05	1.07	0.21	1.37
12	1.25	1.27	0.25	1.35
14	1.42	1.45	0.29	1.33
16	1.76	1.80	0.36	1.29
18	1.91	1.95	0.39	1.29
20	2.10	2.16	0.43	1.28
30	3.29	3.45	0.69	1.24
40	4.45	4.75	0.95	1.21
50	5.45	5.91	1.18	1.20
60	6.45	7.09	1.42	1.19
70	7.25	8.08	1.62	1.19
80	8.15	9.18	1.84	1.19
90	9.00	10.28	2.06	1.19
100	9.72	11.24	2.25	1.19

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[1] This Journal, 10, 679 (1906).

CHROMIC ACID AND THE ANALOGOUS REACTIONS

The difficulty of inventing any hypothetical mechanism to explain the part played by the bichromate is enhanced by the circumstance that this case stands alone. Mr. Dushman[1] has shown that potassium bichromate is without action on the rate of the reaction between iodic and hydriodic acids; and by means of a few measurements I have ascertained that the rates of the reactions between

Iodic and hydrobromic acids
Bromic and hydrobromic acids
Chloric and hydrobromic acids and
Chloric and hydriodic acids

are likewise uninfluenced by the presence of potassium bichromate.

Summary

(1) Addition of potassium bichromate to a solution containing bromic and hydriodic acids brings a new reaction into operation, which consists in the liberation of iodine at a rate proportional to the concentrations of the bromate, iodide, bichromate and acid, without reduction of the bichromate. The normal reaction, whose rate is proportional to the concentration of the bromate and iodide and to the square of that of the acid, goes on unaffected by the presence of the bichromate.

(2) The processes of oxidation of hydriodic and hydrobromic acids by the oxyacids of the halogens, other than that of hydriodic by bromic acid, are not affected by the presence of potassium bichromate. Although in other respects the members of this group of reactions resemble one another closely from the kinetic point of view as well as from that of pure chemistry, the analogy fails at this point.

In both respects this case of catalysis is unique.

I desire to express my thanks to Prof. W. Lash Miller, under whose direction these measurements were carried out in the winter of 1904-5.

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[1] Jour. Phys. Chem., 8, 453 (1904).

The University of Toronto
February, 1907

THE PHOSPHATES OF MAGNESIUM AND IRON[1]

BY F. K. CAMERON AND J. M. BELL

The behavior of phosphates of calcium in phosphoric acid solutions has been discussed in former papers from this laboratory[2]. Two crystalline phosphates of calcium have been shown to exist in equilibrium with solutions containing free phosphoric acid: monocalcium phosphate, which at 25° exists in equilibrium with solutions containing over 317 grams of phosphoric acid (P_2O_5) per liter; and dicalcium phosphate, which is stable below this concentration. At very low concentrations (up to about 5 grams phosphoric acid per liter) the stable solid was found to be a solid solution consisting of lime and phosphoric acid.

Both these crystalline phosphates of lime suffer decomposition when water is added to the solid, the resulting solution becoming richer in phosphoric acid and the solid poorer in phosphoric acid than the original compounds. The phosphates of magnesium are also decomposed by water, yielding solutions which are more strongly acid than the original solid, and the composition of the various acid solutions which can exist in contact with magnesium phosphates have been determined at 25°. In a similar way the phosphates of iron suffer decomposition when treated with pure water and compositions of various acid solutions in contact with ferric phosphate have been determined at 25°. The composition of the solid in contact with these solutions is shown to be variable, that is, the solids are solid solutions.

Phosphates of Magnesium.—Solid dimagnesium phosphate was added in excess to solutions of phosphoric acid in varying concentrations. These mixtures were constantly agitated in a thermostat at 25°, and at the expiration of two months

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[1] Read before the American Chemical Society, Ithaca, June, 1906, by permission of the Secretary of Agriculture.

[2] Cameron, Seidell, and Bell: Jour. Am. Chem. Soc., 27, 1503, 1512 (1905).

the solutions were analyzed for magnesia and for phosphoric acid. Magnesia was determined by adding ammonium chloride to the solution for analysis and then ammonia was slowly added to the solution until the solution became alkaline; the resulting precipitate was filtered, washed, and weighed as magnesium pyrophosphate. To determine phosphates ammonium chloride was added to the solution for analysis, then ammonia was added slowly with constant stirring until the solution became alkaline, then magnesia mixture was added in excess until all the phosphoric acid was precipitated as magnesium ammonium phosphate.

The composition of the solutions is given in Table I and Fig. 1.

TABLE I

MgO per liter. Grams	P_2O_5 per liter. Grams	Density $\frac{25°}{25°}$
0.207	0.486	—
0.280	0.732	—
0.553	1.917	—
1.438	4.85	—
2.23	7.35	1.006
4.73	16.84	1.017
11.19	38.59	1.042
17.33	61.21	1.069
26.09	93.09	1.109
37.40	130.7	1.144
75.5	281.8	1.285
109.5	439.0	—
122.6	498.4	1.470
129.9	546.5	—
140.0	584.0	—
146.8	623.3	1.595
147.3	625.9	—
150.3	645.8	—
155.5	680.7	—
87.1	779.6	1.626
77.1	809.6	1.644
70.6	835.1	1.654

From the above table it appears that there are three series of solutions which exist in contact with the phosphates

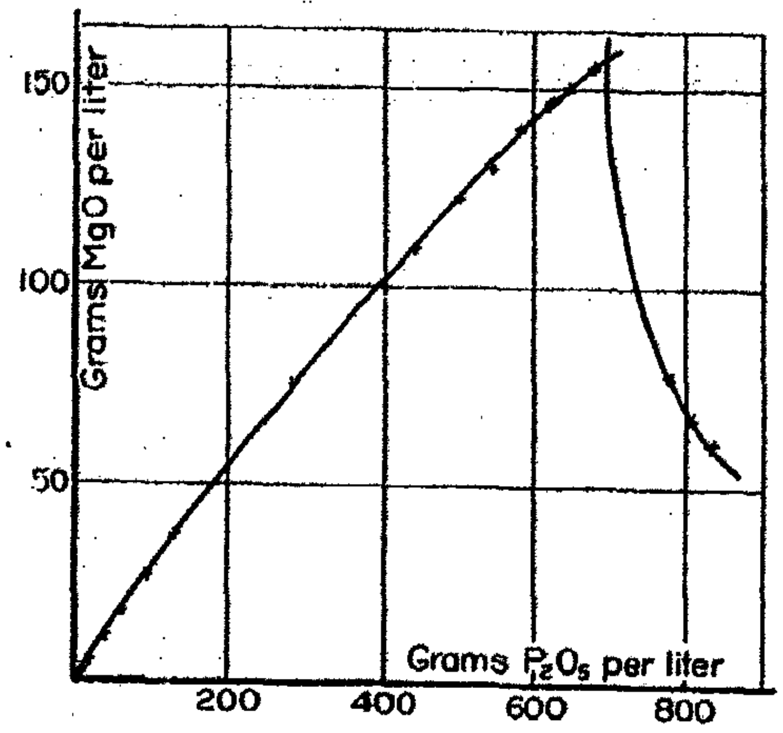

Fig. 1

of magnesia. With the solutions very concentrated with respect to phosphoric acid the content of magnesia phosphate decreased with increasing quantities of phosphoric acid, but with more dilute solutions both magnesia and phosphoric acid increase regularly. The stable solid in contact with the more dilute solutions was dimagnesium phosphate ($MgHPO_4.3H_2O$) and in concentrated solutions monomagnesium phosphate ($MgH_4(PO_4)_2.xH_2O$). The constant solution contains about 700 grams of phosphoric acid (P_2O_5), and about 160 grams magnesia (MgO) per liter. In all but the last three solutions described in the table the solid phase is dimagnesium phosphate and in the last three, described in the table, monomagnesium phosphate. A magnesium phosphate more basic than the diphosphate exists at 25° only in very dilute solutions of phosphoric acid, and over a range of concentration too narrow to be determined with precision.

Phosphates of Iron.—The action of water upon the phosphates of iron resembles in a striking manner the action of water upon the phosphates of calcium and magnesium. They undergo the same decomposition whereby the acid is removed at a different rate from the base, resulting in the formation of a more basic precipitate and the formation of a solution which is acid. Lachowicz[1] has investigated the decomposition action of water upon ferric phosphates, and it is shown that the continued leaching of a substance corresponding closely to the formula $FePO_4$ gave a solution which was acid. Relatively very minute quantities of iron were found in the acid solution. The results of Lachowicz have been confirmed by Cameron and Hurst,[2] who have shown that the action of water upon ferric phosphate cannot be considered as one of mere solution only. If it were a simple solution phenomenon the solution resulting from a mixture of phosphate and water would have the same composition regardless of the quantity of the solid residue, and also the ratio of iron to phosphoric acid in the solution would be the same as in the original solid.

In recent experiments in this laboratory solid ferric phosphate, whose composition was not determined, was placed in contact with phosphoric acid solution of varying concentration up to 5 percent; after four months constant agitation at 25°, the solutions were analyzed for phosphoric acid and for iron and the density having been determined, the percentage of each component could be calculated. The iron in solution was determined as ferrous sulphide by precipitation from the solution which had previously been made alkaline by an excess of ammonia which dissolves the precipitate formed when the solution is just neutral. The iron was weighed as ferric oxide. Phosphoric acid in the filter was determined by precipitation with magnesium mixture. The solid phase was freed as far as possible from the solution and a weighed quantity was dissolved with hydrochloric acid. Aliquot portions were analyzed by the above method for both phosphoric acid and lime. The results of these analyses are given in Table II and have been plotted in Fig. 2.

The lines joining corresponding points in the diagram do not intersect but are approximately parallel, and hence

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[1] Monatshefte, 13, 357 (1892).

[2] Jour. Am. Chem. Soc., 26, 885 (1904).

TABLE II

Solution			Residue	
Phosphoric acid P_2O_5. Per cent	Ferric oxide Fe_2O_3. Per cent	Density $\frac{25°}{25°}$	Phosphoric acid P_2O_5. Per cent	Ferric oxide Fe_2O_3. Per cent
0.942	0.0105	1.0074	13.81	15.11
1.984	0.0205	1.0162	17.90	19.35
2.838	0.0384	1.0244	22.54	23.11
3.770	0.0611	1.0310	17.73	15.13
4.706	0.0849	1.0383	23.37	20.43

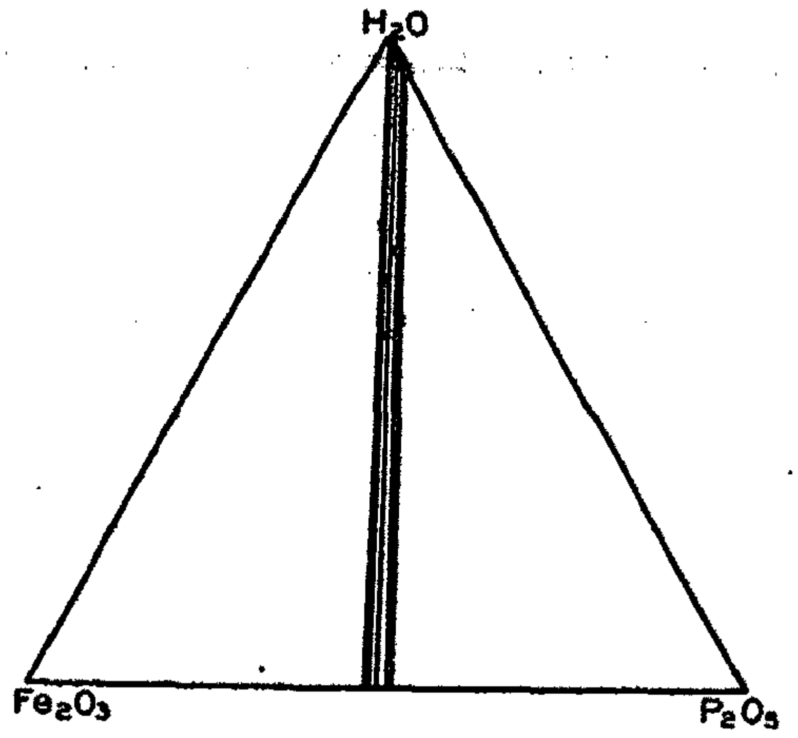

Fig. 2

the solid phase is a solid solution, for it is evident that its composition varies continuously. The ratio of ferric oxide to phosphoric acid in the limiting solid solution is very close to that represented by $FePO_4$, and if any one of these solid solutions be subjected to continued leaching by water, the resulting solid will not be far in composition from $FePO_4$. It is also apparent from the table that phosphoric acid is washed from the solid at a much more rapid rate than is iron, and continual leaching will cause very little loss of iron but will reduce the phosphoric acid content of the solid very rapidly until a limiting solid solution results.

With concentrations higher in phosphoric acid than those of the above table definite chemical compounds may be formed, as in case of lime and magnesium. The behavior of iron phosphate in these more concentrated solutions will be investigated further.

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ELECTROLYTIC PRECIPITATION OF ZINC

BY RALPH C. SNOWDON

In the spring of 1904 I made a preliminary examination of some of the conditions affecting the electrodeposition of zinc. I have not been able to take the question up more carefully and I have therefore decided to publish the data, as they bring out some points which are not matters of common knowledge. The variables taken into account were: concentration, degree of acidity and alkalinity, reducing agent, current density, and temperature. While the cathode was rotated in every case, no attempt was made to measure the rate of rotation carefully or to keep it constant. It was thought that differences in speed would be of minor importance provided a fairly high rate of speed were maintained. The results of the experiments have proved that this was a delusion. It is scarcely overstating the matter to say that the limiting current density at which the deposit begins to become bad depends more on the rate of stirring than on all the other factors combined.

In Table I are given the solutions which were studied.

TABLE I

Sol.	Composition
A	M/2 $ZnSO_4$ + M/50 H_2SO_4.
B	M/2 $ZnSO_4$ + M/5 H_2SO_4.
C	M/2 $ZnSO_4$ + M/50 H_2SO_4 + M/10 resorcinol.
D	M/10 $ZnSO_4$ + M/50 H_2SO_4.
E	M/10 $ZnSO_4$ + M/5 H_2SO_4.
F	M/10 $ZnSO_4$ + M/50 H_2SO_4 + M/10 resorcinol.
G	Saturated solution of ZnO_2H_2 in 3M NaOH.
H	Add 60g solid NaOH (3M/2) per liter of solution G.
I	Add 11g resorcinol (M/10) per liter of solution G.
K	Dilute solution G to one-fourth with 3M NaOH.
L	Add 60g solid NaOH (3M/2) per liter of solution K
M	Add 11g resorcinol (3M/2) per liter of solution K.

Measurements were made with each solution at 20°, 40° and 70°, using a large sheet-iron water-bath heated by Bunsen burners. In this bath a given temperature could be kept to within 2°–3° of the temperature desired. This bath would accommodate four solutions at one time and so the runs were made in sets of four each. The solutions were contained in 500 cc beakers, each cell having two zinc anodes with a rotating cathode placed between them. The cathodes were zinc tubes, one centimeter in diameter and dipped full five centimeters into the solution, making a total cathode surface of a trifle over, sixteen square centimeters. Each cathode was turned by an individual motor, making 200–300 revolutions per minute. The current and voltages were all taken on the specially brightened surface of the connector which held the rotating cathode fast to the shaft of the motor. In each particular case the readings were quite constant but that of course does not mean that they were free from error. An imperfect contact between the voltmeter lead and the rotating cathode, an imperfect contact between the rotating connector and the rotating cathode, or a slight fluctuation in the temperature would all introduce quite serious errors. While it is hoped and believed that errors due to these causes were small, the measurement of the voltages was a secondary matter and it would not be safe to base conclusions on minor fluctuations in the voltages. The polarization voltages were not determined in any case.

By means of a sliding resistance, current densities were varied in steps of 0.5 ampere usually up to 7 amp/dm^2. After that the current density was increased rapidly up to the values at which the deposits became hopeless.

In Tables II–X are given all the data except the limiting current densities, these last being put all together in Table XI.

In the runs with solutions A, B, C and D at 20° the immersed portion of the cathode was twice what it was in the later runs and the motor gave a lower speed. The limiting values in Table XI are not comparable therefore with the corresponding values at 40° and 70°. To show that this difference is due to rate of stirring, a couple of runs were made

TABLE II
Temperature 20°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks
A	1.0	0.55	All deposits granular and spiral	A	1.5	0.91	All deposits granular but spreading
B	1.0	0.32		B	1.5	0.41	
C	1.0	0.41		C	1.5	0.55	
D	1.0	0.84		D	1.5	1.23	
A	2.0	0.97	Deposits granular but becoming smoother	A	2.5	1.34	Same as preceding but C smoother
B	2.0	0.54		B	2.5	0.86	
C	2.0	0.73		C	2.5	1.10	
D	2.0	1.90		D	2.5	2.82	
A	3.0	1.55	All deposits smoother	A	3.5	1.70	Deposits still granular but very metallic looking
B	3.0	0.97		B	3.5	1.10	
C	3.0	1.55		C	3.5	1.65	
D	3.0	3.10		D	3.5	3.20	
A	4.0	1.90	All deposits stronger and smoother	A	4.5	2.00	No change in deposits
B	4.0	1.40		B	4.5	1.50	
C	4.0	1.90		C	4.5	2.10	
D	4.0	3.60		D	4.5	4.00	
A	5.5	2.15	A, B and C good; D poor	A	6.0	2.65	Same as in preceding run
B	5.5	1.60		B	6.0	1.70	
C	5.5	2.00		C	6.0	2.40	
D	5.5	4.00		D	6.0	4.50	
A	6.5	2.90	A, B and C good; D bad	A	7.0	3.00	All deposits fair
B	6.5	2.15		B	7.0	2.20	
C	6.5	2.50		C	7.0	2.65	
D	6.5	4.30					
A	7.5	3.20	All deposits fair	A	8.0	3.30	All treeing
B	7.5	2.20		B	8.0	2.50	
C	7.5	2.80		C	8.0	3.30	
C	8.5	3.50	Only fair	C	9.0	3.50	Poor and non-adherent

TABLE III

Temperature 40°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks
A	0.5	0.50	No precipitate on B; rest granular. Not very adherent	A	1.0	0.39	Becoming finely granular and more adherent
B	0.5	0.15		B	1.0	0.30	
C	0.5	0.35		C	1.0	0.46	
D	0.5	0.30		D	1.0	0.36	
A	1.5	0.54	All deposits finely crystalline and adherent. D very hard and fine	A	2.0	0.77	All good and adherent, somewhat spiral. A poorest, D best
B	1.5	0.36		B	2.0	0.41	
C	1.5	0.57		C	2.0	0.78	
D	1.5	0.53		D	2.0	0.96	
A	2.5	0.96	All deposits good, especially A which was very smooth though not bright	A	3.0	0.93	All deposits fine
B	2.5	0.60		B	3.0	0.36	
C	2.5	0.87		C	3.0	0.98	
D	2.5	1.46		D	3.0	1.60	
A	3.5	1.00	A, B, C fine: B a bit too granular. All adherent	A	4.0	1.20	All deposits fine
B	3.5	0.35		B	4.0	0.40	
C	3.5	1.30		C	4.0	1.25	
D	3.5	1.80		D	4.0	2.10	
A	4.5	1.30	All deposits fine	A	5.0	1.50	A, C, D fine. B slightly spotted but adherent
B	4.5	0.60		B	5.0	0.90	
C	4.5	1.40		C	5.0	1.60	
D	4.5	2.10		D	5.0	2.50	
A	5.5	1.60	A, C, D good, B hard and spotted	A	6.0	1.90	A, C, D good, B hard and spotted
B	5.5	1.00		B	6.0	1.10	
C	5.5	1.90		C	6.0	2.00	
D	5.5	2.90		D	6.0	3.10	
A	15.0	4.00	All deposits good	A	16.0	4.10	A, B, C good, D poor
B	15.0	2.60		B	16.0	2.80	
C	15.0	4.70		C	16.0	4.90	
D	15.0	6.50		D	16.0	7.40	

TABLE IV
Temperature 70°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks
A	0.5	0.30	All deposits consist of large separate crystals	A	1.0	0.33	All deposits crystalline and adherent. D best
B	0.5	0.15		B	1.0	0.16	
C	0.5	0.30		C	1.0	0.28	
D	0.5	0.20		D	1.0	0.36	
A	1.5	0.39	All deposits crystalline and adherent	A	2.0	0.51	Same as preceding
B	1.5	0.20		B	2.0	0.25	
C	1.5	0.45		C	2.0	0.55	
D	1.5	0.44		D	2.0	0.60	
A	2.5	0.72	Same as preceding	A	3.0	1.10	Same as preceding
B	2.5	0.26		B	3.0	0.30	
C	2.5	0.65		C	3.0	0.69	
D	2.5	0.70		D	3.0	0.79	
A	3.5	1.32	Same as preceding	A	4.0	1.20	All deposits adherent, C most so. All crystalline, D least so
B	3.5	0.35		B	4.0	0.44	
C	3.5	0.78		C	4.0	0.86	
D	3.5	1.10		D	4.0	1.30	

TABLE V
Temperature 20°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks
E	0.5	0.35	Crystalline and non-adherent	E	1.0	0.37	E, G, H good and adherent; F crystalline and non-adherent
F	0.5	0.40		F	1.0	0.55	
G	0.5	0.10		G	1.0	0.28	
H	0.5	0.18		H	1.0	0.32	
E	1.5	0.40	All good, E and F the better	E	2.0	0.52	All good
F	1.5	0.68		F	2.0	0.90	
G	1.5	0.18		G	2.0	0.38	
H	1.5	0.33		H	2.0	0.35	
E	2.5	0.52	All good, G and H smooth and adherent	E	3.0	0.56	E fair, F crystalline, G and H good
F	2.5	1.05		F	3.0	1.32	
G	2.5	0.29		G	3.0	0.36	
H	2.5	0.39		H	3.0	0.42	
E	4.0	0.78	F, G, H good, E fair				
F	4.0	1.80					
G	4.0	0.44					
H	4.0	0.47					

TABLE VI
Temperature 40°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks
E	0.5	0.30	All deposits fair and crystalline	E	1.0	0.42	F and G good, E and H fair
F	0.5	0.41		F	1.0	0.56	
G	0.5	0.04		G	1.0	0.06	
H	0.5	0.07		H	1.0	0.09	
E	1.5	0.60	All deposits good	E	2.0	0.63	All deposits good
F	1.5	0.80		F	2.0	1.04	
G	1.5	0.06		G	2.0	0.07	
H	1.5	0.09		H	2.0	0.12	
E	2.5	0.76	All deposits good	E	3.0	0.90	All deposits good
F	2.5	1.33		F	3.0	1.70	
G	2.5	0.09		G	3.0	0.11	
H	2.5	0.14		H	3.0	0.19	
E	3.5	1.00	All deposits good	E	4.0	1.12	All deposits good
F	3.5	1.90		F	4.0	2.00	
G	3.5	0.12		G	4.0	0.13	
H	3.5	0.26		H	4.0	0.28	

TABLE VII
Temperature 70°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	Remarks
E	0.5	0.13	E and H good, F and G nonadherent	E	1.0	0.20	Same as preceding
F	0.5	0.23		F	1.0	0.30	
G	0.5	0.02		G	1.0	0.03	
H	0.5	0.02		H	1.0	0.03	
E	1.5	0.29	Same as preceding	E	2.0	0.36	Same as preceding
F	1.5	0.53		F	2.0	0.75	
G	1.5	0.04		G	2.0	0.05	
H	1.5	0.04		H	2.0	0.04	
E	2.5	0.43	All deposits good	E	3.0	0.53	All deposits good
F	2.5	0.92		F	3.0	1.13	
G	2.5	0.06		G	3.0	0.06	
H	2.5	0.05		H	3.0	0.05	
E	3.5	0.65	All deposits good	E	4.0	0.75	E, F and G good, D poor
F	3.5	1.26		F	4.0	1.55	
G	3.5	0.07		G	4.0	0.08	
H	3.5	0.06		H	4.0	0.07	

TABLE VIII

Temperature 20°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volt	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volt	Remarks
I	0.5	0.05	All deposits light but good	I	1.0	0.06	I, K and L good, M fair
K	0.5	0.05		K	1.0	0.07	
L	0.5	0.08		L	1.0	0.07	
M	0.5	0.05		M	1.0	0.07	
I	1.5	0.08	I, K and L good, M fair	I	2.0	0.09	All deposits good
K	1.5	0.08		K	2.0	0.09	
L	1.5	0.08		L	2.0	0.09	
M	1.5	0.08		M	2.0	0.09	
I	2.5	0.10	All deposits good	I	3.0	0.12	All deposits good
K	2.5	0.11		K	3.0	0.12	
L	2.5	0.10		L	3.0	0.12	
M	2.5	0.10		M	3.0	0.12	
I	3.5	0.14	All deposits good	I	4.0	0.15	I good, K very fair, L fine, smooth and adherent, M only fair
K	3.5	0.14		K	4.0	0.16	
L	3.5	0.14		L	4.0	0.16	
M	3.5	0.14		M	4.0	0.15	

TABLE IX

Temperature 40°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volt	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volt	Remarks
I	0.5	0.04	I, K and L good, M fair	I	1.0	0.05	All deposits good
K	0.5	0.04		K	1.0	0.05	
L	0.5	0.04		L	1.0	0.05	
M	0.5	0.05		M	1.0	0.06	
I	1.5	0.06	All deposits good	I	2.0	0.08	All deposits good
K	1.5	0.07		K	2.0	0.08	
L	1.5	0.06		L	2.0	0.08	
M	1.5	0.07		M	2.0	0.08	
I	2.5	0.09	All deposits good	I	3.0	0.10	All deposits good
K	2.5	0.09		K	3.0	0.10	
L	2.5	0.09		L	3.0	0.11	
M	2.5	0.09		M	3.0	0.10	
I	3.5	0.12	All deposits good	I	4.0	0.13	I, K and L good, M fair. M good zinc but thin
K	3.5	0.13		K	4.0	0.14	
L	3.5	0.12		L	4.0	0.13	
M	3.5	0.11		M	4.0	0.14	

TABLE X

Temperature 70°

Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volt	Remarks	Sol.	$\frac{\text{Amp}}{\text{dm}^2}$	Volt	Remarks
I	0.5	0.03	I thin and fair, K good. L fair, M good	I	1.0	0.03	K, L and M good, I very poor
K	0.5	0.03		K	1.0	0.04	
L	0.5	0.03		L	1.0	0.04	
M	0.5	0.04		M	1.0	0.05	
I	1.5	0.04	Same as preceding	I	2.0	0.05	Same as preceding
K	1.5	0.05		K	2.0	0.05	
L	1.5	0.05		L	2.0	0.05	
M	1.5	0.06		M	2.0	0.06	
I	2.5	0.05	Same as preceding	I	3.0	0.06	Same as preceding
K	2.5	0.07		K	3.0	0.08	
L	2.5	0.06		L	3.0	0.07	
M	2.5	0.07		M	3.0	0.08	
I	3.5	0.07	Same as preceding	I	4.0	0.08	Same as preceding
K	3.5	0.09		K	4.0	0.10	
L	3.5	0.07		L	4.0	0.09	
M	3.5	0.08		M	4.0	0.10	

TABLE XI

Current densities at which deposits go bad

Sol.	Temperature 20°		Temperature 40°		Temperature 70°	
	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	$\frac{\text{Amp}}{\text{dm}^2}$	Volts	$\frac{\text{Amp}}{\text{dm}^2}$	Volts
A	8.0[1]	3.30	46.5	12.0	59.0	7.2
B	8.0[1]	2.50	49.5	9.9	55.8	4.5
C	8.0[1]	3.30	50.2	12.0	65.0	6.0
D	5.5[1]	4.00	31.0	11.6	43.5	9.4
E	34.0	6.0	28.0	5.0	28.0	3.9
F	34.0	15.3	18.6	6.1	15.2	4.6
G	18.6	1.7	54.0[2]	1.45	48.0[2]	0.8
H	15.5	0.9	18.2	0.7	4.0	0.07
I	18.6	—	18.6	0.48	1.0	0.03
K	12.4	—	9.3	0.30	15.2	0.30
L	12.4	—	9.3	0.25	9.3	0.15
M	15.2	—	12.4	0.35	21.7	0.35

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[1] Run at slower speed than the others.

[2] Run at higher speed than the others.

on February 16, 1907, with solution A and another motor. By varying the speed of the motor, the current density at which the deposit became bad could be varied at will. With the highest speed, about 1200 R. P. M., treeing began at the lower edges of the cathode when the current density was 60–65 amp/dm^2. Even at these values there were no signs of spongy zinc and the deposit was excellent over the bulk of the cathode surface. The limiting value for solution G at 40° and at 70° were obtained on a special run made in 1906. These enormous fluctuations, which were entirely unforeseen when the work was planned, make the actual figures for the current densities of practically no value so far as comparisons are concerned. They are valuable in showing what high current densities may be used both in acid and alkaline solutions provided precautions are taken to prevent impoverishment at the surface of the cathode. In fact there is really no evidence that there would be any upper limit in most cases if one could prevent all impoverishment at the cathode surface. On the other hand it must be remembered that the danger from treeing increases rapidly with increasing fall of potential through the electrolyte.

In general, the alkaline solutions begin to give bad results at a lower current density than the acid solutions. Against this we must set the facts that the deposits from the alkaline solutions are smoother than those from the acid solutions, that the current efficiency is apparently higher, and that the voltage across the terminals is very low. This last is because zinc will precipitate readily from a strongly alkaline solution while it does not come out so readily from strongly acid solutions. The presence of resorcinol seems to have very little effect one way or the other.

A few runs on current efficiency were made. The solutions selected were C at 70°, G at 70°, I at 40° and a plating solution at 20°. The plating solution had the composition: $ZnSO_4.7H_2O$, 82.7 grams; $(NH_4)_2SO_4$, 22.6 grams; water, 500 cc. Stationary cathodes were used, consisting of thin copper plates carefully cleaned. The solutions were run in series with a copper coulometer. With a current density of 1.5 amp/dm², the deposits from solutions G and I soon became so bad as to be unweighable. The following results were obtained with solution C at 70° and with the plating solution at 20° in a run lasting sixty-four minutes.

TABLE XII

Solution	Current density	Deposit	Percent efficiency
C at 70°	1.5 amp/dm²	1.670g	89.3
Plater at 20°	1.5 amp/dm²	1.845g	98.7

The deposit from the plating solution was much better than that from solution C; but both solutions showed signs of severe impoverishment around the cathode. The deposits were streaked and porous, that from solution C being decidedly granular. One run was made with alkaline solutions G and I at the much lower current density of 0.5 amp/dm², the run lasting thirty minutes. An apparent efficiency of 105.0 percent was obtained for G and of 104.5 percent for I. This false efficiency is due to the impossibility of drying the spongy precipitates without causing oxidation, which would give an increased weight. This illustrates very clearly the effect due to stirring. With a rotating cathode the current densities could have been increased enormously without causing the deposits to become bad. On account of the erroneous results which were originally obtained, certain experiments have been tried lately to redetermine the current efficiency in alkaline solutions[1] and to test the effect of a rapidly rotating cathode upon the quality of the deposit. For this purpose, solution G was employed as the electrolyte and the cathode was rotated at a rate of 1200 to 1800 R. P. M., such speed being used as would favor the deposition of good adherent metal. The apparatus was practically the same as that used in making the original volt-ampere runs, with the addition of a copper coulometer. The numerical results are given in Table XIII.

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[1] February, 1907.

TABLE XIII

Solution	Volt	Current density	Time deposit	Percent efficiency
G at 20°	0.13	3.2 amp/dm^2	40 min 0.394g	99.49
G at 20°	0.6	20.0 amp/dm^2	15 min 0.930g	100.70

The zinc obtained with a current density of 3.2 amp/dm^2 was most excellent in quality, there being only a slight roughening on the cathode at the surface of the electrolyte. The zinc deposited at the higher current density appeared as rounded granules of the metal adhering slightly to a very finely crystalline under deposit. These runs also show the extremely low voltage at which zinc is precipitated from its alkaline solutions.

In the experiments previously described, the deposits were not saved as it was necessary to use the cathodes over and over again. A few subsequent runs were made for the special purpose of studying the quality of the deposit under the microscope. The cathodes were copper plates 5 x 15 cm, immersed to a depth of 10 cm in the solutions. These plates received a thin coating of zinc from a cyanide plating solution so that there might be no evolution of hydrogen due to local action between the zinc and the copper. This plating solution was made up as follows:

Dissolve 1 gram neutral $ZnSO_4.7H_2O$ to 20–30 cc water. Add enough potassium cyanide solution to redissolve the precipitated zinc cyanide and dilute to 150 cc solution per gram of hydrated zinc sulphate originally taken. Electrolyze at any temperature with a current density of 5.0 amp/dm^2.

To test the effect of varying conditions, the following runs were made:

Effect of temperature

Solution A, 10 amp/dm^2, at 20°, 40°, 70°.
Solution A, 1 amp/dm^2, at 40°, 70°.

Effect of current density

Solution A, 1.0 amp/dm^2 and 10 amp/dm^2, at 70°.

Solution A, 1.0 amp/dm^2 and 10 amp/dm^2, at 40°.
Solution A + 20 cc 40 percent formaldehyde, 1.0 amp/dm^2 and 10 amp/dm^2 at 40°.

Effect of concentration

Solutions A and D, 1.0 amp/dm^2, at 40°.
Solutions A and D, 10 amp/dm^2, at 40°.
Solutions G and K, 3.0 amp/dm^2, at 40°.
Solutions G + 20 cc 40 percent formaldehyde and K + 20 cc 40 percent formaldehyde, 3.0 amp/dm^2, at 40°.

Effect of reducing agent[1]

Solutions A and A + 20 cc 40 percent formaldehyde, 1.0 amp/dm^2, at 40°.
Solutions A and A + 20 cc 40 percent formaldehyde, 10 amp/dm^2, at 40°.
Solutions G and G + 20 cc 40 percent formaldehyde, 3.0 amp/dm^2, at 40°.
Solutions K and K + 20 cc 40 percent formaldehyde, 3.0 amp/dm^2, at 40°.

The solutions were all stirred thoroughly to prevent the collection of bubbles on the surface of the cathode, the acid solutions by means of a swiftly revolving test-tube brush and the alkaline ones with a revolving zinc plate. Both methods were effective. One anode and one cathode were used and the solutions were contained in 500 cc beakers. Zinc anodes and the prepared copper (practically zinc) cathodes were always used.

From these runs it could in general be said that an increase in concentration or in temperature causes an increase in crystal size, while an increase in current density has the opposite effect and decreases the size of the crystals. Formaldehyde makes the deposit nearly amorphous. From sodium zincate solutions we get a deposit which is very finely crystalline.

The general results of this paper may be summed up:

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[1] Formaldehyde was used instead of resorcinol in these runs because there was less likelihood of any formation of a complex salt and because the decomposition products are cleaner.

1. Good deposits of zinc may be obtained from acid or alkaline solutions even at such high current densities as 60 amp/dm^2.

2. The rate of rotation of the cathode has an enormous effect on the upper limit of the current density.

3. Since zinc will precipitate readily from strongly alkaline solutions, the resistance of these solutions and consequently the voltage across the terminals can be made very low for any given current density.

4. A high current efficiency may be obtained in alkaline solutions.

5. More finely crystalline deposits are obtained from alkaline than from acid solutions.

6. Increasing temperature or concentration increases coarseness of crystals.

7. Presence of formaldehyde decreases the size of the crystals.

8. Increasing the current density decreases the size of the crystals.

This investigation was suggested by Professor Bancroft and carried out under his supervision.

Cornell University

POLARIZATION VOLTAGES OF SILVER NITRATE SOLUTIONS

BY J. A. WILKINSON AND H. W. GILLETT

Some qualitative experiments having shown that the decomposition voltage for acidified silver nitrate solutions varied with the concentration of the acid, experiments were made to determine the various factors. The electrodes consisted of two smooth stiff platinum electrodes, each having a surface of 14.64 cm^2. These were placed 3 cm apart in a beaker which required 150 cc of solution to fill it to the upper edge of the electrodes. This same amount of solution was used in each case. Instead of determining the decomposition voltage or point at which the current begins to increase beyond the residual current it was found better to measure the polarization voltage or counter-electromotive force given by the cell after it had been polarized by a charging current. To do this, the charging circuit was broken and the cell short-circuited on a high-resistance voltmeter. Readings were taken every quarter minute and plotted with voltages and time as the co-ordinates. The horizontal portion of the curve is taken as the polarization voltage. In cases where there is no good horizontal portion, the apparent inversion point of the curve was taken. In Table I is given a good example. The charging current was 6.5 milliamperes for 1.25 minutes, and the polarization voltage is clearly 1.02 volts.

The polarization voltage, as thus determined, is identical with the decomposition voltage when the reaction is reversible. When there is no acid at all in the solution, the readings are not congruent. When there is a large amount of acid in the solution or when the temperature is high, it is hard to get a satisfactory polarization voltage because the chemical action is increased and the deposit dissolves too quickly. The charging or polarization current was varied to meet the exigencies of each particular case, being larger when the concentration of acid or when the temperature was high. When

TABLE I

Temperature 18.5°

3.75 g $AgNO_3$ and 7 g HNO_3 per 150 cc

Voltage readings every quarter minute

1.08	1.02	1.015	0.84	0.27	0.16
1.05	1.02	1.01	0.75	0.25	0.15
1.04	1.02	1.01	0.67	0.24	0.14
1.03	1.02	1.00	0.59	0.22	0.14
1.025	1.02	1.00	0.51	0.21	0.13
1.02	1.02	0.99	0.40	0.20	0.13
1.02	1.02	0.97	0.35	0.19	0.12
1.02	1.02	0.94	0.32	0.18	0.12
1.02	1.015	0.90	0.37	0.16	0.11

difficulties were encountered, readings were taken every five seconds. In every case the observations were checked by repeating them under the same conditions. A calibration curve for the Weston voltmeter was obtained by checking against a standard one belonging to the Department of Physics.

There are four variables to be considered: temperature, silver nitrate, acid, and water. In our experiments we have let each one of these vary by itself, keeping the other three constant. Thus, keeping the acid, water and silver nitrate constant, we varied the temperature. Keeping the temperature and the ratio of acid to water constant, we varied the concentration of the silver nitrate. Keeping the temperature and the ratio of silver nitrate to water constant, we varied the concentration of the acid. Keeping the temperature and the ratio of acid to silver nitrate constant, we varied the concentration of the water. In this way a pretty fair idea can be obtained of the effect due to each of the variables although it was not attempted to make the treatment exhaustive. The silver nitrate was from the stock room and was not purified further. The acid was so-called, pure, concentrated nitric acid from the stock room and its specific gravity was 1.41.

In Table II are two runs to show effect of temperature.

TABLE II

EFFECT OF TEMPERATURE

Solution A = 3.75 g $AgNO_3$ + 0.7 g HNO_3 per 150 cc

Temp.	Volt	Temp.	Volt	Temp.	Volt
14°	0.89	46.5°	0.928	68°	0.948
20	0.89	55.0	0.928	70	0.953
32	0.91	66.0	0.938	—	—

Solution B = 11.296 g $AgNO_3$ + 2.80 g HNO_3 per 150 cc

Temp.	Volt	Temp.	Volt	Temp.	Volt
0°	0.91	20°	0.924	39.5°	0.938
11.5	0.913	27	0.928	50.0	0.944
15.0	0.918	31	0.929	61.0	0.952

When these results are plotted it is seen that the data for solution B lie fairly accurately on a straight line while those for solution A vary irregularly from a straight line parallel to that for solution B. We may therefore consider the temperature coefficient as approximately linear over this range of temperatures and concentrations. The value of the temperature coefficient is approximately +0.0008 volt per degree.

In the next series, the concentration of the silver nitrate was the only variable. A solution of 10 cc HNO_3 and 990 cc H_2O was made up, and varying amounts of $AgNO_3$ were dissolved in 150 cc portions. No corrections were made for expansion or contraction when the silver nitrate dissolved. There was a fluctuation of temperature between the first three and the last five observations; but this change of one degree means a correction of less than one millivolt. The data are given in Table III, and are shown graphically in Fig. 1.

The polarization voltage increases with decreasing concentration but is not a linear function. By extrapolation to zero concentration of silver nitrate, an apparent value of about 1.06 volts is obtained. Of course there is no certainty

Table III
EFFECT OF SILVER NITRATE

g $AgNO_3$ per 150 cc	g HNO_3 per 150 cc	Volts	Temperature
5.473	1.05	0.91	23°
2.923	1.05	0.928	23
1.928	1.05	0.948	23
1.069	1.05	0.967	24
0.623	1.05	0.985	24
0.427	1.05	1.005	24
0.201	1.05	1.025	24
0.100	1.05	1.040	24

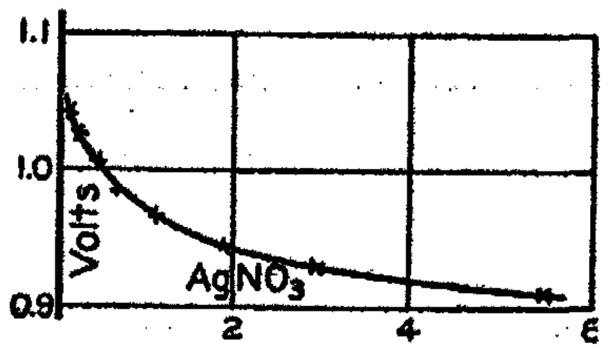

Fig. 1

that this extrapolation is justified but it does not seem an impossible value. The change of 0.13 volt, while the silver nitrate concentration varies in the ratio of 1:55, is unexpectedly large.

In Table IV are the data obtained when nitric acid was the variable. A correction for temperature must be applied before the results are strictly comparable. The results are shown graphically in Fig. 2.

Increasing the nitric acid concentration increases the polarization voltage, at first very much but afterwards less. With no nitric acid this concentration of silver nitrate gives a polarization voltage of about 0.65. Addition of 0.14 gram HNO_3 per 150 cc raises the value to 0.818 and apparently causes the formation of the peroxide or peroxynitrate at the anode. The increase in concentration from 0.14 gram HNO_3 to 10.5 grams raises the polarization voltage by 0.24 volt.

In the experiments to determine the effect of water as a

Table IV
EFFECT OF HNO_3
3 g $AgNO_3$ per 150 cc

g HNO_3 per 150 cc	Volt	Temp.	g HNO_3 per 150 cc	Volts	Temp.
0.14	0.818	25°	2.24	0.986	19.5°
0.28	0.861	25	2.80	0.995	21
0.42	0.915	25	3.08	1.005	20
0.84	0.927	25	3.36	1.005	20
1.12	0.947	25	3.64	1.015	20
1.36	0.948	19.5	4.20	1.025	21
1.40	0.952	25	4.90	1.033	21
1.68	0.965	20	6.16	1.034	25
1.82	0.966	25	7.70	1.044	21
1.96	0.972	19.5	10.50	1.058	21
2.16	0.981	20	—	—	—

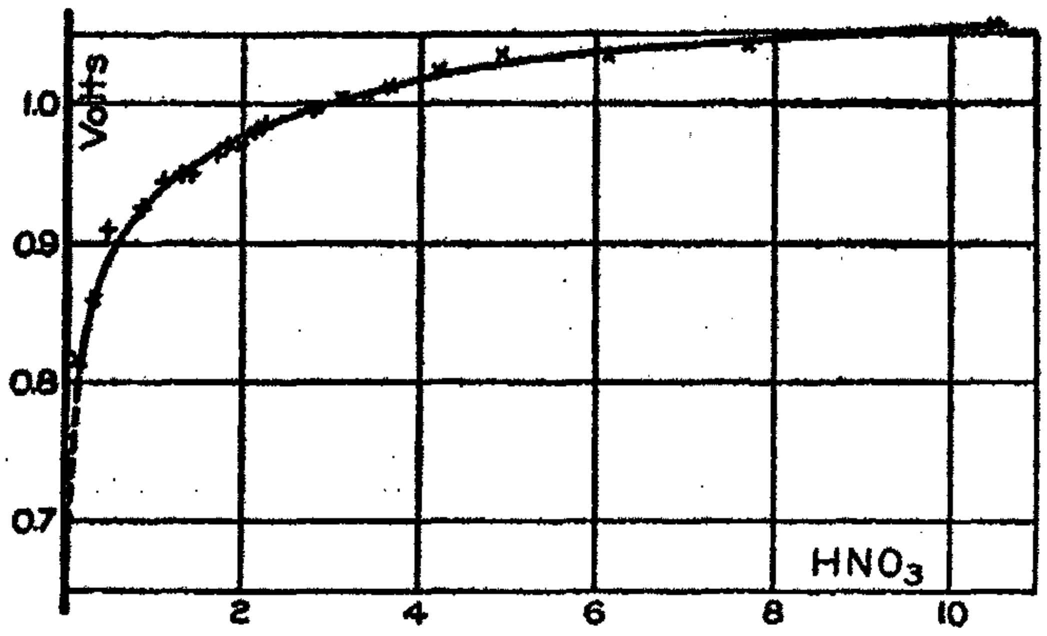

Fig. 2

variable, the ratio of acid to silver nitrate was kept constant. The results are given in Table V and in Fig. 3.

With increasing dilution the values for the polarization voltage fall off slowly at first, but decrease very rapidly for the very dilute solutions. It is not clear what would be the significance of an extrapolation to infinite dilution. It must also be kept in mind that the product formed at the anode probably changes when the polarization voltage falls distinctly below 0.8 volt though this is not a point on which we have any evidence to offer.

Table V

EFFECT OF WATER

g $AgNO_3$ per 150 cc	g HNO_3 per 150 cc	Volts	Temp.
Ratio of $AgNO_3$ to $HNO_3 = 4.13$			
11.296	2.735	0.924	20°
7.527	1.823	0.91	20
5.090	1.234	0.90	22
2.545	0.617	0.89	22.5
1.273	0.308	0.866	24
0.636	0.154	0.832	24.5
0.318	0.077	0.745	24.5
0.159	0.038	0.620	25
Ratio of $AgNO_3$ to $HNO_3 = 18.7$			
13.030	0.700	0.851	21°
4.340	0.233	0.817	21
2.170	0.116	0.793	21
1.085	0.058	0.755	21
0.870	0.046	0.655	24
0.543	0.029	0.630	24
0.435	0.435	0.639	24

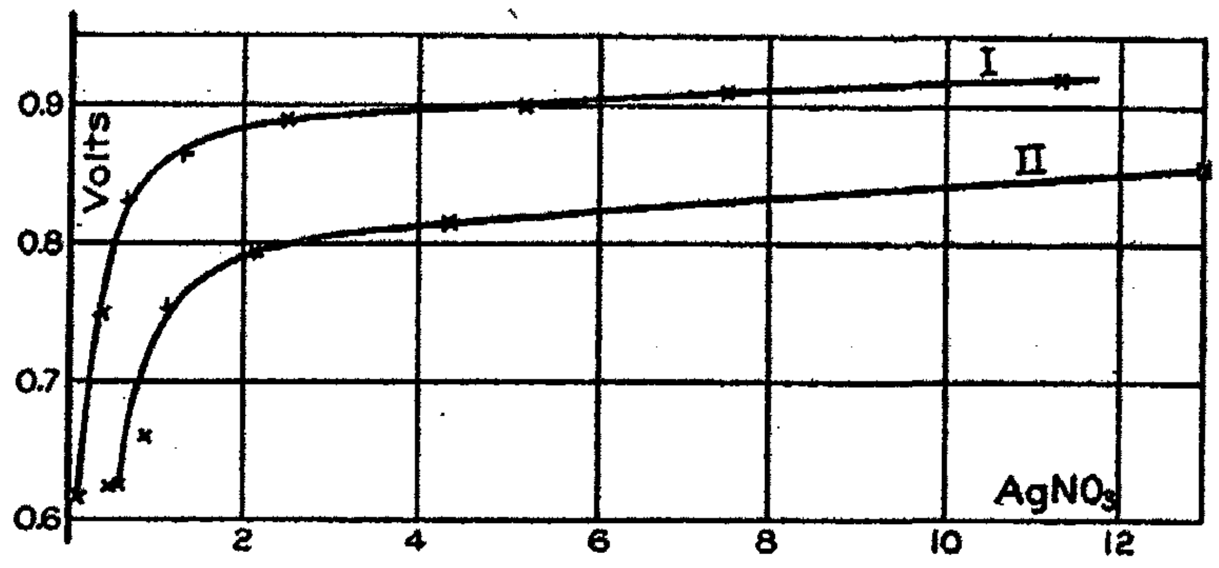

Fig. 3

From the last three tables we see that the polarization voltage rises when the concentration of silver nitrate decreases and that of nitric acid remains constant; that it falls when the concentration of nitric acid decreases and that of silver nitrate remains constant; and that it falls when the concentrations of silver nitrate and nitric acid decrease in the same ratio. Owing to the marked effect thus due to the nitric acid, a few experiments were made to determine the effect of nitric acid at each electrode.

The same two platinum electrodes and the acidified silver nitrate solution were placed inside a porous cup which dipped into a beaker containing H_2SO_4 (1 : 5), Hg_2SO_4Hg. The porous cup had previously been boiled out with a potassium nitrate solution to prevent the precipitation of silver sulphate in the pores. The mercurous sulphate was prepared by the method of Hulett[1]. The connections were so arranged that it was possible to polarize the platinum electrodes and then to connect either one of them through the voltmeter with the mercury electrode. Using a voltmeter one measures potential differences instead of electromotive forces; but this is immaterial so far as studying the relative effect of acid on the two polarized electrodes. The mercury electrode is the anode in all cases. The data are given in Table VI and are plotted in Fig. 4.

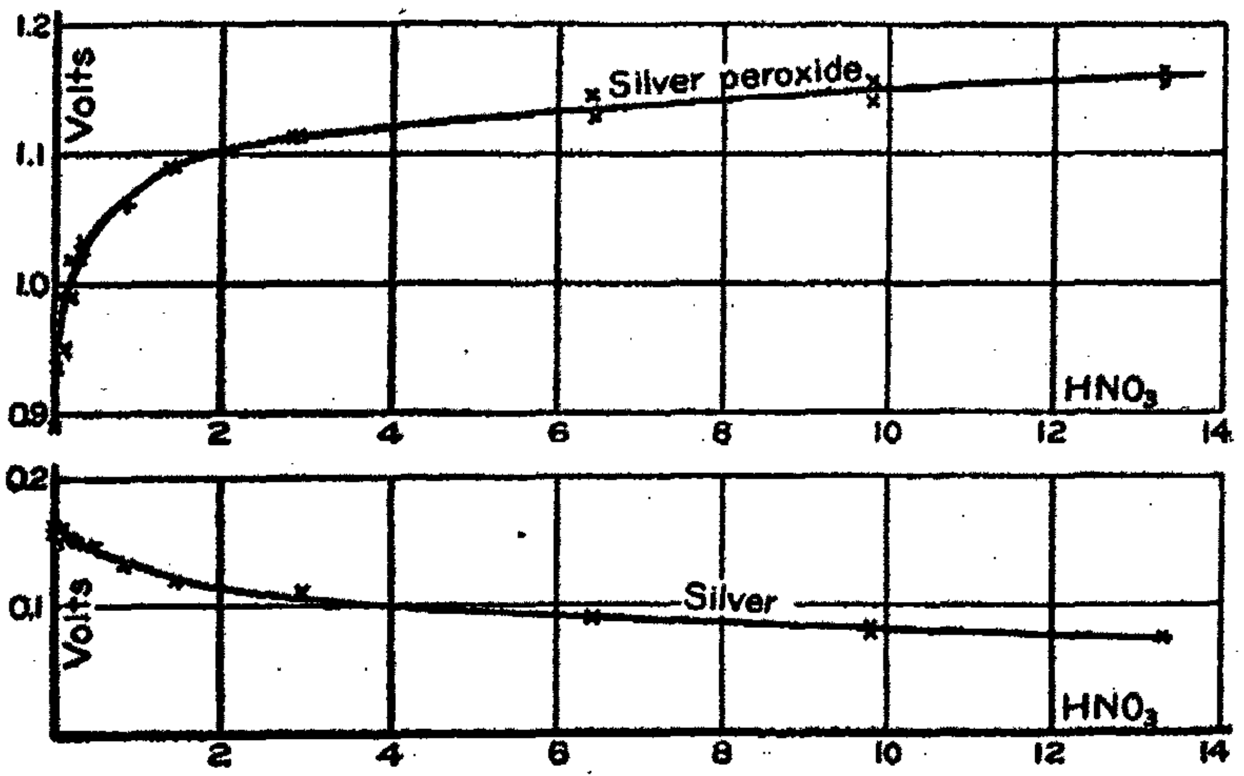

Fig. 4

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[1] Trans. Am. Electrochem. Soc., 6, 109 (1904).

From Table VI it is clear that addition of nitric acid decreases slightly the potential difference between silver and the electrolyte and increases largely the potential difference between the peroxide electrode and the electrolyte. The result is not what one might have expected. The addition of nitric acid might reasonably have been expected to force back the dissociation of silver nitrate to some extent and thus to have increased the potential difference. On the other hand it must be remembered that the addition of nitric acid has an effect on the potential difference between the solutions. If we ignore the potassium sulphate in the walls of the porous cup and the silver nitrate in the cathode chamber, the effect due to the nitric acid is of the same general order as that required by Nernst's formula.

TABLE VI

Temp.	g $AgNO_3$ per 150 cc	g HNO_3 per 150 cc	Volts Hg-Ag	Volts Hg-peroxide
19°	3.00	0.00	0.16	0.89
20	3.00	0.07	0.16	0.948
20	3.00	0.14	0.15	0.987
20	3.00	0.28	0.145	1.015
20	3.00	0.42	0.14+	1.035
20	3.00	0.77	0.135	1.055
20.5	3.00	1.47	0.12	1.09
21	3.00	2.94	0.115	1.107
22	3.00	6.37	0.085	1.148
23	3.00	9.80	0.08	1.154
24	3.00	13.3	0.06+	1.16
19°	3.00	0.00	0.155	0.933
22	3.00	0.07	0.15	0.987
22	3.00	0.135	0.145	1.015
22	3.00	0.28	0.14	1.03
22.5	3.00	0.49	0.135	1.045
22.5	3.00	0.77	0.125	1.058
22.5	3.00	1.47	0.12	1.078
23	3.00	2.80	0.105	1.098
24.5	3.00	6.30	0.08	1.120
25	3.00	9.80	0.07+	1.135
26	3.00	13.3	0.06+	1.150

It is an interesting question whether one is justified in assuming that the solution pressure of silver in aqueous silver nitrate is the same as in that of a solution of silver nitrate in aqueous nitric acid. Kahlenberg[1] has shown that the addition of pyridine to aqueous silver nitrate changes the solution pressure. Pyridine is an organic liquid, miscible in all proportions with water. Nitric acid is an inorganic liquid, miscible in all proportions with water. It would be very interesting—though entirely outside the scope of these experiments—to determine the so-called single potentials for silver and silver nitrate in a solvent varying continuously from pure water to practically pure nitric acid.

The effect of acid at the peroxide electrode is qualitatively what one would expect. It is impossible to discuss the quantitative side until more is known about the real composition of what is called silver peroxide.

The general results are as follows:

1. The polarization voltage of acidified silver nitrate solutions may be made to vary from 0.625 volt to 1.05 volts.
2. The polarization voltage varies with variations of temperature, silver nitrate, nitric acid and water.
3. The temperature coefficient is approximately 0.8 millivolt per degree over a fair range of compositions and temperatures.
4. A decrease in the concentration of silver nitrate increases the polarization voltage if the concentration of nitric acid be kept constant.
5. A decrease in the concentration of nitric acid decreases the polarization voltage if the concentration of silver nitrate be kept constant.
6. The polarization voltage decreases if the concentration of silver nitrate and nitric acid are decreased in the same ratio.
7. When measured against a sulphuric acid, mercurous sulphate, mercury electrode, the potential difference between silver and the electrolyte is decreased slightly by the addition

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[1] Jour. Phys. Chem., 3, 403 (1899).

of nitric acid, while the potential difference between peroxide and electrolyte is apparently increased a good deal.

8. The abnormal result with the silver electrode may be due to a change in the potential difference between the solutions.

9. There is nothing in the data obtained to show whether or when the product formed at the anode changes from peroxide to oxygen.

This work was suggested by Professor Bancroft and has been carried on under his supervision.

Cornell University

A MANOSTAT

BY W. LASH MILLER

In connection with Mr. Stevenson's article in a recent number of this Journal,[1] a short account of a manostat used in this laboratory between 1895 and 1898 may be of interest.

In its final form the apparatus consisted of two cylinders of eight-inch iron pipe (steam pipe), three feet six inches high, framed together, and connected to the apparatus to be kept at constant pressure and to the air pump respectively. The cylinders were connected by the "electric tap," operated by a solenoid which was actuated through a relay by a manometer as in Brown's manostat, and which took the place of the electromagnetic clutches and moving shaft employed by him. A string from the solenoid passed round a groove in the edge of a circular plate attached to the barrel of the tap, and the whole was adjusted once for all so that the tap was only very slightly opened by the pull of the solenoid; this prevented a rush of air, and regulated the interval during which the tap remained open.

In addition to the electric tap, the cylinders were connected by the "by-path," a tap opened by hand and provided with pointer and scale so that its position could easily be adjusted and recorded. When the apparatus was working, this by-path was set so that the electric tap opened about four or five times per minute, remaining open about two seconds each time. The pressure in the cylinder directly connected to the pump was kept within a few inches of that in the other by means of a tap, with pointer and scale, opening to the air.

From the point of view of Stevenson's classification, therefore, this regulator consisted of a manostat of class *ii* in series with a rougher apparatus of class *i*. We used it for pressures between 1000 mm and 50 mm; its very satisfactory performance must be ascribed to the large capacity of the

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[1] Jour. Phys. Chem., 11, 107 (1907).

cylinders, the provision of a by-path, the regulation of pressure in the cylinder connected to the pump, and the proper adjustment of the opening of the electric tap.

The apparatus was not difficult to construct, all the connections being made of $^1/_4$-inch gas pipe, threaded in the usual manner and well covered with paint. To avoid leaks at the electric tap, the barrel was made two inches long and almost cylindrical; it was placed in a cup of vaseline; to prevent binding, it turned on a point whose height could be adjusted by a screw. The solenoid consisted of two pounds No. 28 copper wire, wound on a hollow spool as it came from the shop; the plunger was of soft iron three inches long and half an inch in diameter. To complete the magnetic circuit, the spool stood on an iron casting with a knob projecting about an inch into the spool, the outside of the coil was covered with sixteenth-inch iron, and a circular disc of the same material was attached to the plunger. The rod with the electric connection to the mercury of the manometer carried a pointer which moved over a scale; when set to any desired pressure it was clamped to the scale, and subsequent changes in the barometer were corrected for by a screw which moved scale, rod, and all, past a stationary mark.

The University of Toronto,
April, 1907.

THE COMPOSITION OF SOLID PHASES IN FOUR-COMPONENT SYSTEMS[1]

BY JAMES M. BELL

A method for the determination of the composition of solid phases which cannot be completely separated from the mother-liquor by washing with water on account of the instability of the solid phase on the addition of pure water has been proposed by Schreinemakers[2] and later by Bancroft.[3] This method consists in the use of a triangular diagram, on which are plotted the composition of the mother-liquor and that of the solid with some of the adhering mother-liquor. The line joining the two points passes through the point representing the composition of the solid phase. By determining several such lines, the intersection gives the composition of the solid phase. In this way an indirect analysis has been accomplished of solid phases without separation from the solution. The method has hitherto been employed only for three-component systems, where the solid phase which is stable along any boundary curve was to be analyzed. In the case of four-component systems, one solid phase exists over a field and so long as only one solid is present, a modification in the above triangular diagram method may be employed to determine the composition of the solid phase.

The present method involves the use of two such diagrams. Analyses are made as before for all four components in the mother-liquor and in the solid with adhering mother-liquor, at two different points taken on the same field. The results are then plotted on the first of the diagrams, in which the distances from the sides of the triangle represent the percentage of A, of B, and of the sum of C and D, respectively. The point of intersection of two lines gives the percentage of A, of B, and of the sum of C and D in the solid phase. The

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[1] Published by permission of the Secretary of Agriculture.

[2] Zeit. phys. Chem., 11, 81 (1893).

[3] Jour. Phys. Chem., 6, 178 (1902).

same results are then plotted in another diagram in which the coordinates are the percentages of C, of D, and of the sum of A and B, respectively. From the two diagrams the percentage composition of all four components may be determined graphically.

This method has been applied in the following paper on the solubility of some alkali salts, to determine the composition of a double compound which was encountered. The first of the two figures on page 418 shows that there was no sodium chloride in the compound and also that there was 61 percent sodium sulphate. Owing to the very acute angle at which the lines happen to meet, in the second figure, the present instance does not afford a good example of the application of this method. However, assuming that the lines meet as they are drawn—and it is shown by a different method that they do—the second figure shows that neither sodium chloride nor water is present in the solid phase, and that the solid phase consisted of 39 percent calcium sulphate and 61 percent sodium sulphate, or $2CaSO_4.3Na_2SO_4$. Of course, if the combination of components should happen to be chosen originally as in the second diagram, it would be unnecessary to draw another diagram. In other words, if the solid consists of only two of the components, and if the proper combination should happen to be chosen, a second diagram becomes unnecessary.

This method is subject to the same limitation as in the case of a single diagram. If two lines cross at a very small angle, a very slight error in analysis causes a very great error in the determination of the intersection of the lines.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.

THE SOLUBILITY OF CERTAIN SALTS PRESENT IN ALKALI SOILS[1]

BY F. K. CAMERON, J. M. BELL, AND W. O. ROBINSON

Statement of the Problem.—In previous papers from this laboratory results have been reported for a number of the possible systems which may exist containing the salts commonly found in the soils of arid regions. In the present investigation one of the simplest systems was taken as a starting point and by the successive addition of other components more complex systems were realized, since in this way the bounding isotherms and fields could be most readily determined. As the primary object of the investigation was to obtain information regarding the salts occurring in nature as "alkali," certain conditions were imposed on the several systems, thus approximating field conditions and at the same time materially simplifying the problem. The data here given are for equilibrium conditions at 25° C.

The first results given are for the mutual solubilities of the chlorides of calcium and sodium, and they show that solid calcium chloride does not exist in contact with a solution containing sodium chloride except at very low concentrations of the latter, and at very high concentrations of calcium chloride. It is, therefore, highly improbable that solid calcium chloride exists under normal alkali conditions.[2]

The second system contains sodium chloride, sodium sulphate and water. The solubility curves and the solid phases in contact with the several sets of solutions were determined. This system shows three solubility curves, one representing solutions in contact with the solid decahydrate of sodium sulphate, a second curve for solutions in contact with the solid anhydrous sodium sulphate, and the third curve

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[1] Published by permission of the Secretary of Agriculture.

[2] For illustrations of the occurrence of calcium chloride under unusual conditions, see Bull. No. 18, Division of Soils, U. S. Dept. Agriculture (1901), pp. 44-45.

in contact with sodium chloride. This system was the starting point for the more complex systems considered in this investigation.

The third system was realized by adding calcium sulphate to the second system. In addition to the fields for the decahydrate of sodium sulphate, anhydrous sodium sulphate, and sodium chloride, this system was also found to contain fields for gypsum and for a double sulphate of sodium and calcium whose composition has been determined. The position of the boundary curves and the composition of all constant solutions was also determined.

Several systems containing calcium carbonate have also been studied, *viz.*, the solubility of calcium carbonate in various sodium chloride and sodium sulphate solutions, from which free carbon dioxide has been excluded; also the solubility of calcium carbonate in sodium chloride solutions saturated with carbon dioxide.

System VII was realized by adding calcium carbonate to System II, taking precaution to exclude any free carbon dioxide. The boundary curves in System II were but slightly displaced by the addition of the new component to the system, and but one new field was thereby introduced, namely, the field for solid calcium carbonate.

System VIII was formed by adding both calcium sulphate and calcium carbonate to System II, taking precautions as in the case of System VII to exclude free carbon dioxide. In this case it was found that the boundary curves as they exist in System III are but slightly displaced. No new fields were found, though now, of course, each field represents solutions in contact with two solid phases, one of which was calcium carbonate in every case. The composition of all constant solutions and the position of the boundary curves were determined.

Finally the ninth system was obtained by saturating all solutions of System VIII with carbon dioxide at a pressure equal to the atmospheric pressure; that is, the total pressure of the vapor phase was equal to the atmospheric pressure.

In this system none of the solid phases in System VIII disappeared, nor were any new phases recognized. There was, however, a well-marked displacement of the position of some of the boundary curves as they exist in that system, and consequently in the composition of the constant solutions. Each field in this system represents but two solid phases, although it might be supposed that, by the introduction of the new component, carbon dioxide, a field should represent three solid phases; but coincident with the introduction of the new component the condition was imposed that the pressure of the vapor phase should be the atmospheric pressure, thus arbitrarily reducing the variance of the system by one, or in other words, to the same variance as that of System VIII.

Analytical Methods.—In this work it has been necessary to determine sodium chloride, sodium sulphate, calcium sulphate, calcium carbonate, carbonic acid otherwise combined, and, in a few cases, water. The sodium chloride was determined volumetrically by titrating with standard silver nitrate solution, using potassium chromate as indicator. The sulphates were determined by precipitation with barium chloride in the usual manner. The sodium was not directly determined but was calculated by difference. The calcium was precipitated as the oxalate, with due precautions, and, in general, weighed after blasting to the oxide. When small in quantity, however, the calcium oxalate was titrated in a warm dilute sulphuric acid solution with a dilute solution of potassium permanganate. The carbonates were determined by adding a slight excess of standard sulphuric acid, boiling to expel the freed carbon dioxide, and titrating the excess of acid with a standard solution of sodium hydroxide, using phenolphthalein as indicator, the results being calculated as calcium carbonate.

System I. Calcium Chloride, Sodium Chloride, Water.—The mutual solubility of calcium chloride and of sodium chloride in aqueous solution was determined at 25°. A preliminary experiment showed that there could be but two curves; *i. e.*, but two stable solid phases under these conditions. It was found from data for the cooling curve that the temperature at which calcium chloride hexahydrate changes to the tetrahydrate in the presence of solid sodium chloride was 29.0°. As the stable hydrate of calcium chloride at 25°, both when no other salt is present and also in the presence of sodium chloride is the hexahydrate, this is the only stable form at that temperature.

Table I

Mutual solubility of calcium chloride and sodium chloride in water at 25° C

Density $\frac{25^\circ}{25^\circ}$	$CaCl_2$ per 100 grams H_2O	NaCl per 100 grams H_2O	Solid phase
	Grams	Grams	
—	84.0[1]	0.0	$CaCl_2.6H_2O$
1.4441	78.49	1.846	$CaCl_2.6H_2O$, NaCl
1.3651	58.48	1.637	NaCl
1.3463	53.47	1.799	"
1.2831	36.80	7.77	"
1.2653	30.08	10.70	"
1.2367	19.53	18.85	"
1.2080	3.92	32.48	"
1.2030	0.0	35.80	"

System II. Sodium Chloride, Sodium Sulphate and Water.—The three-component system, sodium chloride, sodium sulphate and water, has been investigated by Meyerhoffer and Saunders[2] while working on the effect of foreign salts, in solu-

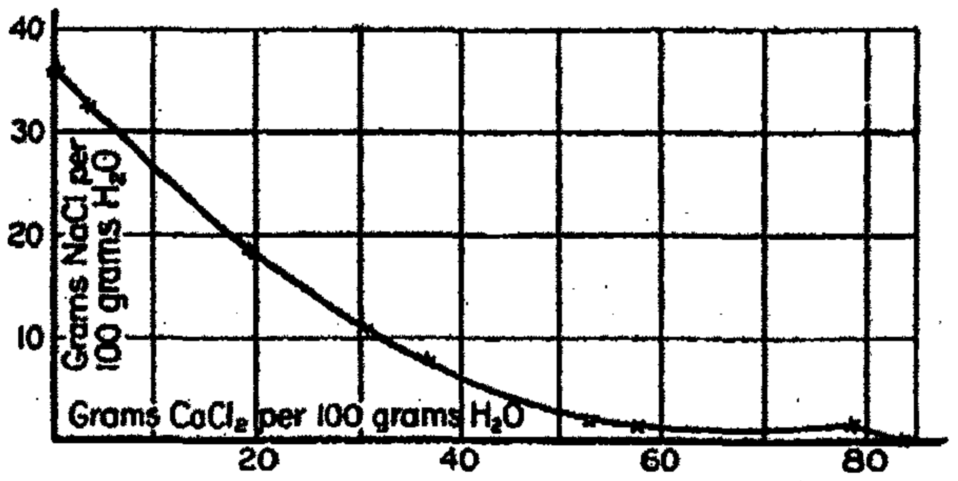

Fig. 1

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[1] From Landolt-Börnstein, Physikalisch-Chemische Tabellen (1905), p. 526.

[2] Zeit. phys. Chem., 31, 373 (1899).

tion, upon the inversion points of hydrated salts. It was found that the change from Glauber's salt to anhydrous sodium sulphate, which takes place in aqueous solution at 32.8°, occurs at 17.9° when the solution is saturated with respect to sodium chloride. It is apparent that at intermediate temperatures either form of sodium sulphate may be stable in solutions containing sodium chloride, depending upon the concentration of the latter salt. Of course for a definite temperature, the solutions in contact with the decahydrate are less concentrated with respect to sodium chloride than the solutions in contact with the anhydrous sulphate.

Browne[1] has also investigated this system, in part, when testing the "indirect method of analysis" proposed by Schreinemakers[2] and Bancroft[3] for the determination of the composition of solid phases which would undergo decomposition if washed with water to remove the mother-liquor. In this work by Browne solutions of sodium chloride containing from 0 to 11.7 percent sodium chloride were saturated with sodium sulphate at 33° and cooled down to 23°. The solid crystallizing out was found to be the decahydrate of sodium sulphate.

Seidell,[4] in this laboratory, studied the problem through the entire range of concentrations and at various temperatures between 10° and 35°. His results confirm the observations of Meyerhoffer and Saunders. Below 18° he found that the complete solubility curve consisted of two branches along which the stable solids were the decahydrate of sodium sulphate, and sodium chloride. Between 18° and 33° there were three branches representing solutions in equilibrium with the decahydrate of sodium sulphate, anhydrous sodium sulphate, and sodium chloride. Above 33° the decahydrate no longer exists and there are, therefore, but two branches.

The curves at 25° have been redetermined and the stable

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[1] Jour. Phys. Chem., 5, 287 (1902).

[2] Zeit. phys. Chem., 11, 81 (1893).

[3] Jour. Phys. Chem., 6, 178 (1902).

[4] Am. Chem. Jour., 28, 52 (1902).

solid phases present have been established by the indirect method. The following Table (II) gives the data, and Fig. 2 their graphical presentation.

TABLE II

Data for the solubility curves in the system, sodium chloride, sodium sulphate and water, at 25° C

Density $\frac{25°}{25°}$	NaCl in		Na_2SO_4 in		Solid phase
	100 cc solution	100 gms. H_2O	100 cc solution	100 gms. H_2O	
	Grams	Grams	Grams	Grams	
1.2180	0.00	0.00	26.93	28.55	$Na_2SO_4.10H_2O$
1.2173	2.77	2.96	24.88	26.60	"
1.2162	5.37	5.79	22.62	24.32	"
1.2150	7.92	9.90	19.73	21.41	"
1.2275	12.20	13.43	17.86	19.62	"
1.2385	14.38	15.82	17.86	19.64	"
1.2571	17.10	19.13	18.55	20.73	$Na_2SO_4.10H_2O$; Na_2SO_4
1.2476	20.67	23.22	14.50	16.28	Na_2SO_4
1.2429	23.81	26.54	11.32	12.62	"
1.2438	27.26	31.06	8.76	9.98	"
1.2451	28.22	32.41	8.65	9.93	"
1.2453	28.59	33.00	8.54	9.84	Na_2SO_4; NaCl
1.2309	29.44	33.81	5.81	6.66	NaCl
1.2162	30.30	34.60	2.97	3.38	"
1.2002	31.52	35.80	0.00	0.00	"

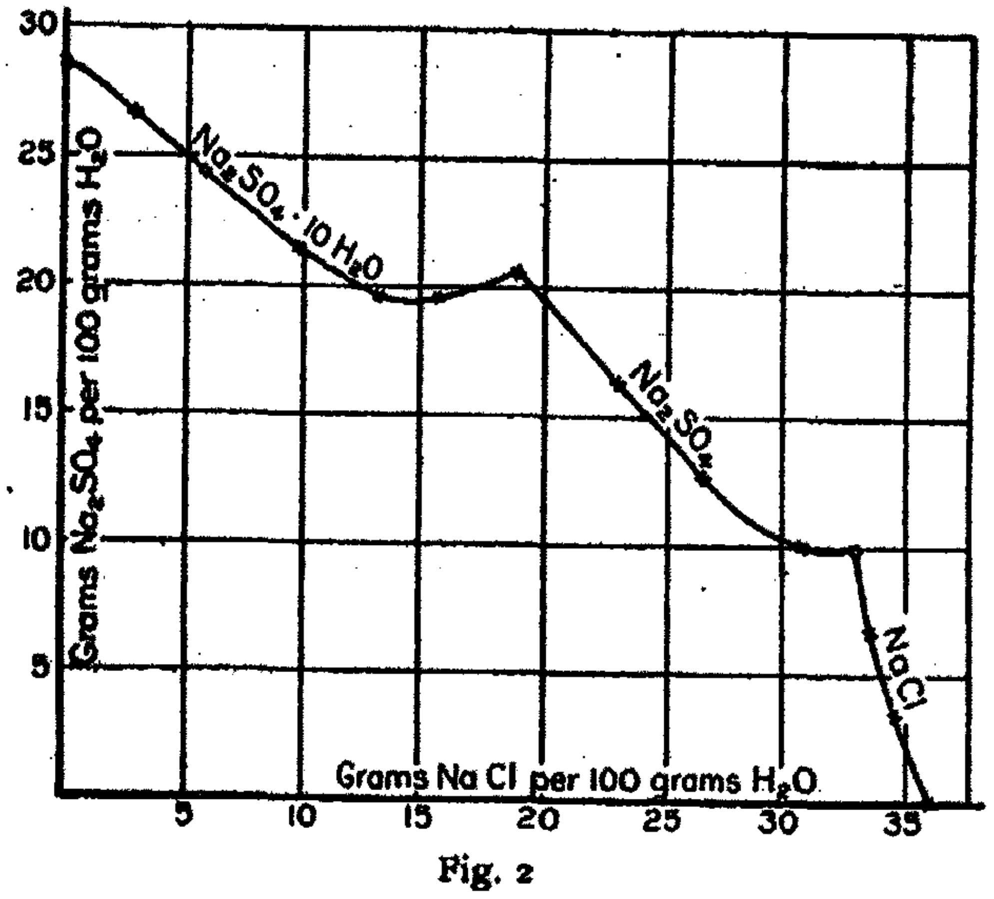

Fig. 2

The composition of the solution in equilibrium with anhydrous sodium sulphate and sodium chloride, at 25°, has been determined by van't Hoff,[1] who found 33.1 grams sodium anhydrous sodium sulphate and sodium chloride, at 25°, has been determined by van't Hoff,[1] who found 33.1 grams sodium chloride and 9.9 grams sodium sulphate to 100 grams water. The figures in the above table are in good agreement with these.

To identify the solid phases, solutions were taken corresponding to two points on each curve. In selecting each pair of points, they were chosen as far apart as could conveniently be done. These solutions were then analyzed for chlorides and sulphates. The solids in contact with these solutions were partially freed from mother-liquor and each mixture of solid with adhering mother-liquor was analyzed for the same constituents as were determined in the free solutions. By plotting the data thus obtained, the intersections representing the solid phases, were found to correspond to the decahydrate of sodium sulphate, to anhydrous sodium sulphate and to sodium chloride. The analytical data are given in Table III and are plotted in Fig. 3.

TABLE III

Data for identification of solid phases in the system, sodium chloride, sodium sulphate, and water, at 25° C., by the indirect method.

	Density	Mother-liquor			Mother-liquor and solid	
		NaCl	Na_2SO_4		NaCl	Na_2SO_4
		Per cent	Per cent		Per cent	Per cent
E	1.2099	3.43	19.01	G	1.68	33.74
F	1.2201	8.26	15.93	H	2.57	35.62
K	1.2512	14.96	13.40	M	8.80	49.49
L	1.2431	22.10	7.12	N	7.88	66.80
L	1.2431	22.10	7.12	N'	9.21	59.30
P	1.2374	23.20	5.88	R	58.46	2.39
Q	1.2117	25.17	1.75	S	62.30	0.90

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[1] Sitzungsber. Akad. Wiss. Berlin, 1899, 810.

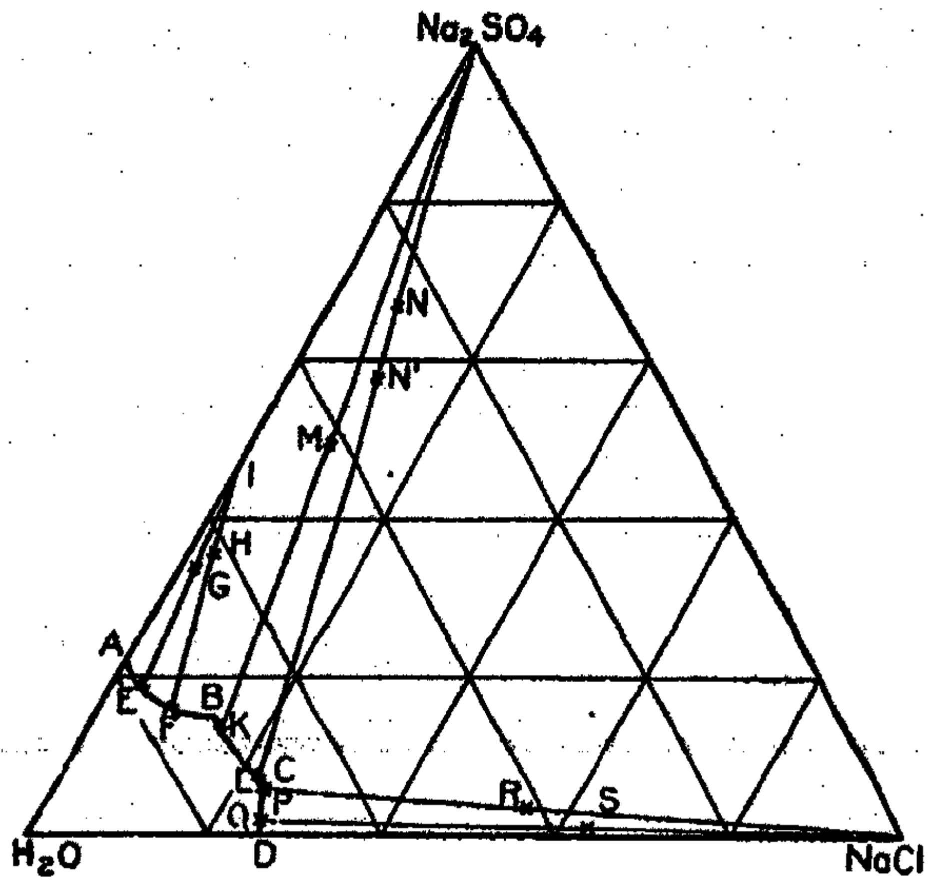

Fig. 3

System III. Sodium Chloride, Sodium Sulphate, Calcium Sulphate and Water.—This system may be considered as made up of the following components, namely, Na_2O, CaO, HCl, SO_3 and H_2O. It is therefore a five-component system. But since in this investigation the condition was imposed that the sum of the bases should be exactly equivalent to the acids one degree of freedom is thereby lost and the system, to all intents and purposes, becomes one of four components. It will be simpler for the present purpose to consider as components, NaCl, Na_2SO_4, $CaSO_4$ and H_2O, and to regard the problem presented by this system as the solubility of calcium sulphate, or of a double salt containing it, in mixed solutions of sodium chloride and sodium sulphate. It will be desirable therefore to consider first the solubility of calcium sulphate in solutions of each of the sodium salts.

The solubility of calcium sulphate in aqueous solutions of sodium chloride has been studied by Droeze,[1] Tilden and

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[1] Ber. chem. Ges. Berlin, 10, 330 (1877).

Shenstone,[1] Lunge,[2] Cameron,[3] Orloff,[4] Cloez[5] and d'Anselme.[6] The details of these several investigations have been brought together recently in another publication.[7] It appears that the solubility curve at ordinary temperatures for solutions in which calcium sulphate or gypsum is the solid phase, passes through a maximum point. At 26° the concentration is approximately 140 grams sodium chloride and 7.2 grams calcium sulphate per liter of solution, and these figures must be nearly correct for 25°, since it has been repeatedly shown that small differences in temperature in this neighborhood produce very small differences in the solubility curve. The concentration of the "constant solution" with both calcium sulphate and sodium chloride present as solid phases, at 25° has been found by Cameron and Brown[8] to be 318.3 grams sodium chloride and 5.52 grams calcium sulphate per liter. In this system no new solid phases appeared.

The solubility of calcium sulphate in aqueous solutions of sodium sulphate has been studied by Droeze,[9] Cameron and Seidell,[10] Cameron and Breazeale,[11] and details of the investigations have been brought together recently in the bulletin cited above.[12] The solubility curve for 25° with calcium sulphate as the solid in contact with the solutions, passes through a minimum point at a concentration, approximately, of 15 grams sodium sulphate and 1.4 grams calcium sulphate per liter of solution. The concentration of the solution in contact with both solid sulphates at 25°, has been found by Cameron

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[1] Proc. Roy. Soc., 38, 331 (1885).

[2] Jour. Soc. Chem. Ind., 4, 31 (1885).

[3] Jour. Phys. Chem., 5, 556 (1901); Bull. No. 18, Division of Soils U. S. Dept. Agriculture (1901).

[4] Jour. Russ. Phys. Chem. Soc., 34, 949 (1902).

[5] Bull. Soc. Chim. Paris [3], 29, 167 (1903).

[6] Ibid., 29, 372 (1903).

[7] Bull. No. 33, Bureau of Soils, U. S. Dept. Agriculture (1906).

[8] Jour. Phys. Chem., 9, 210 (1905).

[9] Ber. chem. Ges. Berlin, 10, 330 (1877).

[10] Jour. Phys. Chem., 5, 643 (1901).

[11] Ibid., 8, 335 (1904).

[12] Bull. No. 33, Bureau of Soils, U. S. Dept. Agriculture (1906).

and Brown to be 254.6 grams sodium sulphate and 2.58 grams calcium sulphate per liter. At this temperature no new solid phase appeared in this system.

The positions of some of the boundary curves for this four-component system were found by adding an excess of gypsum to each of the solutions described in Table II. When equilibrium had been established, each solid was found by microscopic examination to be composed of at least two and sometimes three kinds of crystals. In cases where two solids were found the solutions were on boundary curves and where three solids were found, the solution was a "constant solution," as at a fixed temperature the greatest number of solids which can exist in such a system is three, unless the temperature happens to be that of an invariant point, when four solid phases may coexist. The examination of the solids under the microscope showed the presence of one new crystalline form, which existed over a rather wide range of concentration. This was found to be a double sulphate of sodium and calcium and for the present it will be designated as "double sulphate." Analyses of these solutions for the various components are given in Table IV, and also the solid phases with which each solution is in contact have been given.

By comparison of Table II and IV it will be seen that the presence of gypsum in solution depresses the solubility of sodium sulphate considerably and also depresses the solubility of sodium chloride but to a lesser extent. The position of the points B and C of Fig. 2 have been slightly displaced also by the addition of calcium sulphate. The new positions of these points have been shown in Fig. 4 A, B, C and D. This figure has been distorted somewhat to magnify some of the differences which if drawn to scale would not be recognizable. The quantity of calcium sulphate in solution at these points is also widely different and this has been indicated by the width of the strip ABCDD'C'B'A', the points B and B' and the points C and C' respectively being quite close together. The table also indicates that for a certain distance along A'B' and for a certain distance along D'C' gypsum is the solid

TABLE IV

Data for boundary curves in the system, sodium chloride, sodium sulphate, calcium sulphate and water at 25° C

Density $\frac{25°}{25°}$	NaCl in		Na_2SO_4 in		$CaSO_4$	Solid phases
	100 cc solution	100 gms. H_2O	100 cc solution	100 gms. H_2O	per 100 gms. H_2O	
	Grams	Grams	Grams	Grams	Gram	
1.2123	0.00	0.00	25.63	27.12	0.2648	$Na_2SO_4.10H_2O$ and $CaSO_4.2H_2O$
1.2100	2.76	2.95	23.78	25.37	0.2308	" " "
1.2107	5.52	5.93	21.97	23.39	0.2033	" " "
1.2176	9.29	10.05	19.57	21.25	0.1779	" " "
—	—	—	—	—	0.1330	" " "
—	—	—	—	—	0.0841	$Na_2SO_4.10H_2O$ and double sulphate
1.2573	17.06	19.23	19.34	21.79	0.0354	$Na_2SO_4.10H_2O$, double sulphate, and Na_2SO_4
1.2485	20.44	23.00	15.20	17.02	0.0313	Na_2SO_4 and double sulphate
1.2468	23.19	26.40	11.77	13.40	0.0319	" " " "
—	—	—	—	—	0.0311	" " " "
—	—	—	—	—	0.0310	" " " "
1.2442	28.12	32.18	8.52	9.50	0.0312	Na_2SO_4, double sulphate, and NaCl
—	—	—	—	—	0.0968	NaCl and double sulphate
—	—	—	—	—	0.1795	NaCl and $CaSO_4.2H_2O$
1.2051	31.02	35.09	0.00	0.00	0.6333	" " "

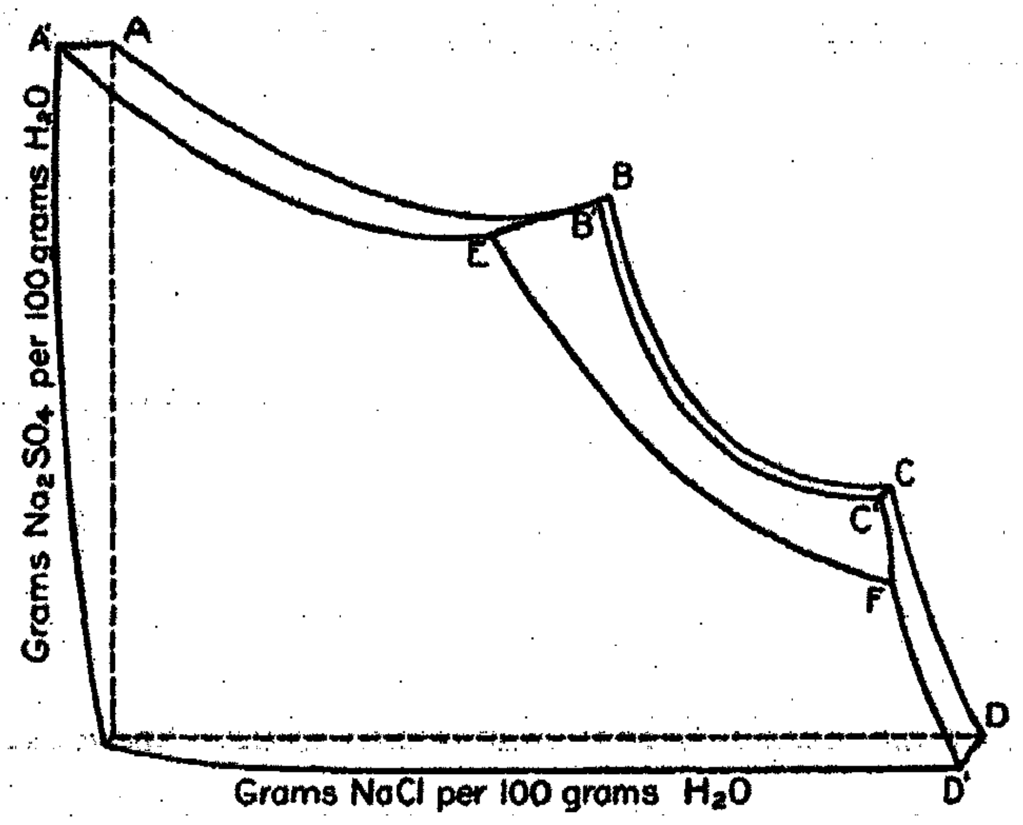

Fig. 4

phase. While the remainder of the curve A'B'C'D' represents solutions in contact with the "double sulphate" and another solid phase or phases. The part of the diagram A'B'C'D'G must therefore be divided into at least two fields, one for gypsum and one for the double sulphate. The boundary between the gypsum and "double sulphate" fields was found to be a continuous curve between the point E on the curve A'B' to the point F on the curve C'D'. It is therefore apparent that there are no fields, other than these two. The data for the boundary curve between these two fields are given in Table V.

It was thought at first that an anhydrite field would be found in this system. Actually, no anhydrite crystals could be found in any of the solutions. Van't Hoff and Armstrong[1] have shown that in any system where the solution has a vapor pressure above 17.2 mm at 25° gypsum is more stable than anhydrite and below this vapor pressure anhydrite is the more stable form of calcium sulphate. Thus the boundary curve at 25° between a gypsum field and an anhydrite field becomes a curve of constant vapor pressure. In the present system no

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[1] Sitzungsber. Akad. Wiss. Berlin, 1900, p. 559.

TABLE V

Data for boundary curve between the field for gypsum and the double sulphate of calcium and sodium in the system, sodium chloride, sodium sulphate, calcium sulphate and water, at 25° C

Density $\frac{25°}{25°}$	NaCl in		Na_2SO_4 in	
	100 cc solution	100 gms. H_2O	100 cc solution	100 gms. H_2O
1.2119	14.20	15.96	17.39	19.54
1.2250	15.73	17.50	16.44	18.29
1.2223	15.80	17.47	16.46	18.20
1.2249	18.29	20.69	13.42	14.91
1.2312	21.38	23.70	11.06	12.24
1.2208	23.82	26.79	8.92	10.09
1.2234	27.25	30.80	6.96	7.85
1.2293	29.23	33.07	4.78	5.41

solution could be found which had a vapor pressure of 17.2 mm or less and consequently if any form of calcium sulphate is stable, it is gypsum and not anhydrite. The solutions which would have the lowest vapor pressures in this system would be those along the boundary curves ABCD and A′B′C′D′. The vapor pressure of a saturated solution of sodium chloride at 25° is 17.7 mm; a solution saturated with respect to anhydrous sodium sulphate, and sodium chloride has a vapor pressure of 17.5 mm. As sodium sulphate decahydrate and sodium sulphate anhydrous coexist at 25° at a vapor pressure of 19 mm, the vapor pressure at the point B of Fig. 4 is 19 mm, and no point on the curve AB will have a vapor pressure below 19 mm. The two solutions E and F of Fig. 4 lost over one percent in weight when standing over a solution of sulphuric acid having a vapor pressure of 17.5 mm. From these results it follows that there is no solution having a vapor pressure as low as 17.2 mm and consequently there can be no anhydrite field.

The composition of the constant solutions have been tabulated below, together with the solid phases with which the solutions are in contact.

TABLE VI

Constant solutions and corresponding solid phases at 25°

Point	Concentration of solution in grams per 100 grams H_2O			Solid phase
	NaCl	Na_2SO_4	$CaSO_4$	
A	0.00	28.55	0.000	$Na_2SO_4.10H_2O$
B	19.13	20.73	0.000	$Na_2SO_4.10H_2O$ and Na_2SO_4
C	33.0	9.84	0.000	Na_2SO_4 and NaCl
D	35.80	0.00	0.000	NaCl
A′	0.00	27.12	0.2648	$Na_2SO_4.10H_2O$ and $CaSO_4.2H_2O$
E	15.96	19.54	0.0347	$Na_2SO_4.10H_2O$, $CaSO_4.2H_2O$ and double sulphate
B′	19.23	21.79	0.0354	$Na_2SO_4.10H_2O$, double sulphate and Na_2SO_4
C′	32.18	9.50	0.0312	Na_2SO_4, double sulphate, and NaCl
F	33.07	5.41	0.0892	NaCl, double sulphate, and $CaSO_4.2H_2O$
D′	35.09	0.00	0.6333	NaCl and $CaSO_4$ $2H_2O$

The Double Sulphate of Calcium and Sodium in Sodium Chloride Solutions at 25° C.—The artificial preparation of a double sulphate of calcium and sodium in the wet way was first accomplished by Fritzsche[1] while preparing hydrochloric acid by mixing sulphuric acid and sodium chloride containing gypsum. He obtained long, acicular needles which somewhat resembled gypsum crystals in appearance but from the action of water upon it, it was apparent that it was a double salt. Fritzsche also prepared the compound by treating gypsum with a saturated solution of sodium sulphate at 80 C. By analysis he decided the composition of this feathery-like compound to be represented by the formula $2Na_2SO_4.CaSO_4.2H_2O$. By continued heating of the pasty mass of feather-like crystals and mother-liquor, it was found that the crystals disappeared, the mother-liquor appeared to clear up, and rhomboidal crystals precipitated. These last crystals could be readily filtered from the mother-liquor, and the substance was found to have the composition $Na_2SO_4.CaSO_4$ and to be in fact an artificial glauberite. Subsequently Hannay[2] found this same compound in the flues of a chemical factory and

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[1] Jour. prakt. Chem., 72, 291 (1857).

[2] Chem. News, 34, 256 (1876).

Volhard[1] obtained it as a by-product in the manufacture of sodium acetate from calcium acetate and sodium sulphate.

Van't Hoff and Chiaraviglio[2] prepared glauberite by the reaction of gypsum with a solution containing 33 percent sulphuric acid saturated with Glauber's salt at 80°. They prepared the acicular compound of Fritzsche by bringing together 53 grams of dry calcium chloride and 34 grams of Glauber's salt in a half liter of water and evaporating. Gypsum first formed but subsequently disappeared, the acicular double salt being formed. On continued boiling, this latter was entirely transformed to glauberite. The Fritzsche formula for these acicular crystals has generally been misquoted as $Na_2SO_4.CaSO_4.2H_2O$; and van't Hoff,[3] from the analogies this substance shows to syngenite, concluded that it contained but one molecule of water and designated it as sodium syngenite.

In a paper just cited van't Hoff has demonstrated that at 29° a solution saturated with both Glauber's salt and gypsum undergoes a change and a new solid phase, glauberite, crystallizes out. In other words, there is an invariant point at 29°, three solid phases being in equilibrium. It is also shown that another invariant point exists at 30.2°, at which point the three phases, Glauber's salt, gypsum and "sodium syngenite" are present. It is obvious that in the neighborhood of 29° the stable double salt is glauberite, and that the second of these invariant points is metastable.

In the work which has been described in the preceding chapter, the double salt, was, however, composed of acicular crystals and no evidence of any rhomboidal crystals at any time appeared. The following dilatometric measurements were made in order to determine which of these double salts was the stable form under the conditions of the experiments. Four dilatometers were charged with these acicular crystals which had been freed, as far as possible, from the mother-

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[1] Chem. News, 43, 6 (1881).

[2] Sitzungsber. Akad. Wiss. Berlin, 1899, p. 810.

[3] Ibid., 1905, 478.

liquor in which they were prepared, and the solutions used were those at the points E,F,B′ and C′, respectively, of Fig. 4. Four similar dilatometers were charged with glauberite prepared by Fritzsche's method and the solutions were the same as for the other four dilatometers. If the field EFB′C′ of Fig. 4 were in reality the sum of two fields, one for each double salt, such would have been indicated, for the stable double salt could not have been the same at all four points. As a matter of fact, these measurements showed conclusively that in all cases where the solid was composed of the acicular crystals, there was no appreciable change of volume in the system, but where the rhomboidal glauberite crystals were used, there was in all four cases a decided increase in the volume of the system, showing that the acicular crystals are stable under these conditions.

The composition of the double compound has been determined by three methods, all of which indicate that the acicular crystals are not sodium syngenite, but correspond to the formula $2CaSO_4.3Na_2SO_4$.

The first method was by the use of two triangular diagrams, which method has been described by Bell.[1] The solutions and residues have been analyzed and plotted on two such diagrams, and in spite of the fact that the points are too close together to prove absolutely the formula which has been given above, yet the lines joining the corresponding points pass very close to the point representing the above compound, and the lines do not pass near the point which would represent a compound of formula $CaSO_4.NaSO_4.H_2O$. The quantity of calcium in the solutions was so small that it was not necessary to determine it at all.

It will be observed that in the first diagram the lines cross on one of the sides of the triangle. The solid compound therefore contains no sodium chloride, and from the position of the point of intersection it contains 61 percent sodium sulphate which is the quantity present in $3Na_2SO_4.2CaSO_4$. Neither diagram, however, proves conclusively that the

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[1] Preceding article.

TABLE VII

Composition of solutions and residues

	Solution		Residue			
	$NaCl$	Na_2SO_4	$NaCl$	Na_2SO_4	$CaSO_4$	H_2O
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
I	20.90	6.66	18 71	12.82	4.16	64.38
II	14.00	11.75	12.36	17.17	4 49	65.82

crystals contain no water. Owing to the feather-like nature of the crystals the quantity of adhering mother-liquor was very large and the points in the diagrams lie close together. A small experimental error in any determination would cause a great difference in the crossing point of two lines which meet at such a small angle.

To find the quantity of water contained in the crystals a "zero method" was employed. To 180 cc of a solution in the double salt field, which had reached equilibrium with the double salt, were added 4.26 grams anhydrous sodium sulphate and 2.72 grams calcium sulphate, which are in the ratio corresponding to $3Na_2SO_4.2CaSO_4$. The density of the solution was determined before and 10 days after the addition of the salts, as was also the sulphuric acid content of the solution. The densities were 1.2188 and 1.2190, respectively, and the barium sulphate from 10 cc of the solution weighed 2.561 and 2.563 grams, respectively, indicating that the solution had undergone no change. As the solution in the field contains but very little calcium sulphate, the union of the sulphates in any other proportion than 3 to 2, would have augmented or decreased the sodium sulphate content of the solution, which would have changed the density and also the sulphuric acid content as determined by precipitation with barium chloride. From this experiment it follows that either no water was removed to form the double salt, or else there were two changes, one in sodium sulphate and the other in water which counterbalanced and gave a solution of the same density and the same sulphate content as the original solution.

This last possibility was excluded by the following experiment. Duplicate mixtures were prepared synthetically which would give a solution in the double salt field. As no sodium chloride exists in the double salt, the same ratio of sodium chloride to water, before and after the double salt is formed would indicate that no water has been removed from solution. This was actually found to be the case, as the following table shows.

TABLE VIII

Composition of the original mixture and of resulting solution

Original mixture	Resulting solution
20 grams $NaCl$	19.99 grams $NaCl$ per 100 grams H_2O
20 grams Na_2SO_4	16.89 grams Na_2SO_4 per 10 grams H_2O
100 grams H_2O	
2.03 grams $CaSO_4$	0.085 gram $CaSO_4$ per 100 grams H_2O

The table shows that the precipitate consists of 1.955 grams calcium sulphate and 3.11 grams sodium sulphate. The molecular ratio is 1 to 1.49 or 2 to 3. The composition of the double salt is therefore $2CaSO_4.3Na_2SO_4$.

System IV. Sodium Chloride, Calcium Carbonate and Water.—In these experiments carbon dioxide was carefully excluded by using distilled water which had been boiled for some time before the solutions were made. This was necessary, for the presence of free carbon dioxide in the solution, increases markedly the solubility of calcium carbonate. Even carbon dioxide at a partial vapor pressure equal to that in the ordinary air is capable of producing a great increase in the solubility in sodium chloride solutions. This may be observed by comparing the following results with those of Cameron and Seidell,[1] in whose experiments the solutions were always in equilibrium with the atmospheric air. They should be compared, also, with the results given in Table X.

System V. Sodium Chloride, Calcium Carbonate, Carbon Dioxide and Water.—The pressure of the vapor phase which

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[1] Jour. Phys. Chem., 6, 50 (1902); Bull. No. 18, Division of Soils, U. S. Dept. Agriculture (1901).

TABLE IX

Solubility of calcium carbonate in sodium chloride solutions free from carbon dioxide at 25°

Density $\frac{25°}{25°}$	NaCl in 100 grams H_2O	$CaCO_3$ in 100 grams H_2O
	Grams	Gram
1.0079	1.601	0.0079
1.0314	5.177	0.0086
1.0466	9.25	0.0094
1.0734	11.48	0.0104
1.0944	16.66	0.0106
1.1346	22.04	0.0115
1.1794	30.50	0.0119

consisted entirely of carbon dioxide and water vapor was one atmosphere. This was attained by saturating the solutions with carbon dioxide at a lower temperature than 25° and removing the stopper of the bottles at intervals to allow the excess of the gas to escape after the bottles had been brought to the temperature of the experiment.

TABLE X

Solubility of calcium carbonate in sodium chloride solutions saturated with carbon dioxide at 25° and one atmosphere pressure

Density $\frac{25°}{25°}$	NaCl in 100 grams H_2O	$CaCO_3$ in 100 grams H_2O
	Grams	Gram
1.0129	1.45	0.150
1.0499	5.69	0.160
1.0501	6.48	0.173
1.0759	11.06	0.174
1.1015	15.83	0.172
1.1246	19.62	0.159
1.1789	29.89	0.123
1.1957	35.85	0.103

System VI. Sodium Sulphate, Calcium Carbonate and Water.—These experiments were similar to those in System IV, except that sodium sulphate was used instead of sodium chloride.

TABLE XI

Solubility of calcium carbonate in sodium sulphate solutions free from carbon dioxide at 25°

Density $\frac{25°}{25°}$	Na_2SO_4 in 100 gms. water	$CaCO_3$ in 100 grams H_2O
	Grams	Gram
1.0081	0.97	0.0151
1.0161	1.65	0.0180
1.0363	4.90	0.0262
1.1084	12.69	0.0313
1.1200	14.55	0.0322
1.1539	19.38	0.0346
1.1615	21.02	0.0343
1.1837	23.90	0.0360

System VII. Sodium Sulphate, Sodium Chloride, Calcium Carbonate and Water.—In the work on the solubility of calcium carbonate in sodium sulphate solutions and in sodium chloride solutions by Cameron and Seidell, the solutions were in equilibrium with the air and consequently contained a small quantity of free carbon dioxide. It was found that with increasing concentration of sodium sulphate, the solubility of calcium carbonate continually increases; on the contrary in sodium chloride solutions, a maximum solubility of calcium carbonate is reached at about 60 grams per liter. It was brought out that at all concentrations the calcium carbonate was much more soluble in sodium sulphate solutions than in sodium chloride solutions. Cantoni and Goguella[1] have recently shown that the solubility of calcium carbonate increases with increasing concentrations of sodium chloride up to a concentration of about 20 grams of the chloride per liter, which was the most concentrated solution used by them.

An excess of solid calcium carbonate was added to solutions containing varying quantities of sodium chloride and sodium sulphate, and after three months at 25°, with frequent shaking, the solutions were analyzed. Table XII gives the data obtained in this work.

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[1] Bull. Soc. Chim. Paris [3], 33, 24 (1905).

TABLE XII

Solubility of calcium carbonate in mixed solutions of sodium chloride and sodium sulphate at 25° C

Density $\frac{25°}{25°}$	NaCl in		Na_2SO_4 in		$CaCO_3$ in 100 g H_2O
	100 cc	100 g H_2O	100 cc	100 g H_2O	
1.2185	0.00	0.00	26.90	28.48	0.0239
1.2113	1.96	2.08	24.83	26.47	0.0192
1.2115	6.43	6.93	21.67	23.36	0.0137
1.2380	10.00	10.78	19.82	21.37	0.0134
1.2378	10.07	10.89	19.39	20.98	0.0137
1.2427	14.62	16.07	18.24	20.07	0.0119
1.2570	17.16	19.18	18.43	20.74	0.0116
1.2435	23.90	26.66	11.30	12.58	0.0044
1.2442	27.30	31.15	8.79	10.00	0.0046
1.2434	27.43	31.52	8.88	10.20	0.0041
1.2470	28.32	32.17	6.74	7.65	0.0043
1.2122	30.38	34.87	2.08	2.35	0.0037
1.2020	31.52	35.70	0.00	0.00	0.0036

These figures are in accord with the previous results in showing that calcium carbonate is more soluble in a saturated sodium sulphate solution than in one saturated with sodium chloride. It will be observed that as the concentration of sodium chloride in solution increases, the quantity of calcium carbonate decreases. The solutions described in this table all lie on the curves of Fig. 2, and consequently the presence of calcium carbonate in these small amounts has not appreciably affected the solubility of the more soluble chlorides and sulphates of sodium.

In all these solutions calcium carbonate was the solid phase, and not a double compound. If a double compound of two calcium salts had been formed, there would have been sodium carbonate in solution which would have caused the solutions to show a decided alkaline reaction. As the solutions were but very faintly alkaline, no such change could have taken place. Further, if a double carbonate had resulted, the solution would have been rich in calcium salts and as the solution carried very little lime, it is again apparent that such a change did not occur.

System VIII.. Sodium Sulphate, Sodium Chloride, Calcium Sulphate, Calcium Carbonate and Water.—Owing to the very slight solubility of calcium carbonate in solutions of sodium chloride and sodium sulphate, it was expected that the presence of a salt with a common ion ($CaSO_4$) would depress this solubility even more. By the same procedure as was described in the preceding chapter, it was demonstrated that calcium carbonate underwent no change in these solutions. Therefore, this system cannot differ essentially from that described by Table IV, as the solubility of calcium carbonate is very slight, and as no new solid phase can appear. An extensive investigation of this system was not necessary as the solutions would have been practically identical in composition with those of Table IV. These conclusions are confirmed by the data in the following table.

TABLE XIII

Data for the solubility of calcium sulphate and calcium carbonate in mixed solutions of sodium chloride and sodium sulphate at 25° C

Density $\frac{25°}{25°}$	NaCl in		Na_2SO_4 in		100 g H_2O contains	
	100 cc	100 g H_2O	100 cc	100 g H_2O	$CaSO_4$	$CaCO_3$
1.2109	2.76	2.94	23.78	25.35	0.2290	0.0163
1.2113	5.52	5.93	21.97	23.39	0.1992	0.0155
1.2442	28.12	32.18	8.52	9.50	0.0301	0.0065

System IX. Sodium Sulphate, Sodium Chloride, Calcium Sulphate, Calcium Carbonate and Water Saturated with Carbon Dioxide.—It has been shown above that the variance of this system is not increased over that of the preceding system by the addition of the new component, carbon dioxide, for at the same time the further condition was imposed, that the pressure of the vapor phase equals atmospheric pressure. In this case a field will represent solutions in contact with two solid phases, a boundary line, solutions in contact with three solid phases. "Constant" solutions will be in equilibrium with four solid phases.

For the experimental work on this system solutions saturated with either sodium sulphate or sodium chloride were put in contact with an excess of calcium carbonate, and the

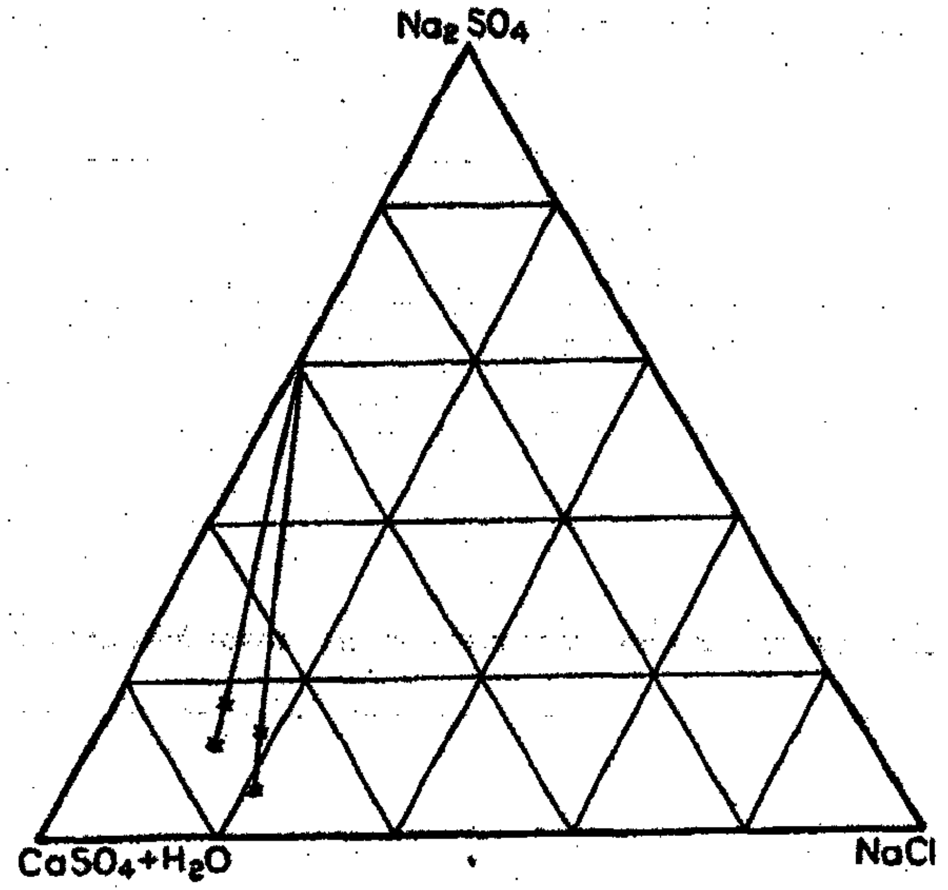

Fig. 5*a*

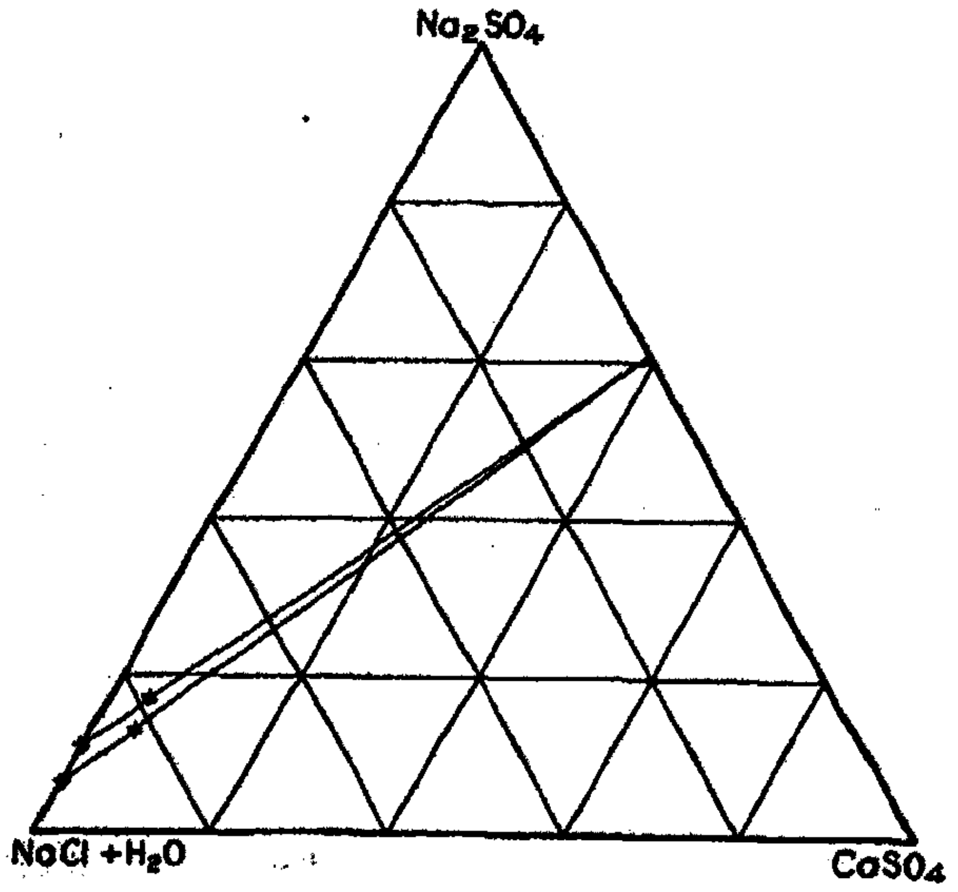

Fig. 5*b*

several solutions were saturated with carbon dioxide by passing the gas under pressure into the solutions at a low temperature. The bottles were then shaken at constant temperature, 25° C., and frequently unstoppered so that the pressure of the vapor phase was finally the atmospheric pressure. In all cases solid calcium sulphate, either as gypsum or a double sulphate, was found. Table XIV gives the analytical data obtained for this system.

TABLE XIV

Solubility of mixtures of calcium sulphate and calcium carbonate in mixed solutions of sodium chloride and sodium sulphate saturated with carbon dioxide at atmospheric pressure, at 25° C

Density $\frac{25°}{25°}$	NaCl in		Na_2SO_4 in		Calcium as calcium oxide in 100 g H_2O
	100 cc	100 g H_2O	100 cc	100 g H_2O	
1.2158	0.00	0.00	25.86	27.12	0.1430
1.2142	2.02	2.13	24.23	25.52	0.1212
1.2109	4.00	4.28	22.81	24.22	0.1148
1.2143	6.00	7.03	21.61	23.10	0.1069
1.2248	9.98	10.77	19.53	21.09	0.0812
1.2224	9.95	10.75	19.73	21.32	0.0826
1.2281	11.31	12.31	19.15	20.84	0.0726
1.2388	13.78	15.50	18.72	20.59	0.0673
1.2590	18.67	20.40	19.80	21.61	—
1.2554	18.80	21.04	16.81	18.81	0.0358
1.2332	21.46	23.81	11.61	12.88	—
1.2474	27.78	31.70	8.70	9.92	0.0183
1.2429	28.47	32.73	5.56	6.26	0.0291
1.2135	30.50	34.48	2.20	2.49	0.0484
1.1957	31.14	35.46	0.00	0.00	0.0490

The diagram representing the system would be almost identical with that shown in Fig. 4, except that each field would represent solutions in contact with two solid phases, one of which would be that shown in Fig. 4 and the other in every case calcium carbonate. The data for the "constant" solutions are given in Table XV.

TABLE XV

Data for constant solutions in the system sodium chloride, sodium sulphate, calcium sulphate, calcium carbonate, carbon dioxide and water, at 25° C

Point	Grams in 100 grams H_2O			Solid phases
	NaCl	Na_2SO_4	CaO	
A	0.00	27.12	0.1430	$Na_2SO_4.10H_2O$, $CaSO_4.2H_2O$ and $CaCO_3$
E	15.50	20.59	0.0673	$Na_2SO_4.10H_2O$, $CaSO_4.2H_2O$, $CaCO_3$ and $2CaSO_4.3Na_2SO_4$
B	20.40	21.61	0.0360	$Na_2SO_4.10H_2O$, $CaCO_3$, $2CaSO_4.3Na_2SO_4$, and Na_2SO_4
C	31.70	9.92	0.0183	$CaCO_3$, NaCl, $2CaSO_4.3Na_2SO_4$, and Na_2SO_4
F	32.73	6.26	0.0291	$CaSO_3$, NaCl, $2CaSO_4.3Na_2SO_4$, and $CaSO_4.2H_2O$
D	35.46	0.00	0.0490	$CaCO_3$, NaCl, and $CaSO_4.2H_2O$

Summary.—In the foregoing pages data have been given for typical systems encountered in studying the chemistry of alkali, or the accumulation of readily soluble salts found in the soils of arid regions. Incidentally it has been shown that solid calcium chloride is not to be expected normally as a component of alkali soils, nor is anhydrite to be expected normally where the salts of sodium and calcium predominate. Further, it has been shown that under certain conditions of concentration a double sulphate of calcium and sodium can exist. At higher temperatures this double salt is the well-known mineral glauberite; at lower temperatures the double salt has been shown to have the composition $2CaSO_4.3NaSO_4$.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.

NEW BOOKS

Qualitative Analysis as a Laboratory Basis for the Study of General Inorganic Chemistry. *By William Conger Morgan. 14 × 22 cm; pp. vii + 351. New York: The Macmillan Company, 1906. Price: bound, $1.90 net.*—"This text presents the course of instruction given by the author to the freshman classes at the University of California where the exigencies of vocational (?) courses render it impracticable for a larger number of students to devote more than one year to general inorganic chemistry and to qualitative analysis as well." "The method of presentation is based principally, though not exclusively, upon the theory of electrolytic dissociation. . . . In the experience of the author, no difficulty in the presentation of the ionic theory has been encountered. Its essentials seem to be grasped as readily and comprehended as correctly as is any other theoretical conception."

"The text is divided into four parts. The general principles underlying any intelligent comprehension of the subject are presented briefly in an introductory part. The reactions of individual elements (arranged according to the Periodic System) comprise the second part. The presentation of analytical methods constitutes the third part while several tables of useful information are found in an appendix."

It is still distinctly a question how much of the electrolytic dissociation theory it is advisable to use when teaching qualitative analysis. The reviewer believes it to be very important for the teacher to be posted; but he does not feel so certain that it is necessary for the student. It is really quite as simple to speak of chlorides as of chlorine ions. Quite irrespective of the question of accuracy, is a freshman to be helped much by the statement, p. 9, that "substances whose activity is increased by dissolving them in water dissociate on going into solution?" It would have been better not to have given the impression, p. 10, that metallic sodium can be precipitated on a platinum electrode from a solution of sodium chloride in pure water "by suitably modifying the apparatus." On p. 8, we have another case of trying to cover too much ground. "Electricity is sometimes called in to aid a chemical reaction as in the production of pure copper. The crude matte is dissolved and the resulting solution electrolyzed with the separation of the metal." From the author's statement, p. 17, the student would naturally suppose that pure zinc precipitates hydrogen as readily, for instance, as iron precipitates copper. Neither on p. 17 nor on p. 327 is there anything to show that the 'potential series' varies with the electrolyte.

These points are emphasized because they have nothing to do with the essential part of the book. They are merely the natural outcome of the feeling that the electrolytic dissociation theory must be shown to be useful everywhere and at all times. An author must make up his mind whether he will expound the dissociation theory with reference to qualitative analysis or whether he will write a manual of qualitative analysis with only such references to physical chemistry as are absolutely necessary. Like those who preceded him, the author has chosen the former course.

These, however, are matters of personal prejudice and what one man does not like, may seem satisfactory to a multitude of others. There can, however, be no excuse for the spellings "kathode" and "kathion," the first of which is German and not English while the second is neither English nor German.

Wilder D. Bancroft

Portland Cement. *Its Composition, Raw Materials, Manufacture, Testing and Analysis. By Richard K. Meade. 15 × 23 cm; pp. viii + 385. Easton: The Chemical Publishing Company, 1906. Price: $3.50.*—The subject is treated under the divisions: introduction; manufacture; analytical methods; physical testing; miscellaneous. The headings of the chapters are: history of the development of the American Portland Cement Industry; chemical composition of Portland cement: raw materials; proportioning the raw materials; quarrying, excavating, drying and mixing the raw materials; grinding the raw material and grinding machinery; kilns and burning; cooling and grinding the clinker, storing and packing the cement; the analysis of cement mixtures, slurry, etc.; the analysis of the raw materials; the inspection of cement; specific gravity; fineness; time of setting; tensile strength; soundness; the detection of adulteration in Portland cement; trial burnings.

Richardson's work on the constitution of Portland cement is quoted at some length; but the author has overlooked the fact that some of Richardson's conclusions are subject to revision. It is interesting to note that we do not yet know whether the reaction between lime and silica is endothermal or exothermal. The question of utilizing the hot kiln gases is also one on which practically no progress has been made. *Wilder D. Bancroft*

Les Origines de la Statique. *By P. Duhem. Tome deuxième. 16 × 25 cm; pp. viii + 364. Paris: A. Hermann, 1906.*—In his first volume Duhem traced the development of the ideas of the "Auctores de ponderibus," authors who looked upon mechanics as applied mathematics and contended for the possibility of a development quite independent of scholastic philosophy. By contrast the earlier part of the present volume considers the contributions due to the scholastics, among which Torricelli's principle of the maximum depression of the center of gravity is prominent. This fruitful postulate seems to have been regarded as "*un axiome, le plus claire et le plus evident qu'on peut demander*," the disciples of the school being unaware of its essential limitation to parallel forces. The enlargement of the principle was brought about by the spread of the doctrines of Copernicus, and most of its corollaries were by these influences eventually put into correct shape. Duhem shows, moreover, in his later chapters how the doctrine of the center of gravity became intermixed with the development of the ideas of medieval philosophers on the figure of the earth.

The book is written in Duhem's well-known, fluent style and the reader is throughout astounded not only by the display of erudition, but at the philological accomplishments of the author. Historical references are very complete and in the original text.

At the present day when mechanics is undergoing its second great transformation, Duhem's scholarly account of the labors of its originators is particularly opportune. *Carl Barus*

An Introduction to Chemical Crystallography. *By P. Groth. Authorized Translation by Hugh Marshall. 12 × 19 cm; pp. vii + 123. New York: John Wiley and Sons, 1906. Price: $1.25 net.*—In the original German this work was published at Leipzig by Engelmann in 1904. It is an attempt on the part of the author "to present the hitherto recognized relations between the properties of crystallized substances and their chemical constitution on the basis of a definite view regarding the structure of crystals."

A few further quotations from the preface may serve to indicate Professor Groth's idea as to the close relationship between the subject of his book and the subject of Physical Chemistry. "However valuable such investigations may be, they can never take the place of the exact examination of the crystallization products themselves (as is evident from the fact that substances have been designated as 'isomorphous' merely on the evidence of the fusion curves of their mixtures, even although nothing was known regarding their crystallographical relationships) . . . . many things of totally distinct nature, whose differentiation still requires further investigation, are thrown together under the name of 'solid solutions.' . . . Chemical crystallography should constitute one of the most highly favored and profitable fields of research in the whole domain of physical chemistry."

The five chapters of the book have the following titles: Crystal Structure, Polymorphism, Morphotropy, Isomorphism, and Molecular Compounds. Each of these topics is illustrated by several well-chosen examples. The treatment assumes a knowledge of elementary crystallography, and thus gives emphasis to the need of that subject for all who would use such words as *isomorphism*, etc., understandingly. Surely, every well-equipped physical chemist should be familiar with the contents of the book under review, as it presents the opinions of one of our most eminent thinkers on points which frequently recur in physical chemical research. *A. C. Gill*

Radioactive Transformations. *By E. Rutherford. 15 × 23 cm; pp. 287. New York: Charles Scribner's Sons, 1906. Price: bound, $3.50, net.*—From an author of Mr. Rutherford's fertility and enthusiasm, any number of books on radioactivity may be expected, each developing the subject from a novel point of view. The present volume in fact deals specifically with chemical aspects, and, therefore, with such subjects as are less frequently included in other collections, as for instance, the treatise on ions, electrons, and corpuscles published by the French Physical Society under the editorship of Abraham and Langevin. Apart from this it seems to us that most of the matter contained in these Silliman lectures is given more succinctly in the second edition of Rutherford's famous treatise on radioactivity (1905). In the case of the α-rays, however, new matter of importance is added. The book, nevertheless, is a connected whole and will be read with pleasure even by those familiar with the more technical work. *Carl Barus*

Abhandlungen zur Kristallographie. *By Quintino Sella. Ostwald's Klassiker der exakten Wissenschaften, No. 155. Herausgegeben von F. Zambonini. 12 × 19 cm; pp. 44. Leipzig: Wilhelm Engelmann, 1906. Price: bound, 0.80 mark.*—This small book constitutes the 155th number in Ostwald's *Klassiker der exakten Wissenschaften*. It reproduces three of Sella's articles on theoretical crystallography, which were previously available only in Italian. They show his genius in applying elementary geometry to crystallographic problems, and also demonstrate for the first time how advantageously determinants may be used in the expression of crystal forms. Six pages of critical and explanatory notes by Zambonini furnish much aid to a proper estimation of Sella's work. *A. C. Gill*

Chemische Krystallographie. *By P. Groth. Erster Teil. 17 × 25 cm; pp. viii + 626. Leipzig: Wilhelm Engelmann, 1906. Price: bound, 20 marks.* —The appearance of the first part of Groth's *Chemical Crystallography* will prove itself both a boon and a disappointment to those who have for years awaited its publication. The disappointing feature of the volume, for which the author is not responsible, is its testimony to the fact that only such an incomplete record has yet been made of the properties of the various known crystalline substances. This incompleteness is only accentuated by a knowledge of the zeal and care with which, for a long series of years and with much competent assistance, Professor Groth has brought together this monumental compilation. His generalizations on the subject have been recently summed up in the Introduction to Chemical Crystallography; see this Journal.

The volume under review presents with abundant references to original sources, the known crystallographic data concerning some 1500 or 1600 substances which are classified as: Elements; Inorganic Substances not to be Characterized as Salts (Metallides, Borides, Oxides, Sulphides, etc.); Halogenides, Cyanides, and Azides; and Double (and Triple) Halogenides and Cyanides. Especial attention is devoted to the comparisons of related chemical compounds,—their molecular volumes, topical axes, polymorphous forms, etc. The book will be found useful as a record of all known crystalline compounds which have been discovered or made, as suggesting new work in filling out important gaps in our knowledge of their properties, as describing material which is suitable for special investigations, etc. In short, every worker with crystallized matter will find an almost unlimited store of suggestion and a very complete summary of our present information in the line of Chemical Crystallography. No investigator in chemistry, physics, or crystallography can afford to be without the book.

It is planned to complete the treatment of all known crystalline substances in three additional volumes which shall appear at intervals of about a year—one on the oxy- and sulpho-salts and related alkyl compounds, and two on the organic substances. *A. C. Gill*

THE CONSTITUTION OF THE ALUMINUM BRONZES.

BY B. E. CURRY

Some work had been done on the copper aluminum series of alloys before this investigation was begun. The freezing point curve had been determined[1] by LeVerrier, Le Chatelier,[2] Campbell,[3] and Guillet.[4] All of these determinations had been made on cooling curves and there is considerable evidence of the effects of supercooling. In general these authors agree as to the general form of the liquidus curve but the data are in no case complete enough to satisfy both the facts and theory. Campbell and Guillet found evidence of heat changes below the solidus but a satisfactory explanation for these was not presented.

These investigators collectively have reported the definite compounds Cu_3Al, Cu_2Al, Cu_8Al_2, Cu_3Al_2, $CuAl_2$, Cu_2Al_6, and also two series of solid solutions. However, there has been no argeement as to what compounds actually are formed. None of these investigators have attempted to present an equilibrium diagram.

Since the data for this work was completed my attention has been called to a report on the same subject by Carpenter and Edwards.[5] They present the first equilibrium diagram for the copper aluminum series of the alloys. Their diagram is reproduced in Fig. 1.

They find the system to consist of five series of solid solutions and the compounds Cu_4Al, Cu_3Al, $CuAl_2$.

The only proof for the compound Cu_4Al is the fact that an alloy of a different composition when dissolved in acid gave a residue which analyzed 90.6 percent Cu and 9.4 percent Al.

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[1] Lejeal: L'Aluminum, p. 168.

[2] Bull. de la Soc. d'Enc., 569 1895.

[3] Journ. Am. Chem. Soc., 24, 265 (1902).

[4] Comptes rendus, 46 (1905).

[5] Eighth Report to the Alloys Research Committee; on the properties of Alloys of Aluminum and Copper.

There is no microscopical evidence to prove the existence of the compound Cu_4Al, and also this composition comes under a minimum in the liquidus curve. This latter fact is in itself sufficient to discredit the existence of the compound Cu_4Al. The alloy of this compostion is inhomogeneous at all temperatures.

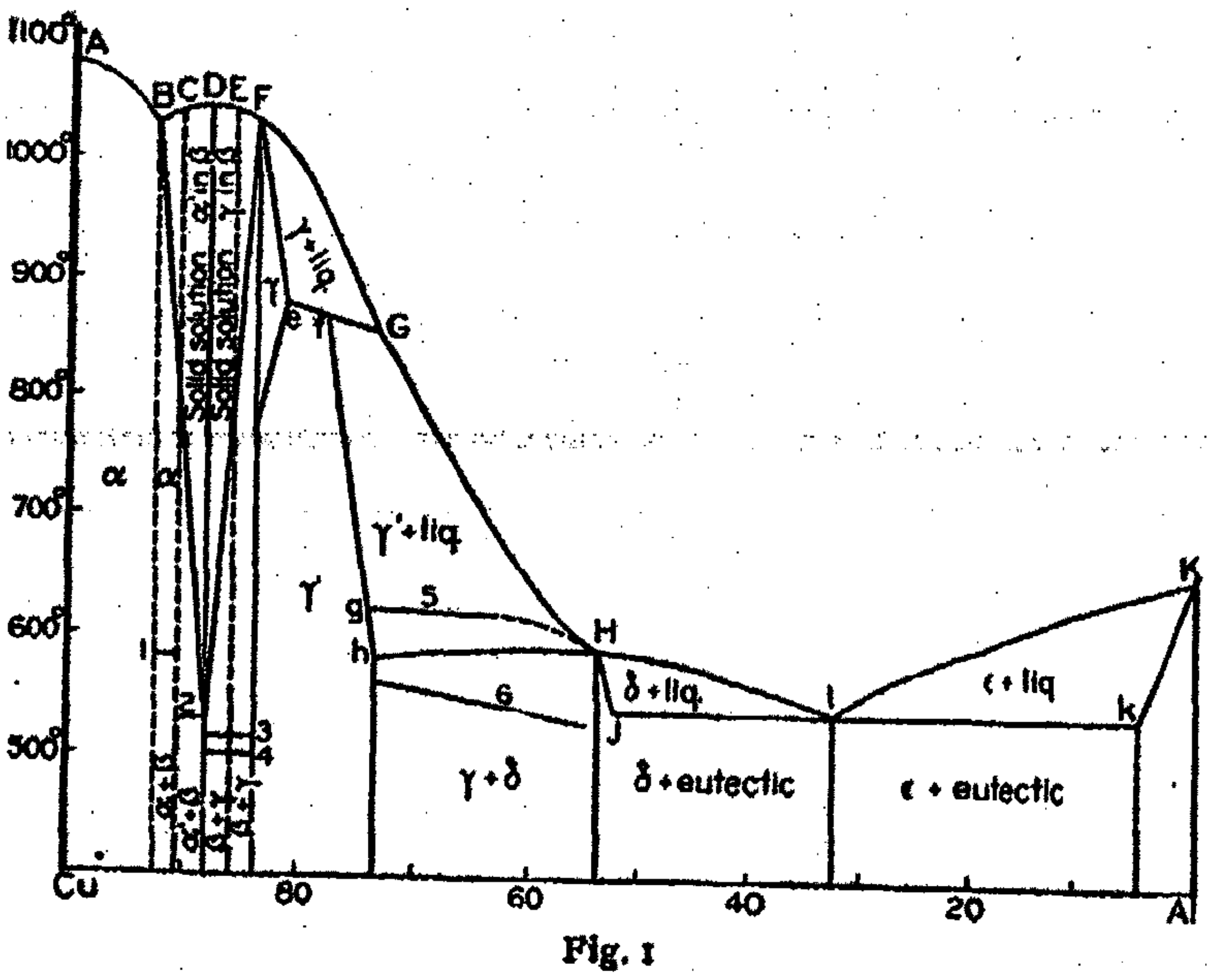

Fig. 1

The compound Cu_3Al occurs in the middle of a series of solid solutions. At present we have no means of determining whether the definite compound is formed under any conditions. We prefer to designate this region of mixed crystals as a simple series of solid solutions. The authors have construed the numerous heat changes which occur between 500° and 600° to mean changes in the solid solutions and to be separate from the so-called compound $CuAl_3$. In other words, that above about 510° the compound $CuAl_3$ exists as a part of a series of mixed crystals while below this temperature the compound exists as such. As will be seen later such is not the fact. The β-phase is *instable* below 566° *either* as a series of *solid solutions* or a *compound.*

The photomicrographs do not confirm the limits of the proposed γ and γ' fields. At 800° the 78 percent alloy is inhomogeneous and this necessitates some change here. The line *d* D is a quadruple line and must, from phase rule considerations, continue at a constant temperature. The region between 53.7 and 73 percent copper is incomplete and does not need further discussion. However, the thermal data for this region must be at variance with the microscopical observations. The exact temperature of these thermal changes will be shown later.

This research was begun with the determination of the melting point curve or the liquidus. The observations for the solidus and other heat changes were made on the same alloys. The time-honored custom of making the observations on cooling curves was abandoned and our data have been taken entirely from heating curves. By this method the annoying effects of supercooling which appear on cooling curves are entirely eliminated. So far as we know the phenomena of superheating does not occur in metals. The heating curves were recorded with a platinum, platinum-rhodium thermo-element and a Wolff potentiometer. The source of heat was a large storage battery. The electromotive force of the element was read directly to micro-volts. These were readily changed to read temperature.

All of the alloys examined were made from pure electrolytic copper and 99.97 percent aluminum.[1] The melts were made in Acheson graphite crucibles. This prevented such contamination of the alloys as would ordinarily be caused by clay crucibles. Before a heating curve was begun, the ingot under examination was placed in the crucible, the pyrometer tube inserted and powdered charcoal added. The crucible was provided with a graphite lid. In this way the oxidation of the alloy was reduced to a minimum. In the heating curve method it is not necessary to stir the melt.

The pyrometric data are given in Table I. In this table the first column represents the composition of the alloy in

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[1] Presented by the Pittsburg Reduction Co.

percentage of copper, the second represents the temperature of the liquidus, the third, the temperature of the solidus, the fourth the temperatures at which other changes occur. The temperatures recorded are correct to ±2°.

Table I

Copper Percent	Liquidus	Solidus	Inversion temperatures	
98	1094°	1082°		
96	1082	—		
95	1074	1050		
92	1058	1042		
91	1052	1038		
90	1040	1039	566°	
87.5	1050	—	566	
86	1042	1034	564	
85	1032	1028	566	
84.4	1026	—	566	954
82.5	1010	900		
80	975	845		
78	950	847		
77	920	846	572	
75	900	650	570	845
72.5	850	630		845
70	800	585	631	
65	725	584	631	
62.5	675	585	630	
60	630	585		
58	615	585		
55	592	584		
54	585			
52	582	543		
50	580	542		
45	575	543		
40	565	543		
35	553	543		
30	552	544		
25	575	543		
20	590	542		
15	615	542		
10	630	544		
5	645	543		

The melting point of aluminum as determined by Holborn and Day is taken as 657°. Heycock and Neville give 1084°

as the melting point for copper in a reducing atmosphere. It is, however, certain from our observations that copper, containing traces of aluminum, melts near 1100°. This may be due to the removal of the last traces of oxide.

The freezing point curve and the equilibrium diagram above 400° is shown in Fig. 2. The freezing point curve consists of seven branches. The branches A B and B C, and the branches F G and G H intersect to form minima at 90.5 percent and 32 percent copper respectively. The one maximum appears at about 87.5 percent copper. There is no evidence of a maximum at 50 percent copper nor of a minimum at 55 percent. The minimum observed here by previous investigators was probably due to supercooling.

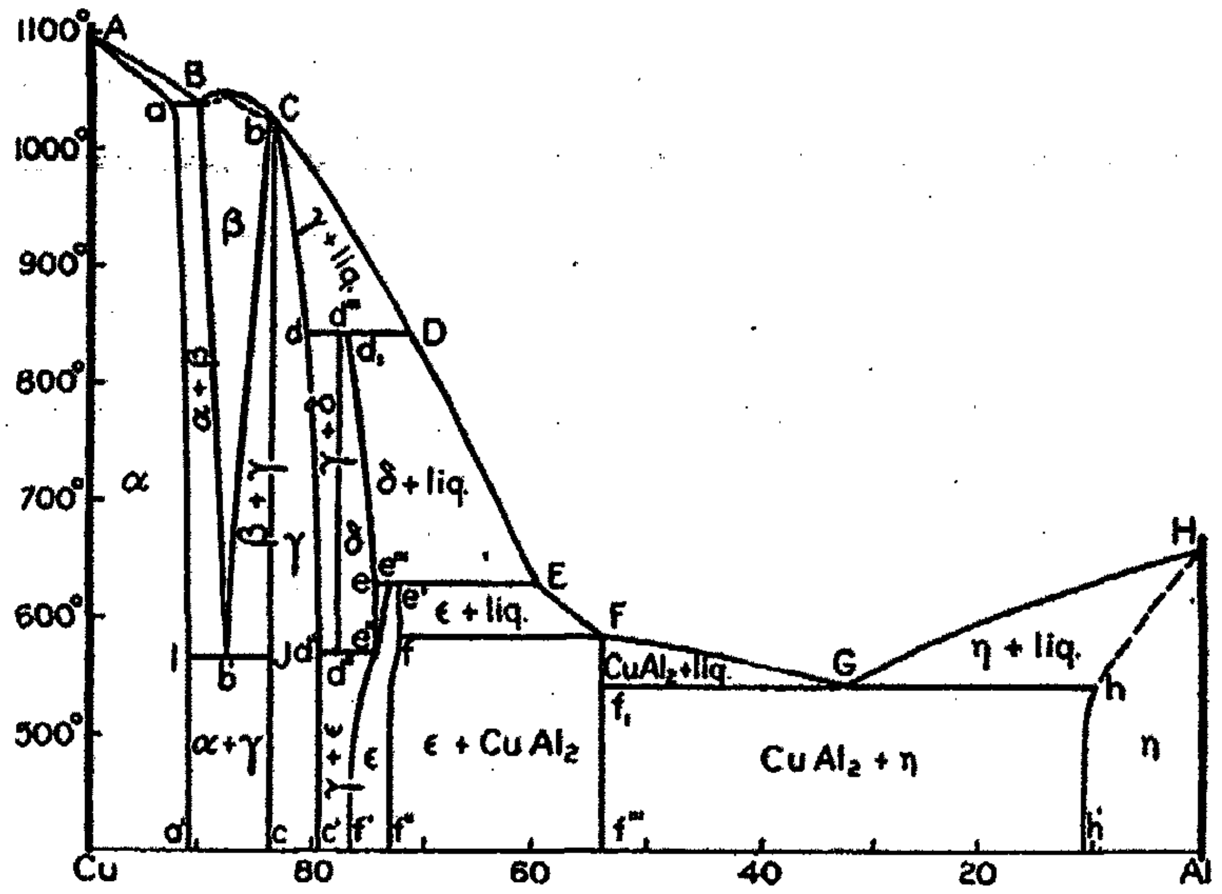

Fig. 2

According to the melting point curve seven phases are stable in contact with the melt. The crystals of the α-series of solid solutions separate along the branch A B. The composition of these crystals varies from pure copper to a 91 percent copper alloy. The limit of the α-field is designated by the line A *a* *a'*. As indicated by this line the α-field is somewhat narrower at the higher temperatures. The α-bronzes vary in color from the characteristic copper red to a golden yellow. In the field A *a* B A, *α*-crystals are in equilibrium with melt.

The field AI *b′* BA is the region in which *α*- and *β*-crystals are found together. The direction of the lines AI and B *b′* were determined by annealing at different temperatures above 566°.

Along the branch B C the *β*-phase crystallizes from the melt. This phase is stable below the solidus[1] between the lines B *b′* and *b′ b*. *β*-crystals are stable only above 566°. At 566° *β* breaks down into a mixture of *α*- and *γ*-crystals. This change was discovered first as a heat absorption in the heating curves over the region 84.3 percent to 91 percent copper. The *β*-crystals are yellow and the alloys falling within the *β*- and *α*- + *β*-fields are also yellow. The fracture of these along the crystal faces is grayish.

β- + *γ*-crystals occur in the field C *b b′* J *c*. These alloys are light yellow when composed chiefly of the *β*-phase. When more of *γ* than *β* is present the yellow disappears and in the edge of the field the alloy is almost white.

Below 566° *α* is in equilibrium with *γ*. The region I *a′ c* J I is composed of varying amounts of the *α*- and *γ*-phases. The color of these alloys is different from that of those over the same composition above 566°. In this field the *γ*-crystals appear over the entire range from 84 to 91 percent copper. For instance, the 87.5 percent alloy above 566° is composed of a yellow constituent. Below 566° practically half of the alloy is composed of the white constituent *γ*. Hence these alloys are less yellow than those of the same composition above 566°. This difference in color is more apparent after long annealing. *α*, *β γ*, and vapor are in equilibrium along IJ.

The *γ*-series of solid solutions crystallize along the branch C D. The lines *c* C *c′* indicate the limits of the field for pure *γ*-crystals.[2] The width of this field varies from about 1 per-

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[1] Theoretically the upper limiting concentration of the *β*-crystals will be different from that of the point *β*. In this case the difference is very slight and is not shown.

[2] It is not asserted that the lines *c* C and *c′* C actually meet at C; but only that the difference, if any, is too small to measure.

cent at 1000° to 5 percent at 400°; no thermal changes occur in the γ-alloys. As already stated, the γ-crystals are almost white. In the field C d D C the crystals of γ are in equilibrium with melt. Between the temperatures 845° and 570°, in the field $d\ d'\ d''\ d'''\ d$, γ is in equilibrium with δ-crystals. Below 570° or in the field $d'\ c'\ f'\ e''\ d'$, γ is in equilibrium with ϵ-crystals.[1] The line $d\ d'''$ is a solidus line while $d'\ e''$ marks the temperature below which ϵ becomes instable. The thermal changes which appear at 845 and 570 are very definite. The γ-alloys are white whether pure or mixed with δ or ϵ.

Along the branch of the curve D E the crystals of δ are stable. δ-crystals are instable above 845° C. If heated above this temperature they are changed over into melt and γ-crystals. The δ-field is designated by the region $d'''\ d''\ e''\ d,\ d'''$. The δ-series of solutions are white as are all of the alloys containing δ-crystals. The δ-phase is instable below 570°. At this temperature the δ-crystals break down to form the γ- and ϵ-phases. In the field D $d'''\ e$ E, δ-crystals are in equilibrium with the melt, and in the small field $e\ e''\ e'''$ the companion phase is ϵ.[1] Along the line $d'\ e''$, δ is in equilibrium with γ and ϵ and vapor.

Along the branch E F the stable phase is ϵ. The ϵ-series of solutions crystallizes white and is stable below 630°. ϵ exists pure over the region $e'''\ f'\ f''\ e'\ e'''$; as is seen from the diagram this field is somewhat irregular and narrow at the higher temperatures. At 400° this field is about 3 percent wide. In the field E $e'\ f$ F E, ϵ is in equilibrium with melt; below 585° or in the field F $f\ f''\ f'''$ F, ϵ occurs with the compound $CuAl_2$.

$CuAl_2$ is the only definite compound of the system and it crystallizes along the branch F G. This compound has a composition of 53.7 percent copper and freezes at a temperature of 585° C.

Along the branch G H the η-series of solid solutions separates from the melt. The heat absorption at the eutectic

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[1] It is not necessary that the point e'' should be on the line $f'\ e'''$. It is very probable that it is slightly to the left of the line.

temperature appears in unannealed alloys that contain 3.5 percent copper.

Guillet and Campbell have done considerable microscopical work on the aluminum bronzes. They have published a series of photomicrographs largely of the cast alloys. The effect of annealing has not received much attention and hence the equilibrium conditions have not been thoroughly investigated. The microscopical work of Carpenter and Edwards, also, is not complete.

The following microscopical data are based upon the annealed alloys. The annealing was of sufficient duration to permit of equilibrium conditions.

So far as the pyrometric observations are concerned, little difference could be expected in the appearance of the alloys with more than 91 percent copper. Both the 92 percent and 91 percent copper ingots show the β-phase when chill-cast. When annealed at 500° the β-phase is no longer in evidence. At 1000° the β-constituent is present in both the 90 percent and 91 percent ingots. The pure α-crystals are very similar to the crystals of α-bronze and α-brass.

The 90.5 percent ingot whether chill-cast or annealed is composed of two phases. If annealed above 500° the α- and β-phases occur together. At 600° the α-phase constitutes the larger part of the alloy; at 850° α and β are present in about equal amounts, while at 1000° there is only a very small amount of α present. The β-phase is instable and is not found in the 90 percent alloy annealed below 566°. At 500° this alloy shows but a small amount of γ appearing between the α-crystals.

The 87.5 percent alloy is typical of the β-series of alloys. When chill-cast or annealed above 566° this alloy shows a mass of fine long needles. Just above the inversion temperature 566° the B field is very narrow but widens at the higher temperatures. The 90 percent alloy is homogeneous or pure β at 1030° but the α-phase appears at slightly lower temperatures. The line B *b′* represents the temperature and concentration where β and α change over from one form to the other.

At 566° the β-alloys undergo a complete change in crystalline structure. Below this temperature, the β-phase breaks down into the α- and γ-phases. The β-structure is very persistent. After annealing the 87.5 percent alloy for 20 days at 500° the partially changed β-crystals or needles are still in evidence. It is not apparent that any change has taken place after this continued annealing when the observation is made with a low magnification. At the end of 30 days the 87.5 percent alloy shows distinctly almost equal proportions of small α- and γ-crystals. At 566° or along the quadruple line I J the α, β γ, and vapor phases are in equilibrium.

The 85 percent alloy is composed of two phases at nearly all temperatures. When annealed at a temperature of 1020° the alloy is homogeneous and is composed entirely of β-crystals. Below this temperature along the line C *b'* the β-crystals begin to change over into γ or vice versa. At 850° practically one-third of the β-constituent has changed over to the γ-phase and at 600° it is practically two-thirds changed. When annealed at 500° β disappears completely and only small amounts of α-crystals appear between the γ-crystals. From the narrowness of the α + β and β + γ field it is at once evident that a shift of one percent in the composition of the alloy changes the relative amount of the two phases very considerably.

The 84 percent alloy is homogeneous when cast. This alloy is typical of the γ-series and when etched shows large broad leaf-like crystals. The 80 percent alloy shows melt when annealed above 845° and is inhomogeneous at 840° or just below 845°. At lower temperatures, about 700°, this alloy becomes homogeneous. Unlike the β- and α-alloys the γ-alloys are very brittle and break with a glass-like or vitreous fracture.

The 78 percent alloy is inhomogeneous at all temperatures. When annealed above 845° the γ phase is in equilibrium with melt. Below 845° and above 570°, γ- and δ-crystals exist together. Below 570° γ and ε are in equilibrium. The γ-phase etches white with nitric acid under all conditions.

The δ-series of solid solutions is stable between 845° and 570°. The 77 percent alloy is typical of this series. This alloy when annealed between the above temperatures is homogeneous with a leaf-like structure. The δ-alloy etch white with nitric acid but appear dark when etched in contact with the γ- and ε-phases. When annealed above 700° the 75 percent alloy shows evidence of melt; below this temperature the alloy becomes homogeneous. At 570° the δ-phase breaks down to form γ and ε. At temperatures below 570° the 77 percent alloy becomes inhomogeneous and when etched shows a network of γ- and ε-crystals.

The ε-series of alloys form at 630°. No one alloy extends throughout the length of this field. At 600° the 72 percent and 73 percent alloy are homogeneous and show large white crystals under the microscope. At 500° the 72 percent alloy has partially broken down into $CuAl_2$ but the 73 percent alloy is very nearly homogeneous. At 550° the 76 percent alloy is almost pure ε and at 500° is entirely so. Pure δ- and pure ε-crystals might be very readily mistaken for γ-crystals.

Between 73 percent and 53.7 percent the ε-phase and the compound $CuAl_2$ exist together. The 63 percent alloy when etched shows about equal amounts of ε and $CuAl_2$. The ε-constituent etches white while the $CuAl_2$ etches dark and tarnishes very readily. This alloy shows a mass of ε-crystals around which is formed a network of $CuAl_2$.

The compound $CuAl_2$ occurs at 53.7 percent and crystallizes as a homogeneous mass of what appears to be equilateral quadrangles when seen under the microscope on a polished surface. If the alloys containing a large amount of $CuAl_2$ are allowed to cool very slowly, long pyramids grow out of the melt. These may easily be grown two or more inches long from a small amount of melt. The alloys rich in $CuAl_2$ present a hackly surface when polished and etched.

In the alloys between 53.7 and 32 percent $CuAl_2$ crystallizes first, leaving a varying amount of the eutectic mixture. With nitric acid the eutectic mixture etches dark over this range. The crystals of $CuAl_2$ are separated by a network of the eutectic composition.

As has been stated, between 0 and 32 percent the η-crystals separate from the melt. In the chill-cast alloys the eutectic mixture appears between the small η-crystals in alloys containing less than 2 percent copper. When these alloys are annealed the η-crystals increase in size and absorb more and more copper. Under equilibrium conditions at 500° the aluminum holds 11 percent of copper in solution. The η-crystals appear as large white plates throughout the field to the right of H *h h'* (Fig. 2). The structure is best seen by etching first with caustic soda and following this with concentrated nitric acid. Also good results may be obtained when the alloy is made anode in alcoholic nitric acid.

Table II shows the composition of the phases found in this series at some of the different temperatures.

TABLE II

Limits of Composition of Crystals

Phase	1000°	At 700°	500°
α	100—92% Cu	100—91% Cu	100—91% Cu
β	90—85% Cu	885—87% Cu	instable
γ..........	84—83% Cu	84—80% Cu	84—79% Cu
δ	melt	87—85% Cu	instable
ε...........	melt	melt	73.5—76% Cu
$CuAl_2$......	melt	melt	53.7% Cu
η...........	melt	melt	0—11% Cu

The α aluminum bronzes are soft and ductile and bend very readily. The β bronzes are much harder and more rigid than the α bronzes and give a very high tensile strength. The presence of a small amount of the β-phase stiffens the α bronzes very markedly. The γ bronze is very hard and breaks with a vitreous fracture. Neither the γ, δ, ε nor $CuAl_2$ bronzes can have any practical value. The addition of copper to aluminum stiffens the alloy very rapidly and at the same time increases the strength. All of the alloys with less than 84 percent copper are white.

The tensile strength of these alloys will be reported in a subsequent paper.[1]

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[1] Jour. Phys. Chem., 9, 461 (1907).

Summary

The equilibrium diagram has been presented for the copper aluminum system above 400°.

It has been shown that copper and aluminum combine to form but one definite compound, namely $CuAl_2$.

In the system there are six series of solid solutions. The limiting concentrations and temperatures have been defined.

Two thermal changes have been found below the solidus. These occur at the temperatures below which the β- and δ-phases are instable.

This investigation was begun and partly finished by Messrs. F. C. Krauskopf and W. M. Kelsey.

A large part of the thermal data was taken in the Geophysical Laboratory of the Carnegie Institute. I wish to thank Dr. A. L. Day for the use of apparatus and the many courtesies extended.

Many valuable criticisms have been received from Mr. E. S. Shepherd.

The expenses of the investigation have been met by a grant from the Carnegie Institution to Professor Bancroft.

This work has been carried on under the supervision of Professor Bancroft. I wish to thank him for his valuable advice and criticism.

Cornell University

ON THE DISSOCIATION OF SERUM GLOBULIN AT VARYING HYDROGEN ION CONCENTRATIONS

BY T. BRAILSFORD ROBERTSON

(From the Rudolph Spreckels Physiological Laboratory of the University of California)

I. INTRODUCTION

In recent papers I have suggested that the proteins may be regarded as amphoteric electrolytes ("ampholytes") and I have pointed out that certain phenomena exhibited by proteins in solution and in the process of hydrolysis by enzymes meet with a simple explanation upon the basis of this hypothesis.[1]

If, however, regarding proteins as amphoteric electrolytes, we endeavor to estimate their dissociation constants when acting as bases, on the one hand, and as acids on the other, it is evident that we cannot, in general, regard one of the functions as negligible while estimating the value of the other. For example, we cannot consider serum globulin in the presence of acid to be acting purely as a base and, regarding it as if it were a simple base, calculate its basic function; for at a definite and comparatively high concentration of acid (in the neighborhood of 10^{-3}N) more than sufficient to carry the globulin into solution, the globulin is "isoelectric," *i. e.*, migrates equally in both directions in an electric field, or, in other words, the concentration of the globulin anion is equal to that of the globulin cation and the protein is acting equally as an acid and as a base, while at lower concentrations of acid, so long as the protein remains in homogeneous solution, the greater part of the protein migrates as an anion, that is, is acting as an acid; and similar considerations doubtless hold good in regard to other ampholytes. Nevertheless, this method of neglecting the acid while estima-

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[1] T. Brailsford Robertson: Jour. Phys. Chem., 10, 524 (1906). Jour. Biol. Chem., 2, 317 (1907).

ting the basic function and *vice versa*, which amounts to neglecting the most characteristic property of the ampholyte while estimating its characteristic constants, has been frequently employed in investigations upon the properties and dissociation constants of ampholytes. As I will show later on, this method can only give even approximately accurate values for the larger function if it be sufficiently large compared with the other; otherwise the dissociation constants obtained in this way are subject to considerable error.

It is, however, possible to estimate the acid and basic functions of an ampholyte by a method which is free from the above objections. Consider the ampholyte HXOH in solution in the presence of the acid HA, and let the concentrations of the various molecules and ions which are present in equilibrium be represented as follows:

$$\begin{array}{cccccccc} H^+ & OH^- & XOH^- & HX^+ & HXOH & XX & A^- & HXA \\ a & b & c & d & e & f & \gamma & \mu \end{array}$$

Then we have, for the equilibrium of the positive and negative ions in pairs:

$$ab = K \quad \text{.....} \quad (1)$$

$$ac = k_a e \quad \text{.....} \quad (2)$$

$$bd = k_b e \quad \text{.....} \quad (3)$$

$$cd = Qf \quad \text{.....} \quad (4)$$

$$d\gamma = S\mu \quad \text{.....} \quad (5)$$

and since the sum of the concentrations of the positive ions must be equal to the sum of the concentrations of the negative ions, we have:

$$a + d = b + c + \gamma \quad \text{.....} \quad (6)$$

In these equations K is the ionic product for water, k_a and k_b are respectively *proportional* to the acid and basic affinity constants of the ampholyte,[1] and Q and S are constants.

From (1), (2) and (3) we obtain the relation:

$$d = \frac{k_b a^2}{K k_a} \quad \text{.....} \quad (7)$$

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[1] J. Walker: Proc. Roy. Soc., 73, 157 (1904). T. Brailsford Robertson: Jour. Phys. Chem., 10, 533 and foot-note, 534 (1906).

Consider the conductivity of this solution, let U be the velocity of the hydrogen ion, V that of the anion A, and v that of the protein ions, assuming that the protein anions and cations, since their mass is practically the same, have identical velocities. From (6), since b is so small compared with a that it can be neglected, we have:

$$\gamma = a + d - c \dots\dots (8)$$

and, if x be the conductivity in reciprocal ohms, we have:

$$1.037 \times 10^{-2}\, x = \mathrm{U}a + \mathrm{V}(a + d - c) + vd + vc$$

Let x_1 be the conductivity the solution would have were the ampholyte absent, then:

$$1.037 \times 10^{-2}\, x_1 = \mathrm{U}a + \mathrm{V}a,$$

the acid HA being supposed to be completely dissociated. Hence:

$$1.037 \times 10^{-2}(x - x_1) = (\mathrm{V} + v)d - (\mathrm{V} - v)c$$

Representing $1.037 \times 10^{-2}\,(x - x_1)$ by λ we have:

$$d = \frac{\mathrm{V} - v}{\mathrm{V} + v}\, c + \frac{\lambda}{\mathrm{V} + v} \dots\dots (9)$$

From (7) and (9), by substitution and rearrangement, we have:

$$c = \frac{\mathrm{K}\frac{k_a}{k_b}\lambda}{(\mathrm{V} + v)\left(a^2 - \frac{\mathrm{V} - v}{\mathrm{V} + v} \cdot \frac{\mathrm{K}k_a}{k_b}\right)} \dots\dots (10)$$

$$d = \frac{a^2\lambda}{(\mathrm{V} + v)\left(a^2 - \frac{\mathrm{V} - v}{\mathrm{V} + v} \cdot \frac{\mathrm{K}k_a}{k_b}\right)} \dots\dots (11)$$

Let a_1 be the total amount of the acid HA which is present, combined or uncombined, in the solution, then, from (8), the amount (μ) which is combined with the ampholyte to form the salt HXA is $a_1 - a - d + c$; let $a_1 - a = m$, then from (8) and (5) we have:

$$d(a + d - c) = \mathrm{S}(m - d + c) \dots\dots (12)$$

From (9):

$$d - c = \frac{\lambda}{\mathrm{V} + v} - \frac{2v}{\mathrm{V} + v}\, c \dots\dots (13)$$

Substituting from (10), (11) and (13) in (12) we have:

$$\frac{a^2\lambda}{(V+v)\left(a^2-\frac{V-v}{V+v}\cdot\frac{Kk_a}{k_b}\right)}\left\{a+\frac{\lambda}{V+v}-\frac{2v\frac{Kk_a}{k_b}\lambda}{(V+v)^2\left(a^2-\frac{V-v}{V+v}\cdot\frac{Kk_a}{k_b}\right)}\right]$$

$$=S\left\{m-\frac{\lambda}{V+v}+\frac{2v\frac{Kk_a}{k_b}\lambda}{(V+v)^2\left(a^2-\frac{V-v}{V+v}\cdot\frac{Kk_a}{k_b}\right)}\right\}\text{......(14)}$$

Let $\frac{V-v}{V+v}\cdot\frac{Kk_a}{k_b}=H$ and $\frac{1}{S(V+v)}=J$, then equation 14 becomes:

$$m=\frac{\lambda}{V+v}-\frac{\frac{2v}{V^2-v^2}H\lambda}{a^2-H}+\frac{Ja^2\lambda\left(a+\frac{\lambda}{V+v}-\frac{\frac{2v}{V^2-v^2}H\lambda}{a^2-H}\right)}{a^2-H}\text{...(15)}$$

In practice it is found that the term

$$\frac{Ja^2\lambda\left(a+\frac{\lambda}{V+v}-\frac{\frac{2v}{V^2-v^2}H\lambda}{a^2-H}\right)}{a^2-H}$$

is negligible, when the ampholyte is chiefly acid, except at comparatively high concentrations of the acid HA, so that for low concentrations of the acid HA we have:

$$m=\frac{\lambda}{V+v}-\frac{\frac{2v}{V^2-v^2}H\lambda}{a^2-H}\text{..................(16)}$$

If, however, the basic function is much larger than the acid function, then H is negligible except at very low concentrations of the acid HA and the equation (15) becomes:

$$m=\frac{\lambda}{V+v}+J\lambda\left(a+\frac{\lambda}{V+v}\right)\text{...............(17)}$$

If, instead of considering the equilibrium of the ampholyte HXOH in the presence of the non-amphoteric acid HA we consider its equilibrium in the presence of the base COH, we obtain equations similar in form except that instead of the constant H we obtain a constant G which $=\frac{U-v}{U+v}\cdot\frac{Kk_b}{k_a}$ where U = the velocity of the cation C. If the basic function is larger than the acid function then at low concentrations of the base COH we have for equilibrium:

$$m = \frac{\lambda}{U+v} - \frac{\frac{2v}{U^2-v^2}G\lambda}{b^2-G} \ldots\ldots\ldots\ldots\ldots\ldots(18)$$

while if $k_a > k_b$, then except at very low concentrations of COH, G is negligible and we have:

$$m = \frac{\lambda}{U+v} + R\lambda\left(b + \frac{\lambda}{U+v}\right) \ldots\ldots\ldots\ldots\ldots(19)$$

In the equations (16) to (19), V and U are, in general, known and the quantities m, and a or b can be measured. Hence from two observations v and the remaining constant in the equation can be obtained. In practice, however, when using the equations (16) and (18) into which v enters as the square as well the first power, it is more convenient to assume a value for v and then, calculating the value of H or of G from one observation, to investigate how closely the equation thus obtained fits the observations. By repeated approximations the values of v and of H or G can in this way be fairly accurately ascertained.

II. EXPERIMENTAL

If the amount of the acid HA which has been added to a solution of an ampholyte and the volume of the solution be accurately known then a_1 is known and if a, the final hydrion concentration, be measured, then $a_1 - a$ gives us m. The conductivity x_1 of a solution of the acid HA of concentration a can be obtained from tables or from the formula $a(U + V) = 1.037 \times 10^{-2} x_1$ where U and V are the velocities of the hydrion and of the anion A respectively, and x_1 is the conductivity of the solution in reciprocal ohms.[1] The conductivity x of the solution of the ampholyte plus the acid HA can be directly measured and $(x - x_1)\ 1.037 \times 10^{-2}$ gives us λ.

The ampholyte which was used throughout in these experiments was the "insoluble" serum globulin[2] prepared

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[1] W. C. D. Whetham: "Theory of Solution," p. 214 (1902).

[2] See Clarence Quinan: Univ. of Calif. Publ. Pathol., 1, 1 (1903); W. B. Hardy: Jour. Physiol., 33, 251 (1905); For literature see Gustav Mann: "Chemistry of the Proteids," p. 363 (1906).

from ox-serum by diluting ten times and saturating with CO_2. The precipitate thus obtained was washed several times with water by allowing the precipitate to settle in tall glass cylinders and then siphoning off the supernatant fluid. It was then dissolved in a minimal amount of normal KCl solution plus a trace of alkali, diluted, precipitated again by CO_2 and repeatedly washed with distilled water. The precipitate, which was never allowed to dry, was then kept standing under water to which toluene had been added as a sterilizer.[1] When globulin was required, the water and precipitate were shaken up and the fine and homogeneous suspension thus obtained was diluted as required. The ash, estimated by igniting slowly at a dull red heat in a platinum crucible, amounted to 0.77 percent of the dried globulin.

The final hydrion concentration, *a*, of the solution was measured by the gas-chain. A calomel electrode in which the solution covering the mercury was N/10 KCl saturated with HgCl formed one extremity of the chain,[2] while an electrode of platinized platinum gauze saturated with hydrogen formed the other extremity. The platinum electrode, which Dr. F. G. Cottrell very kindly prepared for me, consisted of a glass tube bent at right angles at the upper end. A cylinder of platinum gauze was sealed into the lower end and its lower extremity closed by welding the gauze together; a fine platinum wire was threaded in and welded to the gauze and carried up through the glass tube as far as the bend where it passed out into a little cup closed at the bottom and sealed into the tube. Contact was made by means of mercury placed in this cup. The hydrogen was led into the tube and before bubbling through the solution had to pass *through* the platinized gauze —hence equilibrium was very quickly attained.

The hydrogen was prepared from arsenic-free zinc and sulphuric acid and was passed through three Mohr potash bulbs containing (1) alkaline pyrogallol, (2) potassium perman-

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[1] Hardy, Loc. cit., has shown that toluene has no action on globulin.

[2] Richards: Zeit. phys. Chem., 24, 37 (1897).

ganate, and (3) silver nitrate and, finally, through a vessel containing granular calcium chloride.

Since KCl or other neutral salts could not be added to the solutions of serum globulin without, in all probability, displacing the very equilibrium which it was desired to measure, some other device had to be resorted to in order to eliminate the error due to the contact difference of potential between the solution in which the hydrion concentration was being measured and the calomel electrode. The device which was used was to place a saturated solution of KCl in the chain between the solution which was being measured and the calomel electrode.[1] As Bjerrum has shown, this procedure eliminates the contact difference of potential between the solution under investigation and the calomel electrode, and introduces only a small and fairly constant error into the determination. Owing to the foaming of the protein solutions under investigation and the slight pressure thus established, a certain amount of flow was liable to take place in the tube connecting the solution under investigation with the next link in the chain. This tube was therefore not allowed to dip directly into the saturated KCl, but connection was established through another vessel filled with the same solution.

In order to detect the zero point on the bridge a sensitive d'Arsonval galvanometer was employed instead of the capillary electrometer; this method was found in most cases to be very satisfactory, the instrument giving a very distinct throw for 1 mm displacement on the bridge. When measuring the hydrion concentration of solutions of very low conductivity, however, owing to the high internal resistance of the cell formed by the electrodes and the solution, a very low amperage was obtained in the external circuit and the deflection obtained was small. Trouble was not experienced until the conductivity fell to about 2 to 3×10^{-4} reciprocal ohms, but below this the experimental errors in the determination of *a* from this and other causes are considerably increased.

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[1] Tower: Zeit. phys. Chem., 20, 198 (1896); N. Bjerrum: Ibid., 53, 428 (1905).

The general arrangement of the connections was the same as that shown in the figure in Ostwald-Luther's Physico-chemische Messungen 2 Aufl., S. 372. According to Nernst[1] the difference of potential between the hydrogen electrode and 1/IN hydrogen ion solution is +0.277 volt. The potential difference between Hg and N/10 KCl saturated with HgCl is +0.613 volt.[2] Hence the measured difference of potential between the hydrogen electrode and the Hg would be 0.613 volt — 0.277 volt = 0.326 volt. Using carefully standardized[3] N/100 HCl the value of this potential difference which was actually found, using the method of determination described above, was 0.313 volt.

According to the Nernst formula $\pi = \frac{RT}{\eta e} \log \text{nat} \frac{c_2}{c_1}$, where π is the potential difference between two different concentrations of the same ion, R is the gas-constant in volt-coulombs, T is the absolute temperature, η the valency of the ion, and e the Faraday constant.

Hence we have at 20°, at which most of the determinations were made:

$$\pi = \frac{8.316 \times 293}{1 \times 96540} \times \frac{1}{0.4343} \log_{10} \frac{c_2}{c_1} = 0.0581 \log_{10} \frac{c_2}{c_1}.$$

Given that $\pi_1 = 0.313$ volt for normal H^+, then if π_x is the potential difference in volts when C_{H^+} is xN, we have:

$$0.313 - \pi_x = 0.0581 \log_{10} x$$

or

$$\log_{10} x = \frac{0.313 - \pi_x}{0.0581}$$

determinations made upon standard acids and alkali solutions diluted to various strengths gave results agreeing excellently with the titrations of the undiluted solutions.

The following procedure was adopted in all the determinations. The hydrogen was allowed to bubble through the electrode and the solution for $^1/_2$ hour and then a reading

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[1] Quoted after Ostwald-Luther: Loc. cit., S. 384.

[2] Richards: Zeit. phys. Chem., 24, 37 (1897).

[3] Standardized as described below.

was taken. After a further $^1/_4$ hour a second reading was taken, and if the neutral point had not shifted more than 0.5 mm this reading was taken as correct; if a greater shift than this had taken place, a third determination was made after another 15 minutes and so on until a constant reading was obtained. Usually, equilibrium was quickly attained since the solutions under investigation were sufficiently far from neutrality. It was observed, however, that the first determination after the electrode had been allowed to dry and stand in contact with air for some hours was always a long while in coming to equilibrium, so that finally I adopted the plan of simply dipping the electrode in water and passing hydrogen for $^1/_2$ to $^3/_4$ hour before commencing a fresh series of determinations.

The experimental procedure was as follows: A suspension of globulin in distilled water was made up and its concentration determined by evaporating 250 cc and drying at 110° until no further loss of weight could be detected. To 200 cc of this suspension were added 4, 6, 8 cubic centimeters, etc., of acid or alkali of known concentration (approx. N/10) and the total volume of the solution made up to 250 cc with distilled water. The alkali used had been standardized against normal oxalic acid, using lacmoid as indicator; the oxalic acid had been standardized against a solution made up from Kahlbaum's potassium permanganate. The hydrochloric acid solution used was standardized against the KOH thus prepared, using lacmoid indicator, and, finally, a solution of KCl was made by neutralizing the KOH with the HCl; this solution was diluted to N/50 and its conductivity measured; the conductivity was exactly that of a N/50 KCl solution.

The following were the experimental results obtained with HCl.

Concentration of globulin suspension: 0.62 percent.

Hence concentration of globulin in each solution: 0.496 percent.

Conductivity of the water employed 7.3×10^{-6} reciprocal ohms.

Conductivity of globulin suspension alone 9×10^{-6} reciprocal ohms.

Concentration of the HCl employed: 0.1203 N.

The tabulated values of x are the conductivities actually measured less the conductivity of the distilled water. The values tabulated under x_1 are calculated from the formula $1.037 \times 10^{-2} x_1 = a(U + V)$ and U and V are taken as 316×10^{-5} and 65×10^{-5} respectively, and the figures thus obtained are multiplied by 1.12 to reduce to 25°.[1]

Since, in serum-globulin the acid function is much stronger than the basic function,[2] the equation which we have to apply to the above observations is equation (16). Hardy found by direct measurement by the boundary method,[3] that v for globulin was about 10×10^{-5}, but since he had to use very dilute acid and alkali in order to observe the movement of an opalescent boundary, the velocity observed is probably too high on account of the presence of "pseudo-ions," the movements of which in an electric field are due to electric endosmose, as Hardy has pointed out, and are much more rapid than those of true ions. On the other hand, were the observed velocity an ionic velocity, it would be *lower* than the true value, since the migration of the boundary represents the excess of migration in one direction over the migration in the other.

I assumed the values 0, 2.5×10^{-5}, 5×10^{-5}, 7×10^{-5} and 10×10^{-5} for v and substituting them in equation (16) calculated the value of H which most nearly fitted the observations. Of these assumed velocities the one which gave by far the best results was 7×10^{-5} and the value of H which best fitted the observations was found to be 55×10^{-8}.

Hence, since $V = 65 \times 10^{-5}$ equation (16) becomes:

$$m = \frac{\lambda}{72 \times 10^{-5}} - \frac{1.8425 \times 10^{-4}\lambda}{a^2 - 55 \times 10^{-8}}.$$

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[1] See table of ionic velocities in Kohlrausch und Holborn: Leitvermögen der Elektrolyte (1898), S. 200; also table of temperature-coefficients, S. 199.

[2] W. B. Hardy: Loc. cit., p. 255.

[3] W. B. Hardy: Loc. cit.

TABLE I

cc HCl added	a_1	a	m	x	x_1	$1.037 \times 10^{-2} (x - x_1) = \lambda$
4	19.25×10^{-4}	4.37×10^{-4}	14.9×10^{-4}	25.64×10^{-5}	18.1×10^{-5}	7.82×10^{-7}
6	28.9×10^{-4}	8.7×10^{-4}	20.2×10^{-4}	48.9×10^{-5}	35.8×10^{-5}	13.585×10^{-7}
8	38.5×10^{-4}	12.4×10^{-4}	26.1×10^{-4}	71.81×14^{-5}	51.03×10^{-5}	21.55×10^{-7}
12	57.8×10^{-4}	23.8×10^{-4}	34.0×10^{-4}	118.00×10^{-5}	97.93×10^{-5}	20.81×10^{-7}
16	77.0×10^{-4}	36.75×10^{-4}	40.25×10^{-4}	182.4×10^{-5}	151.00×10^{-5}	32.56×10^{-7}
25	120.3×10^{-4}	72.7×10^{-4}	47.6×10^{-4}	331.7×10^{-5}	299.15×10^{-5}	33.754×10^{-7}

In the following table the experimental and calculated values of m are compared.

TABLE II

m Experimental	$\frac{\lambda}{72 \times 10^{-5}}$	a^2	$\frac{1.8425 \times 10^{-4}\lambda}{a^2 - 55 \times 10^{-8}}$	m Calculated
47.6×10^{-4}	46.9×10^{-4}	5285.00×10^{-8}	0.126×10^{-4}	46.77×10^{-4}
40.25×10^{-4}	45.23×10^{-4}	1347.00×10^{-8}	0.492×10^{-4}	44.74×10^{-4}
34.00×10^{-4}	28.9×10^{-4}	566.44×10^{-8}	0.7945×10^{-4}	28.1×10^{-4}
26.1×10^{-4}	29.93×10^{-4}	153.76×10^{-8}	4.02×10^{-4}	25.91×10^{-4}
20.2×10^{-4}	18.86×10^{-4}	75.7×10^{8}	12.09×10^{-4}	6.77×10^{-4}
14.9×10^{-4}	10.83×10^{-4}	19.4×10^{-8}	-4.05×10^{-4}	14.88×10^{-4}

The agreement between the observed and calculated values of m is good except for the value $m = 20.2 \times 10^{-4}$, but in this region it will be noted that equation (16) becomes indeterminate, for when $a^2 = H$ the factor

$$\frac{\frac{2v}{V^2 - v^2} H\lambda}{a^2 - H}$$

becomes infinite while c and d and consequently λ also become infinite and equation (16) takes the form $m = \infty - \frac{\infty}{0}$, which, of course, is indeterminate. Hence for values of a near $a^2 = H$ large discrepancies are to be expected.

From these results it appears that $H = 55 \times 10^{-8}$, and hence $\frac{Kk_a}{k_b} = 68.3 \times 10^{-8}$.

The factor

$$\frac{J_a{}^2\lambda\left(a + \frac{\lambda}{V + v} - \frac{\frac{2v}{V^2 - v^2} H\lambda}{a^2 - H}\right)}{a^2 - H}$$

in equation' (15) is, as we have said, small except when a is large. If we estimate its value from the observation $m = 47.6 \times 10^{-4}$, which is most likely to give the correct value, we find that $J = 2037.6$, and adding this correction factor to the previously calculated values of m we obtain the following results:

TABLE III

m Experimental	m Calculated	$\dfrac{Ja^2\lambda\left(a+\dfrac{\lambda}{V+v}-\dfrac{\frac{2v}{V^2-v^2}H\lambda}{a^2-H}\right)}{a^2-H}$	m Corrected
47.6×10^{-4}	46.77×10^{-4}	0.83×10^{-4}	47.6×10^{-4}
40.25×10^{-4}	44.74×10^{-4}	0.563×10^{-4}	45.3×10^{-4}
34.00×10^{-4}	28.1×10^{-4}	0.243×10^{-4}	28.34×10^{-4}
26.1×10^{-4}	25.91×10^{-4}	0.263×10^{-4}	26.17×10^{-4}
20.2×10^{-4}	6.77×10^{-4}	0.157×10^{-4}	6.93×10^{-4}
14.9×10^{-4}	14.88×10^{-4}	0.01×10^{-4}	14.89×10^{-4}

The following results were obtained when KOH was used:

Concentration of the globulin suspension: 0.26 percent.

Hence concentration of globulin in each solution: 0.208 percent.

Concentration of the KOH employed: 0.0805N.

The tabulated values of x are the conductivities actually measured less the conductivity of the distilled water. The values tabulated under x_1 are the values calculated from the formula $1.037 \times 10^{-2} x_1 = b(U + V)$ where U and V are taken as 64×10^{-5} and 172×10^{-5} and the values thus obtained are multiplied by 1.14 to reduce them to 25.[1]

It is evident that in the presence of alkali m is practically constant for a given amount of serum globulin. Thus serum globulin in the presence of alkali behaves like a strong non-amphoteric acid and the basic function can, for all practical purposes, be neglected.

The values of λ could not be satisfactorily determined with the accuracy required, owing to the rapidity with which hydrolysis of the globulin takes place in alkaline solution, the hydrolysis in acid solution taking place much more slowly. This hydrolysis of the protein has the effect of diminishing the value of a and enhancing that of λ^2 and hence in two of

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[1] See Kohlrausch and Holborn: Loc. cit.

[2] Cf. V. Henri et Larguier des Bancels: Comptes rendus, 136, 1099, 1581 (1903). T. Brailsford Robertson. Jour. Biol. Chem., 2, 317 (1907).

TABLE IV

cc KOH added	b_1	b	m	x	x_1	$1.037 \times 10^{-2} (x - x_1) = \lambda$
4	12.88×10^{-4}	3.143×10^{-4}	9.74×10^{-4}	14.31×10^{-5}	8.15×10^{-5}	6.388×10^{-7}
5	16.1×10^{-4}	6.49×10^{-4}	9.61×10^{-4}	24.74×10^{-5}	16.84×10^{-5}	8.192×10^{-7}
6	19.32×10^{-4}	9.05×10^{-4}	10.27×10^{-4}	32.84×10^{-5}	23.48×10^{-5}	9.706×10^{-7}
8	25.76×10^{-4}	16.41×10^{-4}	9.35×10^{-4}	47.95×10^{-5}	42.58×10^{-5}	5.567×10^{-7}

the observations recorded $\frac{\lambda}{U+v}$ ($U = 64 \times 10^{-5}, v = 7.10^{-5}$) is greater than *m*. This increase in conductivity is greatly accelerated by increase of temperature,[1] while, judging from my experiments upon the reaction-changes in the hydrolysis of casein by acids and alkalies,[2] the relative change with time of the hydrion-concentration should be much less than that of the conductivity. Hence values of *m* constant within the experimental error were readily obtained. I will point out later how from these values k_a for serum globulin can be approximately estimated.

III. THEORETICAL

We have seen that an equation can be obtained connecting *m*, the amount of hydrion or hydroxidion neutralized by an ampholyte in the presence of a non-amphoteric acid or base and the difference between the conductivity of this solution and that of a solution of the non-amphoteric acid or base of the same concentration as that of the hydrogen or hydroxyl ions in the solution containing the ampholyte. This equation does not directly involve the *concentration* of the ampholyte and hence is a useful one to apply to associating ampholytes such as proteins, in which the molecular weight, and therefore the concentration, is usually indeterminate and probably varies with the nature of the solution. The agreement between the observed values of *m* and those calculated by this formula has been shown to be fairly satisfactory.

It is, however, possible to look at the matter from a somewhat different point of view.

From equations (3), (1) and (11) we have:

$$e = \frac{\frac{K}{k_b(V+v)} a\lambda}{a^2 - \frac{V-v}{V+v} \cdot \frac{Kk}{k_b}} \qquad \text{.................... (20)}$$

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[1] Wm. Bayliss: Arch. des Sci. biol., II Suppl., p. 261 (1904); reprinted in the collected papers of the Physiological Laboratory, University College, London, Vol. 13.

[2] T. Brailsford Robertson: Loc. cit.

Now e represents the concentration of the free undissociated ampholytes (type HXOH), that is, the total concentration of the ampholyte *less* the concentration of the association-salts (formed by the union of two ions of the type HX^+ and XOH^-, with the elimination of water), *less*, also, the amount of ampholyte combined with the acid HA to form the salt HXA and *less* the concentration of the ampholyte which is present in ionic form. Now from (8):

$$\gamma = a + d - c$$

and hence the concentration of the salt HXA is $a_1 - \gamma$, that is:

$$m - d + c$$

Hence, from (4):

$$e = c - m - \frac{cd}{Q} - 2c$$

Substituting in equation (20) and rearranging, we have:

$$m = C - Rcd - \frac{Aa\lambda}{a^2 - H} - \frac{2K\frac{k_a}{k_b}\lambda}{(V + v)(a^2 - H)} \cdots\cdots (21)$$

where C represents the total concentration of the ampholyte, $R = \frac{1}{Q}$, $A = \frac{K}{k_b(V + v)}$ and $H = \frac{V - v}{V + v} \cdot \frac{Kk_a}{k_b}$.

In our previous calculations we have found that for globulin in the presence of hydrochloric acid $H = 55 \times 10^{-8}$ and $v = 7 \times 10^{-5}$, hence, since $V = 65 \times 10^{-5}$ equation (21) becomes:

$$m = C - Rcd - \frac{Aa\lambda}{a^2 - 55 \times 10^{-8}} - \frac{18.97 \times 10^{-4}\lambda}{a^2 - 55 \times 10^{-8}}.$$

Substituting in this equation the values of m, c, d, a and λ for the observations $m = 47.6 \times 10^{-4}$, 26.1×10^{-4} and 14.9×10^{-4} we obtain:

$$C = 29.455 \times 10^{-4}$$
$$A = -4.7$$
$$R = 923$$

The negative value of A, at first sight somewhat puzzling, is to be explained by the *association* which the protein undergoes in solution. Consider the molecule HXXOH: if this takes up water and breaks down into two which may be represented by the formula HXOH the molecular concentration is now *double* its former value. We must, in fact, regard a solution of a protein as a system of polymeric modifications of the substance HXOH in equilibrium with each other, this equilibrium being shifted by various alterations in the conditions. For instance, the simplest possible ampholyte, namely, water, has been shown by Arrhenius and by Sutherland[1] to be just such a system of polymeric modifications of the substance HOH, the point of equilibrium being shifted by temperature. Since the concentration, *f*, of the association-salts varies as the product of the concentrations of the negative and positive ampholyte ions in the solution (Equation 4), the mass of the polymeric modifications of HXOH cannot be neglected in a solution of an associating ampholyte such as globulin, when the concentration of the ampholyte acting as an acid is commensurate with the concentration of the basic portion. In a solution of globulin in the presence of a non-amphoteric acid, therefore, the polymeric modifications of the order HXXOH or even of higher orders may be present in concentrations comparable with the total concentration and the *average* molecular concentration may very well be *less* than the sum of the molecular concentrations of the salts HXA, etc., of the association-salts XX, etc., and of the ions HX^+, XOH^-, etc. If this were the case, then in equation (21), $C - m - Rcd - \frac{2K\frac{k_a}{k_b}\lambda}{(V + v)(a^2 - H}$ would be negative and this would, on substituting the observed values of m, c, d, λ and a lead to apparently negative values for A. The fact that the solution of the observation equations *does* lead to a negative value for A may therefore be regarded as evidence in favor of the view that a solution of a protein may be regarded as a system of polymeric modifications of the type HXOH, the point of equilibrium being shifted by any variation in the

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[1] Svante Arrhenius: "Text-book of Electro-chemistry," Trans. by John McCrae, p. 116 (1902). Wm. Sutherland: Phil. Mag., 50, 460 (1900).

conditions (such as the addition of acid, alkali, salts, or the application of heat, etc.) which influences the concentrations of the protein ions.

If this be the case, the question arises whether we are justified in regarding C as a constant, and I think that this question cannot but be answered in the negative, since every addition of acid, base, etc., will shift the equilibrium to a greater or less degree in one sense or in the opposite and, therefore, will alter the average concentration of the whole. Hence equations (16) to (19) are much better adapted for estimating the affinity constants of proteins than equations of the type of equation (21). Unfortunately, the value of H determined from equation (16) does not enable us to determine $\frac{K}{k_b}$ and, substituting in (21), to find out how C varies with the hydrion concentration. As a first approximation we may regard the value of C determined from equation (21) as representing the *average* molecular concentration of the protein over the range of hydrion concentrations covered by the observations, and, if this range be not too great, the error will probably not be large. If C is not constant, however, the value of A determined from equation (21) will, of course, be influenced by its variability. Its value, however, assuming that C is constant, is $4.7 \left(= \frac{K}{k_b(V + v)} \right)$, hence $\frac{K}{k_b} = 6528$.

In the case of globulin in the presence of KOH the problem of determining the affinity constants is simpler; here the comparative constancy of *m* shows that in the presence of alkali we may neglect the basic function of the globulin, or in other words, that *d* (equations 3 and 4) is negligible, hence *f* (equation 4) must also be negligible and C is probably constant.

From equations (2) and (1) we have:

$$e = \frac{Kc}{k_a b} \qquad \text{(22)}$$

and a simple repetition of the investigation which led to equation (10) gives us, for the case of an ampholyte in the presence of excess of hydroxyl ions:

$$c = \frac{b^2\lambda}{(\mathrm{U} + v)\left(b^2 - \frac{\mathrm{K}k_b}{k_a}\right)} \cdots\cdots\cdots\cdots (23)$$

where U is the velocity of the potassium ion (or cation of the base COH). From the value $(= 68.3 \times 10^{-8})$ for $\frac{\mathrm{K}k^a}{k_b}$ which we have already obtained it is evident that $\frac{\mathrm{K}k_b}{k_b}$ is of the order 10^{-18} and is therefore negligible, so that equation (23) becomes:

$$c = \frac{\lambda}{\mathrm{U} + v} \cdots\cdots\cdots\cdots (24)$$

Reasoning similar to that which led to equation (8) shows that in this case, since d is negligible:

$$e = \mathrm{C} - m \cdots\cdots\cdots\cdots (25)$$

Substituting from (25) and (24) in (22) we have:

$$m = \mathrm{C} - \frac{\mathrm{K}}{k_a(\mathrm{U} + v)} \cdot \frac{\lambda}{b} \cdots\cdots\cdots\cdots (26)$$

an equation which would be convenient for determining the value of $\frac{\mathrm{K}}{k_a}$, could our determinations of λ in alkaline solution be relied upon.

If we assume, however, that the salt KXOH is practically *completely dissociated as such*,[1] then, since the amount of un-

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[1] This assumption is certainly a somewhat gratuitous one, but it has nevertheless been repeatedly made in the hitherto published investigations upon ampholytes. That this is so will be more clearly seen from the following alternative derivation of equation (27).

If we neglect d it is obvious that the total concentration $(= e + c)$ of the free ampholyte uncombined with the base COH is equal to $\mathrm{C} - m$.

The concentration of free KOH will be equal to that of the free protein *plus* that of the hydroxyl ions. While the amount of the salt KXOH which is present will, if we neglect d, be equal to the amount of hydroxyl which has been neutralized, that is, to m.

Hence the equation:

$$m(\mathrm{C} - m)(b + \mathrm{C} - m) = \mathrm{G}m$$

If we consider the magnitude of the acid function in serum-globulin as compared with that of the basic function, it is evident that the square of $\mathrm{C} - m$ can be neglected and this equation reduces to:

$$m = \mathrm{C} - \frac{\mathrm{G}m}{b}$$

dissociated salt is equal to $m - c + d$ and d is negligible, we have: $m = c$ and equation (26) becomes:

$$m = C - \frac{K}{k_a} \cdot \frac{m}{b} \qquad (27)$$

Applying equation (27) to the observations in Table IV, we find that $C = 10.58 \times 10^{-4}$ and $\frac{K}{k_a} = 0.27 \times 10^{-4}$. Comparing the values of m calculated from this formula with the observed values, we have:

TABLE V

m Experimental	m Calculated
9.74×10^{-4}	9.74×10^{-4}
9.61×10^{-4}	10.15×10^{-4}
10.27×10^{-4}	10.27×10^{-4}
9.35×10^{-4}	10.41×10^{-4}

On page 448, from observations on globulin in the presence of HCl, we found that $\frac{K}{k_a} = 6528$. From this and from the value of $\frac{K}{k_b}$ just enunciated we find that $\frac{Kk_a}{k_b} = 265 \times 10^{-8}$.

From the value of H calculated from the formula (16) and from the observations on globulin in the presence of hydrochloric acid we obtained the value $\frac{Kk_a}{k_b} = 68.3 \times 10^{-8}$. Considering the errors involved the agreement is good. Since,

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in which $G = \frac{K_1 K}{K_2 k_a}$, where $K_1 =$ the dissociation-constant for the salt KXOH and $K_2 =$ the dissociation-constant for the base, in this instance KOH. (Nernst, "Theoretical Chemistry." Trans. by C. S. Palmer, 1895, p. 443). Assuming that $K_1 = K_2$, that is, that the salt KXOH is practically completely dissociated, we have:

$$m = C - \frac{K}{k_a} \cdot \frac{m}{b},$$

which is identical with equation (27). And the equation derived in this way, in the special case in which $C - m = b$, is the ordinary equation for the hydrolysis of salts of weak acids and has been unhesitatingly applied to amphoteric electrolytes—with, of course, an approach to accuracy only in cases where the salts are strongly dissociated.

in the presence of alkali, we may neglect the ampholyte cation d, the value of C determined from equation (27) represents the molecular concentration of the globulin under these conditions. Hence, knowing the percentage concentration (0.208) of the globulin in the solution, its molecular weight can at once be calculated. In this way the molecular weight in alkaline solution is found to be 1967, a value which agrees fairly with previous estimates of the molecular weight of proteins although it is lower than most of them.[1]

The value of C derived from equation (21) and the observations on globulin in the presence of HCl was 29.455 $\times 10\_{}^{4}$, while the percentage concentration in this case was 0.496; from this the molecular weight would be 1684; very little reliance is, of course, to be placed upon this determination for reasons which have already been discussed; a large part of the value of C, which in this case is inconstant, is probably bound up in the estimated value of A which is probably too high. The value of C obtained from equation (27) is, however, probably as correct as the experimental errors allow, since its value is not affected by the assumption that the salt KXOH is highly dissociated..

From the value of $\frac{Kk_a}{k_b}$ determined from equation (16), the "isoelectric" point for serum globulin, at which c (=concentration of the globulin anion) is equal to d (=concentration of the globulin cation) should be at $C_{H^+} = 8.3 \times 10^{-4}$, which agrees approximately with my own observations upon the migration in an electric field of globulin in acid solution, it would also appear to fit in with those of Pauli,[2] although other proteins besides the globulin which is precipitated by CO_2 are present in the dialyzed serum which Pauli used in his experiments. Of course, the isoelectric point for a protein in solution must not be confounded with the isoelectric point which may be exhibited by the same protein suspended in a

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[1] Compare Schaefer: "Text-book of Physiology," Vol. I, p. 27 (1898). Gustav Mann: "Chemistry of the Proteids," p. 328 (1906).

[2] W. Pauli: Beiträge zur chem. Physiol. und Pathol., 7, 531 (1906).

two-phase system, a phenomenon which may depend upon quite different factors.

A word remains to be said regarding the equations deduced in this paper; throughout the investigation no account has been taken of the ampho-salts (types $KX^+ + OH^-$, $H^+ + XCl^-$) which may be present in the system. From my experiments upon the hydrolysis of casein by trypsin[1] I believe that the error introduced on this account is small except at high protein concentrations or, possibly, at high concentrations of the non-amphoteric acids or bases in the system; the fact that in alkaline solution the value of m is so constant shows that in this case at all events the concentration of the ampho-salts is negligible.

CONCLUSIONS

1. Serum-globulin is shown to exhibit the characteristic behavior of an amphoteric acid in regard to the conductivity of its solution in acid and alkali and the amounts of hydrion and hydroxidion which it neutralizes.

2. The value of $\frac{Kk_a}{k_b}$, where K is the ionic product for water, k_a is the dissociation-constant of globulin acting as an acid, and k_b is its dissociation-constant when acting as a base, has been determined by two different methods from two series of observations. The values obtained were 68.3×10^{-8} and 265×10^{-8}. Of these determinations the first is probably the more accurate.

3. The velocity, v, of the serum globulin ion was estimated by methods described in the paper and was found to be 7×10^{-5} centimeters per second under a potential gradient of a volt per centimeter.

4. In solution in alkali (KOH) serum-globulin behaves like a non-amphoteric acid, that is, the concentration of the globulin cation is so small that it can be neglected.

5. Evidence has been advanced in favor of the view that a solution of a protein may be regarded as a system of polymeric modifications of the type HXOH, the point of equilibrium

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[1] T. Brailsford Robertson: Jour. Biol. Chem., 2, 372 (1907).

being shifted by any variation in the conditions, such, for instance, as the addition of acid, alkali, salts, or the application of heat.

6. Since the concentration of the globulin cation is negligible in alkaline solution, the degree of polymerization and therefore the molecular concentration is constant. Hence, the molecular weight can be calculated from the percentage concentration provided the molecular concentration is known. This was determined by methods described in the paper and the molecular weight in alkaline solution found to be 1967. In acid solution the *average* molecular weight, calculated by similar methods, was estimated at 1684, but this value is probably far from correct since in acid solution the degree of polymerization varies with the amount of acid present.

7. The general behavior and amphoteric character of serum globulin are well exhibited in the following table, calculated from measurements made upon a 0.496 percent solution of serum globulin in various concentrations of HCl.

I desire to express my indebtedness to Drs. A. E. Taylor and F. G. Cottrell for instruction in the manipulation of the gas-chain and for the loan of much of the apparatus used in the experiments.

Table VI

$C_{H^{\cdot}}$	Conc. of $H^{\cdot}$ neutralized by globulin	Excess of conductivity due to presence of globulin. (Recip. ohms)	*d* Active mass of globulin acting as base	*c* Active mass of globulin acting as acid	*f* Association salt type XX
72.7×10^{-4}	47.6×10^{-4}	102.55×10^{-5}	47.38×10^{-4}	0.61×10^{-4}	28.9×10^{-8}
36.75×10^{-4}	40.25×10^{-4}	31.4×10^{-5}	47.15×10^{-4}	2.39×10^{-4}	112.7×10^{-8}
23.8×10^{-4}	34.0×10^{-4}	20.1×10^{-5}	32.01×10^{-4}	3.86×10^{-4}	123.56×10^{-8}
12.4×10^{-4}	26.1×10^{-4}	20.78×10^{-5}	46.68×10^{-4}	20.7×10^{-4}	965.8×10^{-8}
4.37×10^{-4}	14.9×10^{-4}	7.54×10^{-5}	5.62×10^{-4}	20.77×10^{-4}	116.7×10^{-8}

THE TENSILE STRENGTHS OF THE COPPER ALUMINUM ALLOYS

BY B. E. CURRY AND SAMUEL H. WOODS

This work was begun in order to establish the relation between the constitution of the aluminum bronzes and their tensile strengths. About twenty years ago, Tetmajer[1] published data on this subject. His work was handicapped seriously by an incomplete knowledge of the internal constitution of these alloys and by the impure aluminum obtainable at that time. Since then we have been able to obtain very pure aluminum and we now know about the constitution of these alloys.

Aside from the results of Tetmajer we have only incomplete data on this subject. Others have made a greater or less number of individual tests without any very definite knowledge of the internal structure.

The Equilibrium Diagram

In Fig. 1 the equilibrium diagram for the copper aluminum series is shown. The coordinates are temperature and percentage composition. The lines in the diagram mark the occurrence of some physical or chemical change. The upper full line or liquidus represents the temperatures above which the alloys are completely melted. The line just below the liquidus or the solidus line represents the temperatures below which the alloys are completely solid. Between these lines melt and crystals exist together. The lines below the solidus represent the temperatures at which some chemical change takes place.

In the diagram the field designated as α represents the concentration and the temperature over which pure α-crystals are stable under equilibrium conditions. The crystals are composed of a solid solution of aluminum in copper. With

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[1] Tetmajer: Mitteilungen der Materialprüfungsanstalt IX Heft. Methoden und Resultate des Untersuchung des Aluminums und seiner Abkömmlinge.

more than 91 percent copper there is but one form of crystallization.

β, γ, δ, ϵ and η also are other series of solid solutions, each having a definite crystal form. The η-series is formed by the solution of copper in aluminum. The limits of this field are very narrow when determined from chill-cast alloys. The effect of annealing is very marked over this range. The only compound, $CuAl_2$, occurs at 53.7 percent copper.

The fields which are designated as $\alpha + \beta$, $\beta + \gamma$, etc., represent the concentrations and temperatures over which two

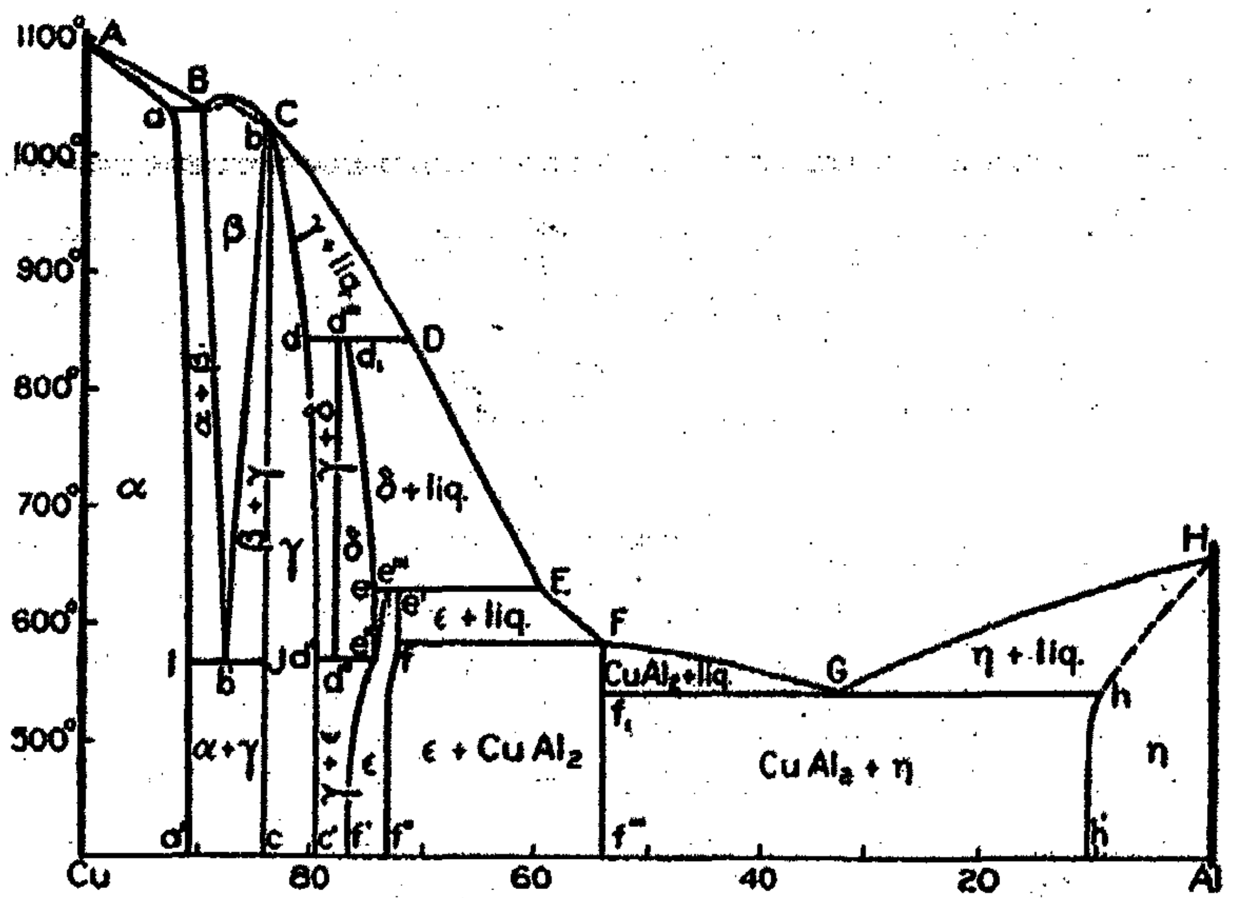

Fig. 1

crystalline formations exist together. A field of this sort occurs between any two successive phases.

There are some chemical changes in this series of alloys which are caused by temperature changes. For example, when an 89 percent melt begins to solidify, β-crystals separate from the mother liquor. These continue to separate as the temperature drops. When the dotted line or solidus is reached the melt freezes completely and the mass is composed of pure β-crystals. As the temperature drops still further the β-crystals begin to break down into α. Then over a considerable temperature α- and β-crystals exist together. At 566° the β-crystals break down completely to form α- and γ-crystals. The β-phase does not appear below 566° under equilibrium conditions. If an 86 percent copper alloy be followed as it cools, changes occur very much as they do in an 89 percent alloy excepting that the β-crystals break down partially to form γ-crystals at the higher temperature. At 566° the β-crystals change over completely to the α- and γ-form. In general all changes in the solid alloys take place most rapidly at the higher temperatures. At ordinary temperatures the reaction rate is practically negligible.

Because of this slow rate at which internal changes take place at ordinary temperatures, an alloy may be heated to a given temperature, and this temperature maintained until equilibrium is established, and then if cooled very rapidly those conditions will remain fixed at ordinary temperatures. If an 88 percent alloy be heated to 700° it will, under equilibrium conditions, be composed of pure β-crystals. If quenched quickly in water from this temperature the β-crystals do not have time to change over into α- and γ-crystals, and at ordinary temperature the alloy retains the same crystalline structure it had at 700°. If allowed to cool more slowly, this alloy undergoes a structural change at 566°. If one wishes to determine the strength of a pure β-alloy an 88 percent alloy, for example, may be annealed at any temperature falling within the β-field until equilibrium is reached and then quenched rapidly. This method is of very general application.

The alloys with a copper content falling between 25 percent and 86 percent are too brittle to be of any technical value. This report is concerned only with the α, α + β, β, β + γ, α + γ, η and η + $CuAl_2$ alloys.

The complete diagram is discussed in a separate paper.[1]

Artificial Acheson graphite was used in making the moulds for the test pieces. This material was first made use of for this purpose by Shepherd and Upton[2] in their investi-

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[1] Journ. Phys. Chem., 11, 425 (1907).

[2] Ibid., 9, 441 (1905).

gation of the bronzes. The material is almost ideal for the purpose; it is easily worked with ordinary wood-working tools and, being usually homogeneous, takes a very smooth finish.

In making the moulds most of the cutting was done with carpenter's gouges, but the grooves for the test section were finished by means of a sharp screw thread of the desired diameter. The centrifugal sprew devised by Shepherd and Upton was made use of. To obtain this the sprew cavity was cut so as to give a corkscrew shape to the sprew. Thus when the molten metal first enters the mould it is given a whirling motion. This prevents splashing which tends to entrap air. The "airtrap" in the sprew was also used. Vents leading from this trap at the grip end and a large riser at the opposite end of the mould were also provided. Very little local necking occurs in the alloys tested, and standard proportions in the test pieces were not necessary. The diameter of the test section was 3/8" and the test length 5". The grip ends were made 3/4" in diameter and about 2" long.

Very little trouble was experienced because of occluded gases or trapped air. Some of the pieces when broken showed small amounts of slag, but this was no fault of the moulds. The only difficulty which could be attributed to the moulds was the breaking of the pieces near the ends. This was found to be caused by a too sharp angle in the test piece where grip end and test section meet. This difficulty disappeared when the angle in the mould was sufficiently rounded off. If the halves of the mould were clamped too tightly, shrinking stresses were often found to develop. Best results were obtained when the halves of the mould were clamped together at the sprew end, the riser ends being held together by means of bricks placed on the floor against the sides.

Oxidation was prevented by addition of powdered charcoal and by passing illuminating gas directly into the crucible. This was found to be very effective in excluding oxygen from the melt. By observing these precautions the composition of the melt was not materially affected by oxidation and the amount of slag was kept at a minimum.

A certain amount of slag and oxide is inevitable. After a test piece had been cast the remaining metal was poured into a small ingot mould and the crucible then jarred on the floor. In this manner all the slag was removed from the crucible after each melt. There was a tendency for the slag to cling to the crucible and the metal was almost always entirely free from slag or oxide as it entered the moulds.

The crucibles were made from cylinders of Acheson graphite about 4 1/2" in diameter. They were turned out by chucking in a lathe and cutting with ordinary machine tools. These crucibles were entirely satisfactory in every respect except durability. No practical means were found for preventing the flames in the furnace from striking the sides of the crucible. When casting the alloys rich in copper, only 15 to 20 pourings could be made from one crucible. With the aluminum-rich alloys many more pourings could be made before the walls burned through.

An ordinary gas furnace equipped with air blast was used for the source of heat. In this a temperature of about 1500° could be obtained. After the furnace became hot the bronzes with the higher melting points could be made quickly. We made it a practice to keep the melt in the furnace the shortest practicable length of time. The time factor has much to do as regards the amount of slag and oxide formed.

The aluminum used in making these alloys was about 99.97 percent. It was presented to us by the Pittsburg Reduction Company to whom we express our thanks. The copper was the best electrolytic product. In making the aluminum-rich alloys it was found practicable to melt the aluminum and then to add the copper. This method was satisfactory when the surface of the metal aluminum was free from slag and the surface of the copper was bright. Otherwise the copper did not always dissolve readily. In making the copper-rich alloys the copper was always melted first and the aluminum added to the melt. Thorough mixture of the two metals was obtained by stirring with a graphite rod.

It was early noted that when aluminum is added to molten copper the temperature rises from 150° to 250°. This was first supposed to be caused by the reduction of copper oxide but this is not the reason. If a second amount of aluminum is added a similar rise in temperature is observed. The phenomena must be due to heat of solution. A like phenomenon occurs when copper is dissolved in molten tin.

All of the test-pieces were repeatedly melted. The composition was checked from time to time by analysis and in nearly every case the variation was less than one-tenth of one percent. The number of meltings did not affect the quality of the copper-rich test-pieces, but after the aluminum-rich alloys were melted several times the average percent of good pieces began to drop.

It was not found necessary to heat the moulds before pouring. In most cases good pieces could be obtained by pouring into a cold mould. It was usually necessary to have the first melt somewhat hotter than the succeeding ones.

The temperature of pouring was kept as low as possible as a matter of economy of fuel, crucibles, and time. It is difficult to say definitely at what temperature any given alloy should be poured, for that is a matter requiring experience and judgment. The best copper-rich test-pieces were made by pouring at such a temperature that the metal would about half fill the riser. If poured colder than this the piece would be likely to be bad at the end. If poured much hotter the lower part of the mould would fill first, then the upper part would fill and a seam, noticeable on the outside of the piece but not apparent on the inside, would be formed. This fault was not a serious one but did not add to the appearance of the piece. This phenomenon did not appear in the aluminum-rich alloys at all. The castings obtained were as nearly perfect as could be desired and the surface in most cases was as smooth as if machined. The part of the casting corresponding to the joint in the mould showed a slight fin in most cases. This was not great enough to cause any inconvenience.

The treatment given the pieces recorded as chill-cast was as uniform as possible. The pieces were poured from about the same temperature head above their melting point. They were then allowed to cool sufficiently to allow handling and then quenched in water. The annealings below 500° were carried on in a specially constructed furnace. This was made of brick and large enough to hold about thirty pieces It was constructed to give an evenly distributed heat. The heat was supplied from two large Bunsen burners, the hot gas passing along the bottom and sides and then over the top of the enclosed muffle in which the pieces were packed.

The temperature was read by means of a pyrometer and could be kept sufficiently constant for our purpose. For the annealings above 565° a coke-fired assay furnace was used. The time required at these temperatures was short and the assay furnace was very satisfactory. The temperature was observed as in the first furnace. The test-pieces were packed in a fire-clay muffle in powdered graphite. The mouth of the muffle was closed with clay or asbestos paper. The aluminum-rich alloys showed no evidence of oxidation due to annealing. There was a marked tendency for the copper-rich pieces to oxidize, and a stream of illuminating gas was passed into the muffle. At the worst, the film of oxide formed on the surface of the bronze pieces was too thin to cause any trouble. In fact the film could be easily removed with the nail or a knife point.

The aluminum-rich alloys were given but one heat treatment; namely, annealing at 400°. The copper-rich pieces were given two heat treatments; 1st, annealing at 500° for 2 days and 2d, annealing above 565° for 30 minutes. In the latter treatment the pieces were quenched from about 750°. The pieces annealed at or below 500° were not quenched but allowed to cool in the muffle.

A few of the bronzes were cast and allowed to cool slowly in the air, protected from draughts.

Testing

Practically all of the tests were made on a 10,000 pound Olsen machine. This machine was well adapted to our purposes because of its small size and accuracy. The cross section of the test-pieces was small and the actual breaking load was only in a few cases greater that 10,000 pounds. Because of this nearly all of the pieces broke within the range of the machine.

The mechanism of this machine was worked by hand. This was found to be advantageous in a number of ways.

The method of procedure in testing was briefly as follows:

The diameters of the test-pieces were carefully measured with micrometer calipers reading directly in thousandths of an inch. The smallest diameter was always the one recorded. The pieces were not perfectly circular but varied slightly in diameter at any one section. Three or four diameters were taken and the average of these was recorded. In some cases the fin, formed by the imperfect fitting of the halves of the mould, was filed away. This fin is not large enough, however, to affect the strength of the piece appreciably, so that the filing was generally omitted.

The records of extension were taken by means of a 6-inch drafting compass fitted with fine steel points. It would have been desirable to use an extensometer for this purpose, but none short enough was obtainable. The method finally adopted was to make a fine prick punch mark at the end of the piece uppermost in the machine, and mark the lower end by means of the point of the compass. Making these two marks exactly 5″ apart results in a considerable saving of time of computation. It was easy to take the extensions quite accurately in this way. After the beam had been balanced with the desired load, the compass was set to coincide with both marks, and the distance thus measured was read on a steel scale divided in hundredths of an inch; with the aid of a magnifying glass, extensions were thus easily read in thousandths.

A few of the stronger pieces were broken in a 100,000 pound Riehlé machine, which has a noticeable throwback. In all the tests run on this machine, the mechanism was run at low speed, and extension readings were taken with the machine running, as the load was raised. By this means, the effect of throwback is eliminated.

In all the tests on both machines, care was taken to have the beam floating at the time of fracture.

After the pieces were broken the halves were removed from the machine and carefully observed. The character of the fracture was recorded in every case. The final extension was obtained by measuring between the marks with the broken ends held together. Care was taken to correct for the opening left between the ends.

Results

The results of the experiments are presented in the accompanying tables, and are shown graphically on the curve sheets. While it might have been desirable to present all the extension data exactly as taken, it would also have been very cumbrous. Extension data are given for representative pieces of every composition tested.

Table I gives records of all the pieces broken, which gave tests which were considered not seriously affected by slag, air holes, or shrinkage strains. Strengths per square inch have been computed from the diameter of the smallest section, measured before testing. Ductilities are computed from the final extension, corrected by adding the initial extension as shown by the stress-strain diagrams, as described later.

Table II gives complete records of the "best" pieces. Since the highest strength obtainable by experiment is the true strength of any material, these records are representative of the various alloys.

Two corresponding sets of curves have been plotted:

Fig. 2 shows the variation of strength and ductility with composition, for the best pieces of the aluminum-rich alloys. Fig. 3 shows the same for the bronzes. The points corresponding to pure copper are taken from the data obtained by Shepherd and Upton in 1904.

Figs. 4–7 are the stress-strain diagrams. The coördinates of such a diagram are, as standardized, load per square inch, as ordinates, and extension from initial length, per inch of length as abscissae. In the present case, since all the pieces were of the same length, actual extensions were used as abscissae.

They are all plotted in accordance with standard practice; that is, zero extension is plotted for initial load, and for the other loads; extensions reckoned from the length at initial load

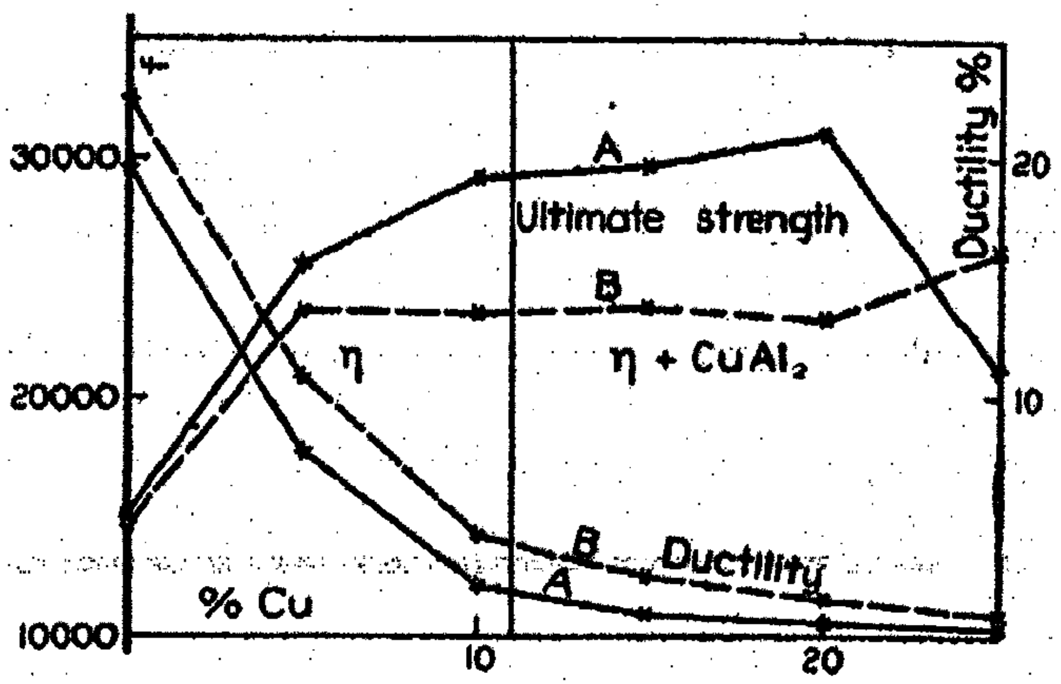

Fig. 2

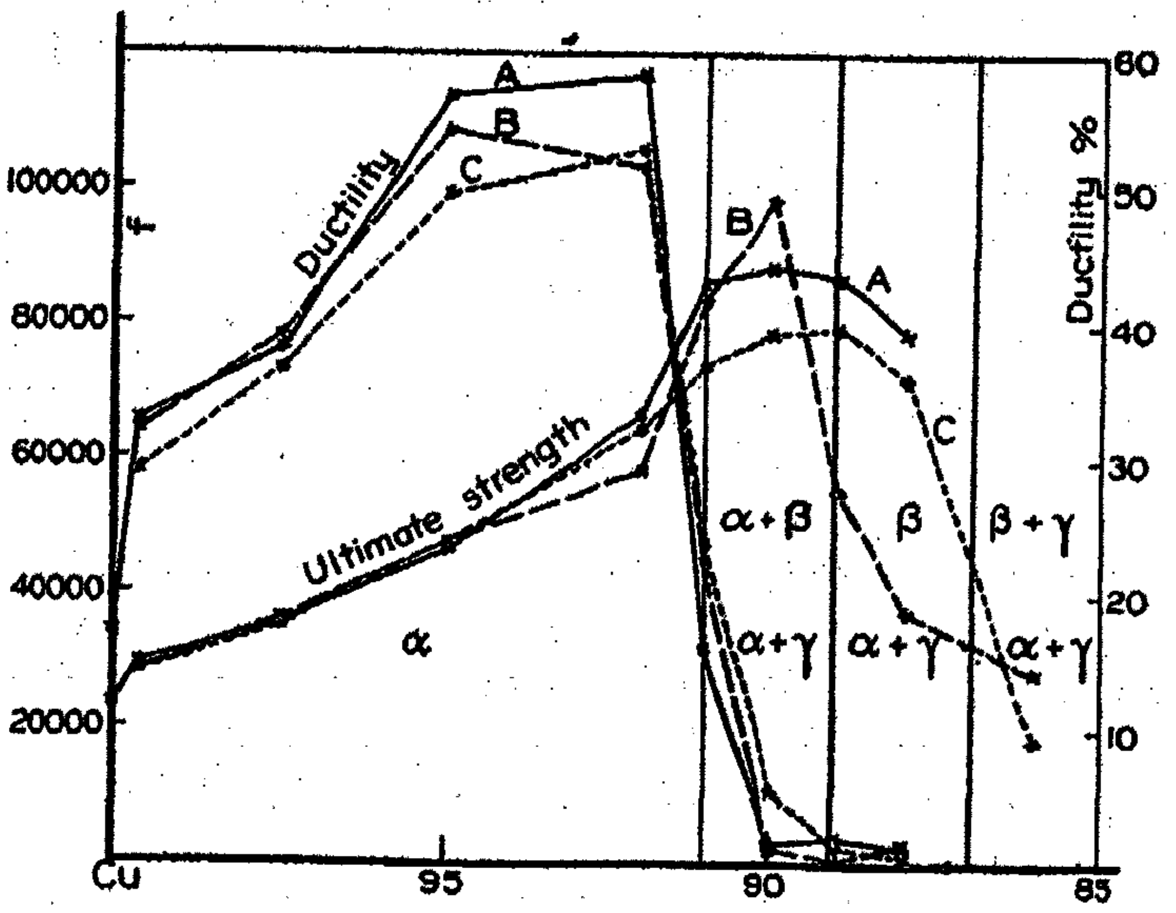

Fig. 3

are plotted. The curve is then drawn, and the intercept on the axis of abscissae noted. This intercept is the extension at the initial load, and the curve is then shifted a distance equal to this intercept, to the right so as to pass through the origin. In all cases the initial load was so small as to give practically no extension.

In all the curves, tables and diagrams, *A* refers to chill-cast pieces; B to pieces annealed at the lower temperatures; C to pieces annealed above 565° for 30 minutes and water-quenched; D to pieces allowed to cool in the air.

Referring to Fig. 2, both the chill-cast and annealed pieces

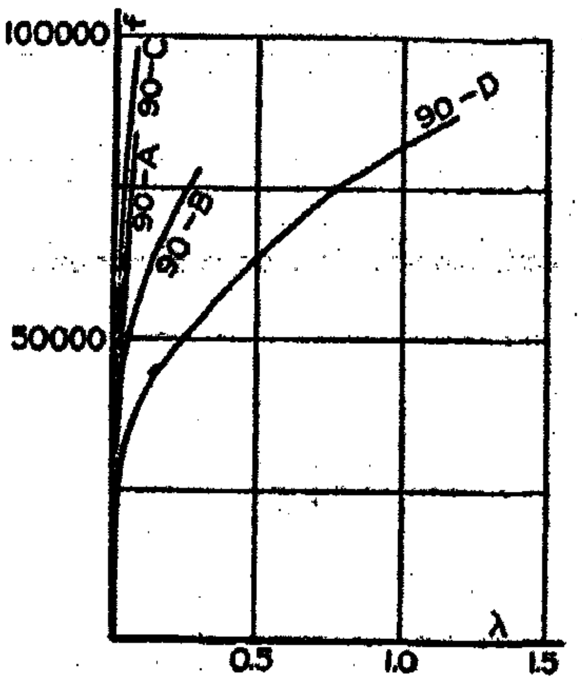

Fig. 4

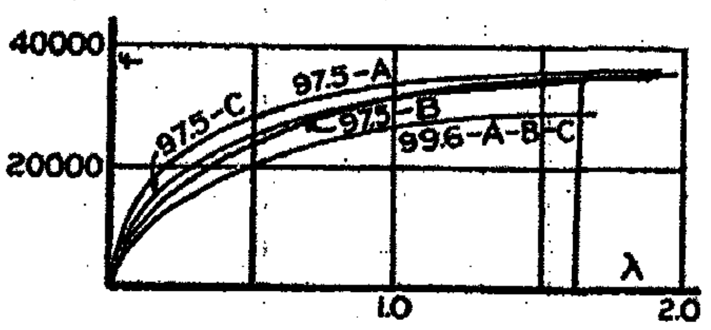

Fig. 5

show a very rapid increase in strength as we go from pure aluminum to the 5 percent alloy. For the chill-cast pieces this increase continues more gradually until we reach the maximum at 20 percent Cu. From here there is a very marked drop to the 25 percent alloy. This may be assigned largely to a peculiarity of the very brittle alloys which we are approaching. When the metal enters the mould, it freezes at the surface, thus forming a skin. When shrinkage takes place, the skin already formed, being very stiff, cannot yield and a void is formed at the center. It seems almost impossible to prevent this. The annealed pieces show almost a constant strength throughout the range from 5 percent copper to 20 percent copper. A considerable rise in strength is noticed at 25 percent copper, due to the fact that the piece showed no signs of the void at the center, which was so noticeable in the other pieces of this composition.

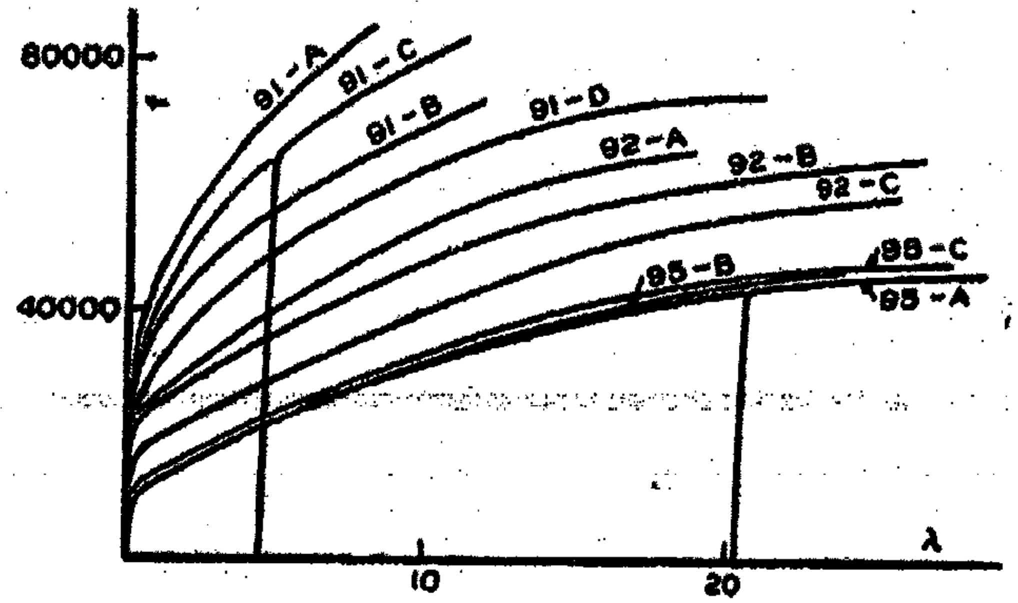

Fig. 6

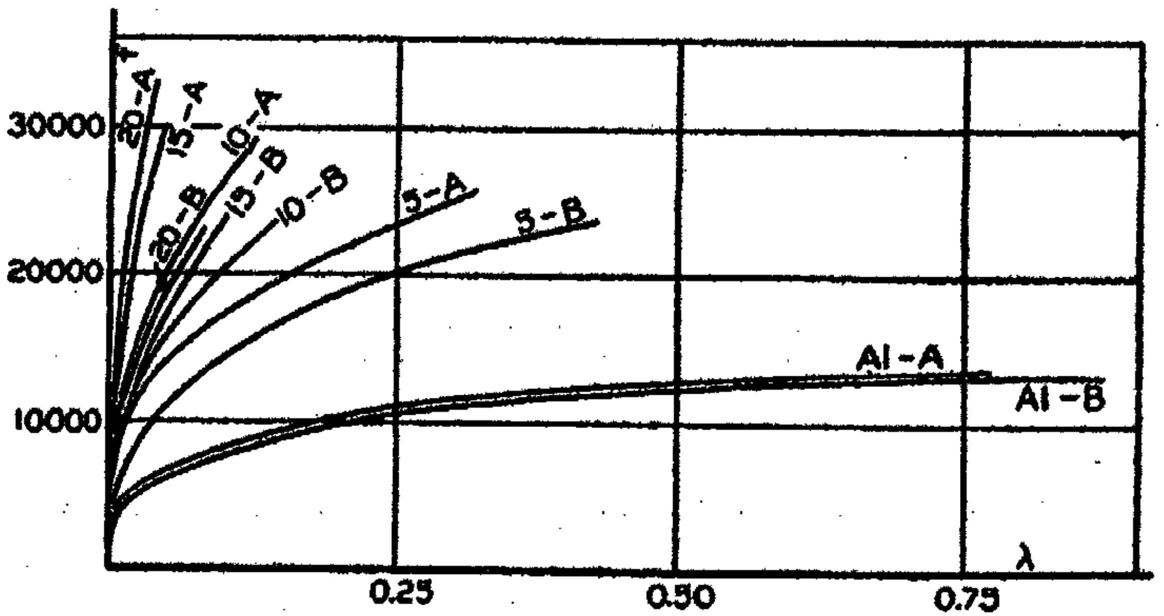

Fig. 7

The curves for ductility show a steady decrease as the copper content increases, rapid at first and then more gradual. This shows very clearly the stiffening effect of the $CuAl_2$ crystals.

Both the strength and ductility curves show the effect of annealing quite markedly. For every alloy tested, barring the 25 percent, the annealing reduces strength and increases ductility. As noted before, the 25 percent copper alloys did not show shrinkage voids, so that this apparent exception to the rule is the result of the absence of these voids and not of structural change. Temperature changes do not affect or change the structure in any way except to increase the size of the crystals. The best *dependable* alloy is about 10 percent copper. This corresponds very closely to the edge of the η-field or to the appearance of $CuAl_2$ crystals as shown in Fig. 1. While some good tests were obtained on alloys with more than 10 percent copper the pieces were by no means uniform.

In the strength curves (Fig. 3) there is very marked increase in strength due to small amounts of aluminum. This is due in all likelihood to two reasons; first, the aluminum removes all traces of copper oxide and produces a sound casting, and second, to the formation of an alloy. From this composition, 99.6 percent copper, the curves for all heat treatments are very nearly coincident and show a gradual rise in strength until the copper content is 92 percent. As the aluminum content is further increased, the curves rise more rapidly and continue to a maximum with 90 percent copper. The curve beigns its rapid rise while in the α-field but very close to the edge where β-crystals first appear, the 91 percent copper alloy is largely made up of α-crystals with traces of the β-phase appearing between. Chill-cast alloys with a composition lying in the α- + β-region (see Fig. 1) contain only these two phases as do the same alloys when annealed above 566°. When these same alloys are air-cooled the β breaks down, partly at least, to form the α- and γ-phases. Under these conditions α-, β- and γ-phases are probably present. The maximum strength was found in an 89.9 percent copper chill-cast piece which broke under a load of 108,200 pounds per square inch. The strength drops slightly again at 89 percent copper and still more at 88 percent, where pure β-crystals are still present. These crystals, as shown by the fractures, are very large, even when cooled rapidly.

The annealing has a very noticeable effect on the strength of the bronzes after we pass the 92 percent alloy. At 92 percent, the strength of the pieces annealed above 566° falls considerably below that of chill-cast pieces and those annealed at 500°, which last run very close together. At 91 percent, the strength of the pieces annealed above 566° runs up nearly to that of the chill-cast, while that of the pieces annealed at 500° is quite a little lower. At 90 percent, the chill-cast pieces have a strength intermediate between the strengths of the annealed pieces, the difference being about 10,000 pounds per square inch with those annealed above 566° highest at 98,000 pounds per square inch.

At 89 percent and 88 percent, the pieces annealed at 500° show about 8,000 pounds per square inch less strength than the chill-cast pieces. For these compositions, the pieces annealed above 565° showed up rather more poorly. This is due to the fact that at the temperature of quenching (about 800°), these alloys soften and tend to bend. Also above 600° the crystals grow very rapidly, and this causes the strength of the alloys to be greatly reduced. The 86 percent alloys were the most brittle with which we had to deal; so much so that if allowed to fall to the floor they were almost certain to break. The strengths recorded mean very little, for the pieces nearly always failed by breaking in the grips.

The variation of ductility in this series of alloys is very remarkable. As with the strength, the ductility increases very rapidly at first as aluminum is added, and then more gradually, though still quite rapidly until the 95 percent bronze is reached. It probably reaches a maximum value between 95 percent and 92 percent, at which latter point the "best" piece, chill-cast showed a slightly greater value than at 95 percent. One 95 percent specimen, annealed above 566°, gave 60.8 percent ductility. In passing from 92 percent to 91 percent the ductility drops from 57.5 percent to 16 percent and again to 1.2 percent at 90 percent. This shows clearly the character of the β-crystals which are exceedingly stiff. The ductility from here remains, as far as our observations continued, very nearly constant.

The effect of annealing on the ductility is not very marked. Chill-cast pieces and those annealed above 566° run very closely together from 99.6 percent to 95 percent copper, while the pieces annealed at 500° show a slightly smaller value. At 92 percent, the chill-cast pieces are the best as regards ductility, the annealed pieces showing somewhat smaller values, both close together. At 91 percent copper, the ductility curves are dropping so rapidly that it would be safe to say only that the ductilities lie in the neighborhood of 20 percent or about 1/3 the value at 92 percent. At 90 percent chill-cast pieces and those annealed above 566° C were very low in ductility, while those annealed at 500° C showed considerably more, 6-8 percent.

A few air-cooled pieces were made—90 percent and 91 percent. These show a rather marked increase in ductility over that of any other specimens of the same composition (see Tables). This gain in ductility does not reduce the strength in the 90 percent alloys, but reduces it slightly in the 91 percent.

From the diagram, Fig. 3, it is evident that the ductility of the β- and γ-crystals is practically zero while the α-crystals have a higher ductility the greater the aluminum content. The ductility appears to decrease at 92 percent before any of the β- or γ-phases has appeared. It is quite possible, however, that the falling off of the ductility with increasing aluminum content is more rapid than is shown by the diagram and that a sample with a copper content of 91.5 percent might have shown as high a ductility as that with 92 percent. No explanation can be offered at present for the fact that annealing appears to decrease the ductility. The opposite effect was observed with the copper-tin bronzes and is quite marked in the aluminum-rich bronzes. At the aluminum end of the series, the ductility of the η-crystals decreases with increasing copper content and becomes very low for $CuAl_2$.

The tensile strength of the β bronzes is higher than that of the γ bronzes, while that of the α bronzes increases with decreasing copper content. The maximum strength does not come at the point where the alloy ceases to be homogeneous. The presence of the stiffer β- or γ-crystals appears to add to the strength of the alloy up to a certain point. A similar phenomenon was observed with the copper-tin bronzes. The essential feature is, however, the amount of the α-crystals present. For this reason the effects due to annealing above and below the inversion point are not so striking as with the copper-tin bronzes. Owing to the greater intrinsic strength of the β-alloys, the maximum strength is greater for the α- and β-alloys than for the α- and γ-alloys. At the aluminum end of the series, the maximum strength occurs in the field for γ and $CuAl_2$ instead of at the boundary curve.

The character of fractures in the aluminum-rich series varies from the fibrous of pure aluminum to semivitreous in the 20 percent and 25 percent copper alloys. It becomes semi-granular in the 5 percent, quite granular at 10 percent, crystalline at 15 percent. Pure aluminum and the 5 percent alloys generally show a cupped or irregular fracture. The 10 percent and 15 percent alloys are usually quite irregular but never cupped. The 20 percent and 25 percent pieces break almost square across, the 25 percent alloy breaking very much like glass.

The bronzes show a cupped, diagonal or irregular, fibrous fracture, from pure copper to the 92 percent bronze. At 91 percent, the fracture is semi-granular and almost straight across. In the 90 percent, two sorts of fractures are noticeable. All the pieces show a crystalline fracture, those annealed at 500° showing a fairly smooth break, while those chill-cast or annealed above 565° were very irregular and showed large β-crystals. The air-cooled pieces were similar to those annealed at 500°, except that the fracture was somewhat more irregular. The 88 percent and 89 percent pieces show a very irregular, coarsely crystalline fracture and that of the 86 percent bronze is quite vitreous.

Alloys containing 5 percent copper or less show a slight local necking. This is also true of bronzes containing 92 percent copper or more.

The color of the aluminum-rich alloys is uniformly white. The alloys containing 10 percent copper or more show a beautifully smooth surface when cast. Below this amount of copper content, the surface of the castings, while smooth, was not nearly so good. Aside from this difference in smoothness, the appearance of all the alloys of this series is the same.

The bronzes show a greater variation in respect to color. The 99.6 percent bronze is very nearly the color of pure copper but slightly lighter. The 97.5 percent copper alloy has a rich gold color with a pinkish tint. The other copper-rich bronzes have a golden color which becomes lighter as the aluminum content increases. With less than 84 percent copper the yellow color disappears.

Little needs to be said about the stress-strain diagrams. These in themselves are graphical descriptions of the behavior of the various alloys. However, for any one alloy the diagrams are of similar form regardless of the heat treatment. The yield point or elastic limit can not be easily located. This, of course, is true of any unworked metal. In a few cases after the load had been run well up it was reduced to zero and then again applied and the extension readings taken. This gives the elastic lines shown in some of the diagrams. From these lines it would be possible to compute the modulus of elasticity.

In the copper-rich alloys which have a high ductility the breaking load is really much greater than the data imply. The reduction in cross-section is considerable, due to the elongation.

In the tables, the following abbreviations have been used:

Both tables, with respect to heat treatment,

A—chill-cast,

B—for aluminum-rich alloys, annealed at 400°, for aluminum bronzes, annealed 2 days at 500°,

C—annealed above 566°, 30 minutes, and quenched in water,

D—air-cooled.

Table I, with respect to character of fracture,
G—good,
B—bad,
f.—fibrous,
gr.—granular,
cr.—crystalline,
v.—vitreous,
ox.—oxide,
irr.—irregular,
diag.—diagonal,
tr.—trace.

Table II,
P = load in pounds,
f = load per sq. in., pounds,
L = length between marks,
γ = extension.

TABLE I

Aluminum-rich alloys

Heat treatment	Diam.	Ultimate strength	Percentage extension	Fracture
		0 percent Cu		
A	0.382	13750	15.4	G—f. cup, necked.
	0.398	13320	17.0	"
B, 4 days	0.381	13130	18.0	"
	0.375	13400	18.0	"
		5 percent Cu		
A	0.383	23750	7.5	B—gr. cr. cup tr. slag
	0.399	23780	9.0	B—gr. cr. irr. tr. slag
	0.394	25750	6.4	G—gr. irr
B, 4 days	0.376	21050	7.0	"
B, 6 days	0.386	23620	8.6	G—f.cup
	0.376	23200	8.4	G—f. diag.

Table I—(*Continued*)

Heat treatment	Diam.	Ultimate strength	Percentage extension	Fracture
10 percent Cu				
A..........	0.376	29150	1.7	G—gr. st
	0.376	28600	1.8	B—tr. ox.
	0.392	27500	1.2	B—tr. ox.
	0.380	26450	2.0	G—gr.
B, 4 days...	0.375	21650	2.78	G—gr. cr. irr.
	0.374	23300	2.8	“
B, 3 days...	0.380	20650	2.6	“
	0.377	21750	2.86	“
	0.375	22150	3.36	“
15 percent Cu				
A..........	0.377	29300	1.4	G—gr. cr. irr.
	0.380	29200	0.9	“
	0.379	29700	0.9	“
	0.374	29550	0.84	“
B, 6 days...	0.379	22550	1.8	B—gr. tr. slag
	0.378	22500	2.0	G—gr.
	0.388	23600	2.0	“
	0.377	23000	1.9	“
20 percent Cu				
A..........	0.376	32700	0.15	G—cr. semi-v.
	0.373	31050	0.4	“
(Test length, 6 inches)	0.375	26950	0.5	“
B, 4 days...	0.379	22800	1.1	“
	0.379	23050	1.2	“
25 percent Cu				
A..........	0.377	17850	0.14	G—v. void
	0.381	18950	0.4	“
	0.381	20000	..	“
	0.382	22700	0.18	“
B, 4 days...	0.379	25650	0.6	G—v. solid
	0.378	13900	..	G—v. void

Table I—(*Continued*)

Aluminum bronzes

Heat treatment	Diam.	Ultimate strength	Percentage extension	Fracture
99.6 percent Cu				
A..........	0.381	28550	33.6	G—f. neck
	0.382	28800	32.8	"
	0.379	29450	33.8	"
B..........	0.375	28900	29.2	"
	0.376	28450	32.6	"
	0.374	28450	35.0	"
	0.375	25600	20.8	G—semi-cr.
	0.376	28100	32.0	G—f. cr. semi-cup
C..........	0.376	28100	33.0	B—f. small air-hole
	0.374	28600	33.0	G—f. cup neck
	0.378	28900	32.0	" "
	0.376	27800	32.0	B—small air-hole
97.5 percent Cu				
A..........	0.378	35600	40.0	G—f. diag. neck
	0.378	35450	37.2	G—f. cup neck
	0.378	35800	38.0	"
B..........	0.371	32500	23.0	"
	0.376	35100	36.6	"
	0.380	34100	27.2	G—cr.
C..........	0.378	35450	37.0	G—f. cup neck
	0.376	35300	38.0	"
	0.377	36000	39.2	"
95 percent Cu				
A..........	0.381	46850	56.6	G—f. semi-cup neck
	0.377	46600	59.7	"
	0.375	45250	47.0	B— " tr. slag
B..........	0.378	43000	57.2	" "
	0.374	46250	46.4	G—f. cr. cup neck
	0.377	47300	49.6	"
	0.375	45250	44.4	B— " small blow-hole
	0.378	45750	54.4	B— " tr. slag
C..........	0.377	47200	58.4	G—f. diag. neck
	0.374	47000	60.8	G—f. cup neck
	0.377	47650	53.8	"
	0.375	47000	54.4	"

Table I—(*Continued*)

Heat treatment	Diam.	Ultimate strength	Percentage extension	Fracture
92 percent Cu				
A	0.386	66200	57.6	B—f. cup tr. slag
	0.378	65400	43.6	G—f. cup neck
	0.372	63000	47.0	B— " tr. slag
B	0.373	56500	42.0	B— " tr. slag
	0.371	64500	53.0	G—f. diag. neck
	0.368	61900	48.4	G—f. cup neck
C	0.372	57900	43.4	B— " tr. slag
	0.376	45100	30.0	B—f. cr. tr. slag
	0.372	50500	38.1	G—f. irr.
	0.369	56350	52.0	G—f. cup neck
	0.370	58600	51.6	"
91 percent Cu				
A	0.372	84200	26.0	B—gr. st. air-hole
	0.369	81800	16.0	G—gr. st.
	0.372	86200	16.2	"
	0.374	76100	25.4	B " tr. slag
B	0.370	74100	24.0	G—gr. st.
	0.372	73400	23.4	"
	0.376	67250	17.2	G—cr. gr.
	0.374	69700	17.1	"
C	0.374	81000	24.2	B— " air hole
	0.375	74700	23.6	B— " tr. slag
	0.370	81800	30.0	G—f. cr.
	0.369	83200	22.6	"
D	0.372	74250	42.8	"
	0.373	74700	42.4	"
90 percent Cu				
A	0.371	88000	1.0	G—cr. st.
	0.370	83700	1.2	"
	0.372	79200	6.4	"
B	0.368	78700	5.6	"
	0.365	72000	8.0	"
	0.374	73000	16.4	"
	0.369	70100	7.2	"
C	0.374	97500	1.2	G—cr. very irr.
	0.369	98000	1.3	"
C	0.363	98400	1.3	G—cr. very irr.
D	0.367	85900	18.4	G—cr. irr.
	0.361	86900	23.6	"
	0.369	86800	20.4	"
	0.369	86250	18.8	"

Table I—(*Continued*)

89 percent Cu

Heat treatment	Diam.	Ultimate strength	Percentage extension	Fracture
A	0.374	83500	1.8	B—coarsely cr. air hole
	0.375	79600	2.0	G—coarsely cr.
	0.373	86900	1.8	"
B	0.368	79800	1.2	"
	0.380	59800	0.6	"
	0.371	57700	0.6	"
	0.373	65700	..	"
C	0.372	55200	0.24	G— "

88 percent Cu

A	0.371	78600	1.4	G—very coarsely cr.
	0.374	56200	1.2	"
	0.372	41450	0.8	B— " bent
B	0.372	71350	0.4	G— " "
	0.371	64600	0.5	" "
	0.371	60100	0.5	" "
	0.373	64000	0.3	" "
C	0.371	23100	1.2	B—very large crystals, bent
	0.368	37600	1.2	These pieces showed tracks developed in heat treatment.
	0.372	29500	1.4	

86 percent Cu

B	0.372	17300	..	Vitreous
C	0.373	28800	..	Vitreous

All the other pieces of this composition broke in the grips.

91.6 percent Cu

C	0.369	85500	27.5	G—gr. f. cr.

89.8 percent Cu

A	0.370	108200	1.25	G—cr. irr.

TABLE II

Aluminum-rich Alloys

Aluminum—A, $d = 0.382$				Aluminum—B, $d = 0.375$			
P	f	L	λ	P	f	L	λ
200	1750	4.987	0	200	1810	5.003	0
400	3500	4.991	0.004	400	3620	5.008	0.005
600	5250	5.016	0.029	600	5430	5.037	0.034
800	7000	5.061	0.074	800	7240	5.084	0.081
1000	8750	5.118	0.131	1000	9050	5.132	0.129
1300	11350	5.266	0.279	1200	10860	5.231	0.228
1460	12750	5.457	0.470	1400	12670	5.440	0.437
1580	13750	5.759	0.772	1480	13400	5.90	0.897
5 percent Cu—A, $d = 0.394$				5 percent Cu—B, $d = 0.386$			
300	2460	5.000	0	300	2560	5.000	0
600	4830	5.008	0.008	600	5130	5.006	0.006
900	7390	5.011	0.011	900	7700	5.011	0.011
1200	9850	5.014	0.014	1200	11350	5.038	0.038
1500	12300	5.031	0.031	1400	12000	5.061	0.061
1800	14800	5.059	0.059	1600	13700	5.082	0.082
2000	16400	5.084	0.084	1800	15400	5.111	0.111
2200	18100	5.112	0.112	2000	17100	5.152	0.152
2500	20500	5.168	0.168	2200	18800	5.200	0.200
2800	23000	5.239	0.239	2400	20500	5.255	0.255
3000	24600	5.289	0.289	2600	22200	5.320	0.320
3120	25750	5.320	0.320	2760	23600	5.430	0.430
10 percent Cu—A, $d = 0.376$				10 percent Cu—B, $d = 0.374$			
200	1800	5.000	0	300	2730	5.002	0
600	5400	5.004	0.004	600	5460	5.006	0.004
1000	9000	5.010	0.010	900	8190	5.012	0.010
1200	10800	5.011	0.011	1200	10920	5.021	0.019
1400	12600	5.013	0.013	1500	13650	5.039	0.037
1600	14400	5.020	0.020	1800	16400	5.054	0.052
1800	16200	5.028	0.028	2000	18200	5.070	0.068
2000	18000	5.036	0.036	2200	20000	5.090	0.088
2200	19800	5.049	0.049	2400	21850	5.117	0.115
2400	21600	5.060	0.060	2500	22700	5.129	0.127
3240	29150	5.120	0.120	2560	23300	5.140	0.138

Table II—(*Continued*)

15 percent Cu—A, $d = 0.379$				15 percent Cu—B, $d = 0.388$			
P	f	L	λ	P	f	L	λ
300	2660	5.002	0	300	2540	5.002	0
600	5320	5.005	0.003	900	7620	5.009	0.007
900	7980	5.007	0.005	1200	10160	5.020	0.018
1500	13300	5.012	0.010	1800	15240	5.040	0.038
2000	17700	5.018	0.016	2000	17100	5.050	0.048
2500	22080	5.022	0.020	2200	18650	5.059	0.057
2700	23900	5.025	0.023	2400	20300	5.071	0.069
3000	26600	5.030	0.028	2600	22050	5.086	0.084
3350	29700	5.045	0.043	2800	23730	5.100	0.098
20 percent Cu—A, $d = 0.376$				20 percent Cu—B, $d = 0.377$			
500	4500	5.002	0	500	4460	5.010	0
1000	9000	5.006	0.004	1000	8900	5.014	0.004
1500	13500	5.009	0.007	1500	13400	5.022	0.012
2000	18000	5.012	0.010	2000	17850	5.042	0.032
2500	22500	5.016	0.014	2400	21400	5.059	0.049
3640	32700	5.023	0.021	2580	23050	5.060	0.050
25 percent Cu—A, $d = 0.381$				25 percent Cu—B, $d = 0.379$			
500	4400	5.010	0	500	4400	5.002	0
1000	8750	5.016	0.006	1000	8850	5.005	0.003
1500	13140	5.020	0.010	1500	13250	5.011	0.009
1800	16000	5.022	0.012	1800	15950	5.016	0.014
2000	17500	5.025	0.015	2000	17700	5.020	0.018
2160	18950	5.028	0.018	2300	20350	5.023	0.021
				2500	22100	5.029	0.027
				2800	24600	5.032	0.030
				2900	25600	5.033	0.031

Aluminum Bronzes

99.6 percent Cu—A, $d = 0.379$				99.6 percent Cu—C, $d = 0.378$			
500	4420	5.020	0	500	4460	5.018	0
1000	8840	5.130	0.110	1000	8920	5.110	0.092
1500	13280	5.230	0.210	1500	13380	5.230	0.212
2000	17680	5.410	0.390	2000	17840	5.400	0.382
2500	22100	5.620	0.600	2400	21400	5.562	0.534
2800	24800	5.790	0.770	2600	22300	5.662	0.644
3000	26500	5.870	0.850	2800	25000	5.850	0.832
3100	27400	6.050	1.030	3000	26800	5.972	0.954
3200	28400	6.190	1.110	3100	27700	6.060	1.042
3300	29200	6.480	1.460	3200	28600	6.260	1.242
3320	29400	6.690	1.670	3250	29000	6.600	1.582

Table II—(*Continued*)

99.6 percent Cu—B, $d = 0.375$

P	f	L	λ
500	4525	5.010	0
1000	9050	5.058	0.048
1500	13575	5.178	0.168
1800	16300	5.278	0.268
2000	18100	5.330	0.320
2300	20800	5.550	0.530
2500	22600	5.586	0.576
2700	24400	5.700	0.690
2900	26300	5.906	0.896
3000	27200	6.025	1.015
3100	28000	6.143	1.133
3190	28900	6.460	1.450

97.5 percent Cu—A, $d = 0.378$				97.5 percent Cu—B, $d = 0.376$			
1500	13400	5.000	0	1000	9000	5.04	0
2000	17850	5.150	0.150	1500	13500	5.120	0.080
2500	22300	5.312	0.312	2000	18000	5.300	0.260
3000	26800	5.493	0.493	2500	22270	5.470	0.430
3500	31200	5.770	0.770	3000	27000	5.660	0.620
3800	33900	6.018	1.018	3500	31500	5.990	0.950
4000	35700	6.370	1.370	3750	34800	6.250	1.210
4020	35900	6.900	1.900	3890	35000	6.830	1.790

97.5 percent Cu—C, $d = 0.377$

P	f	L	λ
1500	13450	5.120	0
3000	26880	5.650	0.530
3500	31400	5.710	0.590
3750	33600	6.130	1.010
4000	35850	6.520	1.400
* *	*	*	* *
1000	8930	6.629	1.503
2000	17360	6.637	1.515
3000	26790	6.640	1.520
4000	35720	6.702	1.582
4020	35900	6.960	1.840

Table II—(*Continued*)

95 percent Cu—A, $d = 0.381$

P	*f*	L	λ
1000	8770	5.012	0
1300	11400	5.042	0.030
1600	14030	5.130	0.118
2000	17540	5.282	0.270
2500	21900	5.495	0.483
3000	26300	5.700	0.688
3500	30700	5.908	0.896
4000	35100	6.190	1.178
45 0	39500	6.537	1.525
5000	43800	7.070	2.058
*	*	*	*
0	0	7.030	2.018
1000	8770	7.040	2.028
2000	17540	7.050	2.038
3000	26300	7.060	2.048
4000	35100	7.070	2.058
5000	43800	7.082	2.070
5200	45500	7.360	2.348
5350	46900	7.830	2.818

95 percent Cu—B, $d = 0.377$

P	*f*	L	λ
1000	8960	5.011	0
1500	13440	5.060	0.049
2000	17920	5.290	0.279
2500	22400	5.500	0.489
3000	26900	5.695	0.684
3500	31400	5.908	0.897
4000	35800	6.198	1.187
4500	40350	6.525	1.514
5000	44800	7.050	2.039
5200	46600	7.338	2.327
5280	47300	7.480	2.469

95 percent Cu—C, $d = 0.377$

1000	8960	5.010	0
2000	17920	5.270	0.260
2500	22400	5.470	0.460
3000	26900	5.670	0.660
3500	31400	5.890	0.880
4000	35800	6.190	1.180
4400	39400	6.470	1.460
4800	43000	6.820	1.810
5000	44800	7.020	2.010
5200	46600	7.370	2.360
5300	47500	7.690	2.680
5320	47650	7.750	2.740

92 percent Cu—A, $d = 0.386$

1000	8550	5.010	0
2000	17100	5.020	0.010
3000	25650	5.100	0.090
3500	29900	5.190	0.180
4000	34200	5.320	0.310
4500	38400	5.450	0.440
5000	42700	5.575	0.565
5500	47000	5.710	0.700
6000	51300	5.870	0.860
6500	55550	6.075	1.065
7000	59800	6.310	1.300
7500	64050	6.640	1.630
7750	66200	6.880	1.870

92 percent Cu—A, $d = 0.371$

1000	9250	5.007	0
2000	18500	5.016	0.009
2500	23050	5.072	0.065
3000	27750	5.191	0.184
3500	32400	5.340	0.333
4500	41600	5.715	0.780
5500	50800	6.160	1.160
6000	55500	6.430	1.423
6500	60100	6.886	1.879
6800	62900	7.230	2.223
6980	64500	7.650	2.643

Table II—(*Continued*)

92 percent Cu—C, *d* = 0.370

P	*f*	L	λ
1000	9300	5.008	0
2000	18600	5.048	0.040
3000	27900	5.400	0.392
3500	32500	5.630	0.622
4000	37200	5.878	0.870
4500	41800	6.160	1.152
5000	46500	6.310	1.302
5500	51150	6.620	1.612
5750	53500	6.820	1.812
6000	55800	7.007	1.999
6250	58100	7.420	2.412
6300	58500	7.580	2.572

91 percent Cu—A, *d* = 0.372

1000	9210	5.000	0
2000	18420	5.003	0.003
3000	27630	5.015	0.015
4000	36840	5.040	0.040
5000	46050	5.100	0.100
6000	55260	5.200	0.200
6500	59800	5.265	0.265
7000	64470	5.350	0.350
7500	69000	5.420	0.420
8000	73500	5.520	0.520
8500	78200	5.620	5.620
9000	82800	5.740	0.720
9378	86400	5.810	0.810

91 percent Cu—A, *d* = 0.370

1000	9300	5.004	0
2000	18600	5.008	0.004
3000	27900	5.020	0.016
3500	32550	5.040	0.036
4000	37200	5.080	0.076
4500	41800	5.150	0.146
5000	46500	5.225	0.221
5500	51100	5.312	0.308
6000	55800	5.470	0.466
6500	60500	5.612	0.608
7000	65100	5.790	0.786
7500	69750	6.015	1.009
7960	74000	6.200	1.196

Table II—(*Continued*)

91 percent Cu—C, $d = 0.369$				91 percent Cu—D, $d = 0.372$			
P	*f*	L	λ	P	*f*	L	λ
2000	18700	5.010	0	1000	9220	5.005	0
3000	28050	5.030	0.020	2000	18400	5.010	0.005
4000	37400	5.065	0.050	3000	27650	5.100	0.095
4500	42060	5.110	0.100	4000	36900	5.198	0.193
5000	46750	5.165	0.155	5000	46100	5.410	0.405
5500	51450	5.275	0.265	6000	55300	5.680	0.675
6000	56100	5.330	0.320	7000	64500	6.080	1.075
*	*	*	*	8000	73500	6.755	1.750
1000	9350	5.457	0.429	8180	74700	7.120	2.115
2000	18700	5.439	0.447				
3000	28050	5.464	0.454				
4000	37400	5.470	0.460				
5000	46750	5.474	0.464				
6000	56100	5.480	0.470				
7000	65450	5.506	0.496				
8000	74800	5.730	0.720				
8500	79500	5.955	0.945				
8900	83200	6.130	1.120				
90 percent Cu—A, $d = 0.371$				90 percent Cu—B, $d = 0.368$			
1000	9250	5.000	0	1000	9410	5.000	0
2000	18500	5.001	0.001	2000	18820	5.001	0.001
3000	27800	5.010	0.010	3000	28230	5.003	0.003
4000	37000	5.015	0.015	4000	37640	5.010	0.010
5000	46200	5.018	0.018	5000	47000	5.023	0.023
6000	55500	5.020	0.020	6000	56460	5.070	0.070
7000	64700	5.030	0.030	6500	61200	5.130	0.130
8000	74000	5.040	0.040	7500	70500	5.210	0.210
9000	83200	5.050	0.050	8000	75280	5.260	0.260
9500	88000	5.060	0.060	8350	78500	5.280	0.280
90 percent Cu—D, $d = 0.361$				90 percent Cu—C, $d = 0.363$			
2000	19560	5.010	0	1000	9680	5.001	0
3000	29340	5.020	0.010	3000	19360	5.009	0.008
4000	39120	5.080	0.070	4000	38700	5.012	0.011
5000	48900	5.220	0.210	5000	49400	5.016	0.015
6000	58680	5.400	0.390	6000	58700	5.025	0.024
7000	68400	5.600	0.590	7000	67700	5.031	0.030
8500	83100	6.060	1.050	8000	77400	5.037	0.036
8900	87000	6.180	1.170	9000	87000	5.043	0.042
				10000	96800	5.062	0.061
				10200	98560	5.066	0.065

Table II—(*Continued*)

89 percent Cu—A, $d = 0.373$

P	f	L	λ
2000	18600	5.005	0
4000	37200	5.010	0.005
6000	55800	5.018	0.013
7000	64100	5.030	0.025
8000	74400	5.038	0.038
9000	82500	5.050	0.045
9500	86900	5.090	0.085

89 percent Cu—B, $d = 0.368$

P	f	L	λ
2000	18800	5.004	0.0
4000	37600	5.010	0.006
6000	56400	5.020	0.016
8000	75200	5.050	0.046
8500	80000	5.060	0.056

89 percent Cu—C, $d = 0.372$

P	f	L	λ
2000	18400	5.000	0
4000	36800	5.010	0.010
6000	55200	5.012	0.012

88 percent Cu—A, $d = 0.371$

2000	18500	5.005	0
3000	27750	5.010	0.005
4000	37000	5.017	0.012
5000	46250	5.020	0.015
6000	55500	5.030	0.025
7000	64750	5.040	0.035
8000	74000	5.070	0.065
8500	78600	5.070	0.065

88 percent Cu—B, $d = 0.372$

2000	18400	5.002	0
3000	27650	5.003	0.001
4000	36800	5.008	0.006
5000	46100	5.010	0.008
6000	55300	5.013	0.011
7000	64500	5.018	0.016
7770	64800	5.020	0.018

88 percent Cu—C, $d = 0.368$

P	f	L	λ
2000	18800	5.028	0
3000	28200	5.040	0.012
4000	37600	5.060	0.032

Conclusions

In summing up the results of our investigations, we may draw the following conclusions:

1. In the aluminum-rich series the maximum dependable

strength occurs in the neighborhood of the 10 per cent copper alloy and its value is about 28,000 pounds per square inch. The alloy is, however, of low ductility. 20 percent copper seems to be the greatest copper content for this series which will give a useful alloy.

2. Throughout the aluminum-rich series, annealing for from 3 to 6 days at 400° reduces tensile strength and increases ductility.

3. In the bronzes with more than 92 percent copper, annealing seems to have no marked effect on either strength or ductility.

4. In the bronzes, between 92 percent and 95 percent copper, tensile strengths varying from 48,000 to 66,000 pounds per square inch with ductilities of from 50 percent to 60 percent may be expected.

5. From 89–91 percent copper, annealing above 565° and quenching in water gives an increased strength, but very low ductility.

6. Bronzes with less than 90 percent copper are brittle and likely to be unreliable; of coarse crystalline structure, and soft at temperatures considerably below the melting point.

7. Air-cooling bronzes of 90-91 percent copper give an increased ductility with but slightly reduced strength.

8. The ductility of the chill-cast bronzes decreases very rapidly in the 91 percent copper content, the ductility in the 92 percent bronze being 50 percent to 60 percent and at 90 percent copper the ductility is only between 6 percent and 8 percent.

9. With 90 percent copper content a strength of 100,000 pounds per square inch may be expected from pieces chill-cast or annealed above 566°. The strength is considerably reduced by annealing below 566°.

10. The β-alloys may be expected to give the highest strengths.

11. Small amounts of the β-phase in contact with α cause a very marked decrease in ductility and a very marked increase in strength.

12. Small amounts of the γ-phase in contact with α increases the strength and decreases the ductility of these alloys.

13. The general effect of annealing is to decrease the ductility of the copper-rich alloy and to increase the ductility of the aluminum-rich alloys.

14. The most dependable high-strength aluminum-rich alloy is found near the edge of the η-field or with a 10 percent copper content.

15. The maximum tensile strength does not occur at a boundary curve.

The expense of this work has been covered by a grant from the Carnegie Institution to Prof. Bancroft.

The testing has been done in the laboratories of Sibley College.

This research has been conducted under the direction of Prof. Bancroft, and we wish here to thank him for his assistance and kindly criticisms.

Cornell University

A SUPPOSED AMMONIUM SYNGENITE[1]

J. M. BELL AND W. C. TABER

In a recent publication J. D'Ans[2] has shown that the double sulphate of ammonium and calcium, which he calls ammonium syngenite, exists at 25° and even at lower temperatures. In our former paper[3] in which we described a double sulphate obtained at 50°, we stated that as Droeze, Cohn and Sullivan had not noticed a double sulphate, it was probable that it was not stable at 25°, the temperature at which Sullivan worked. There was, however, no record that they investigated solutions approaching saturation with respect to ammonium sulphate, and consequently the possibility of a double sulphate at higher concentrations was not excluded.

To the double sulphate of ammonium and calcium D'Ans has given the formula $(NH_4)_2SO_4.CaSO_4.H_2O$, based on its similarity in crystal form to syngenite, and on a determination of the composition of the solid product obtained by washing the double compound free of the mother-liquor by an alcohol-water mixture and then by an alcohol-ether mixture. This treatment is claimed to cause no precipitation from the mother-liquor and also to cause but very slow decomposition of the crystals. In order to determine the effect of this treatment upon the solid residue, we have washed about 20 grams of the residue with about 75 cc of 50 percent alcohol in small portions, followed by washing with about 30 cc of a 50 percent alcohol-ether mixture in three portions, each time removing the wash liquid as far as possible by suction. The residue was then dried at about 40° until no odor of alcohol or ether

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[1] Published by permission of the Secretary of Agriculture.

[2] Berichte, 39, 3326 (1906).

[3] Jour. Phys. Chem., 10, 119 (1906). In this paper we misquoted the formula given by Fritsche (Jour. prakt. Chem., 72, 291 (1857)), for the double sulphate of calcium and sodium, which should have been $2Na_2SO_4.CaSO_4.2H_2O$ and not $Na_2SO_4.CaSO_4.2H_2O$.

could be detected, requiring about ten minutes. In the following table are given the results of the analysis of this residue, and also the results of D'Ans.

	Loss on ignition	Ca weighed as CaO.	SO_3 weighed as $BaSO_4$
D'Ans	52.38	14.28	—
Authors	49.65	15.21	53.46
Calc. from $(NH_4)_2SO_4.CaSO_4.H_2O$	52.45	14.00	55.91
Calc. from $(NH_4)_2SO_4.CaSO_4.2H_2O$	55.3	13.17	52.60

From our results upon the loss on ignition after washing with various mixtures, it is evident that this treatment caused an increase in the quantity of lime in the residue. In other words, even if the formula proposed by D'Ans were correct, the above experiments prove that washing with an alcohol-water mixture decomposes the compound rapidly, and consequently the results of D'Ans with a product so obtained are open to serious doubt. The concordance between the calculated and his observed value of the loss on ignition is probably due to a smaller degree of decomposition than we have observed. As the molecular weight of ammonium sulphate and calcium sulphate are very close, no conclusions can be drawn from the sulphate determinations. Some water may also have been removed by the alcohol-ether treatment.

It is apparent, therefore, that washing with a solvent to remove the mother-liquor, results in the decomposition of the crystals by the removal of ammonium sulphate and possibly of some water. To determine the composition of the crystals, an indirect method must be resorted to. We have repeated two determinations by the indirect method of residues, and both sets of figures confirm the formula which we gave in our former paper. These mixtures have stood at room temperature (20°) for about four months.

By plotting these on a triangular diagram and joining the corresponding points, both lines cross the line representing equi-molecular quantities of the sulphates, at the point representing 11.5 percent of water. From the formula which we have given the compound, $(NH_4)_2SO_4.CaSO_4.2H_2O$, the calculated percentage of water is 11.8. In our former paper another indirect method is given. By adding the three components in the above ratio to a solution in equilibrium with the double sulphate, no change was observed in the composition of the solution. Consequently, it follows that the components must have been added in the ratio in which they were present in the solid phase.

Solution		Residue	
$(NH_4)_2SO_4$ Percent	$CaSO_4$ Percent	$(NH_4)_2SO_4$ Percent	$CaSO_4$ Percent
37.82	0.261	42.15	33.36
38.90	0.226	42.49	32.65

In this paper, we have shown:

1. That the method of D'Ans for removing the mother-liquor causes a rapid decomposition of the crystals, and any analytical results on the composition of the solid so obtained are invalidated.

2. That by indirect methods of analysis, the formula formerly given by us, is correct.

Bureau of Soils,
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Washington, D. C.

CALCIUM SULPHATE IN AQUEOUS SOLUTIONS OF SODIUM CHLORIDE

BY F. K. CAMERON

In a recent publication Arth and Crétien[1] have announced results obtained by dissolving calcium sulphate in solutions of sodium chloride at various temperatures. They found that at temperatures below 62.5°-65° the solutions apparently contained more lime than was equivalent to the sulphuric acid present, while at higher temperatures the reverse was true. In consequence the authors criticize the earlier solubility determinations of Cloez[2] and myself.[3] Assuming the correctness of Arth and Crétien's figures it follows that at temperatures below 62° there would be a marked hydrolysis of calcium sulphate in the presence of solutions of sodium chloride, more lime than sulphuric acid going into solution, and that at higher temperatures a new solid phase separates containing relatively more sulphuric acid than required by the formula $CaSO_4$.

To test these points, Mr. W. C. Taber, of this laboratory, has determined the solubility curve for calcium sulphate in solutions of various concentrations of sodium chloride, at 80° C. In general, the results agreed closely with the earlier work in this laboratory. The curve appears to have a maximum point for a solution containing approximately 7.3 grams calcium sulphate ($CaSO_4$) and 155 grams sodium chloride per liter. None of the solutions were alkaline nor acid. Moreover, analyses showed that even in the presence of solutions containing more than 290 grams sodium chloride per liter, the solid phase contained the lime and sulphuric acid in the ratio required by the formula $CaSO_4$, and that no other base or acid was present in the solid.

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[1] Bull. Soc. Chim. Paris [3], 35, 778 (1906).

[2] Ibid. [3], 29, 167 (1903).

[3] Jour. Phys. Chem., 5, 556 (1901); See also Bull. No. 18, Div. of Soils, U. S. Dept. of Agr. (1901).

In Mr. Taber's experiments he employed a very pure sodium chloride, which had been recrystallized from a high-grade product. Nevertheless, he found, as did Arth and Crétien and previous workers in this laboratory, that in the presence of any considerable amounts of sodium chloride, the amounts of lime and sulphuric acid present in the solutions were not equivalent *as ordinarily determined.* In the present investigation the results from the lime determinations were uniformly higher than those from the sulphuric acid determinations when calculated as calcium sulphate ($CaSO_4$), the variation amounting in some cases to about 1.5 percent. It was found, however, that the lime determinations were usually too high, since the precipitate of calcium oxalate carried down greater or less amounts of sodium chloride, and re-solution with a second precipitation was necessary for accurate results. The solubility of the oxalate in the mother-liquor was small and negligible. On the other hand, the solubility of barium sulphate in the presence of sodium chloride, may be far from negligible, and great care was found necessary to secure an approximately complete precipitation of the sulphuric acid. This has long been known, however, and as far back as 1883 Dircks[1] gave quantitative figures showing that on account of the solubility of the precipitate, that even relatively small amounts of sodium or potassium chloride markedly interferes with the separation of sulphuric acid.

It follows from the foregoing considerations, that:

1. There is no noticeable hydrolysis of calcium sulphate.
2. Within a temperature range from below 25° to upwards of 80°, calcium sulphate forms no double salt in solutions of sodium chloride, at any concentration with respect to the latter.

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[1] Landw. Vers.-Stat., **28**, 185 (1883).

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Washington, D. C.

NEW BOOKS

Electrons, *or the Nature and Properties of Negative Electricity. By Oliver Lodge. 14 × 22 cm; pp. viii + 230. New York: The Macmillan Company. 1906. Price: bound, $2.00 net.*—The new work of the great English expositor has all the features of his earlier writings. We enjoy his direct and incisive style, his very homely but nevertheless apt analogies, his attempt to present the most advanced investigation in a way intelligible to the man of general culture, as well as the intense English sympathy which pervades the whole account. In one respect the present book seems to us to be defective, and that is in the insufficient use of diagrams in the opening chapters; those in other words in which the fundamental conditions of radiation are developed. No doubt a few suggestions will suffice in the case of readers familiar with Poynting's theorem, and who have accustomed themselves to the Fleming rules; but even these will often have to stop and consider whether the magnetic field, or the current or its equivalent, is the thing moving. Thus, for instance, the following pivotal passage will need a few readings, at least, to be adequately grasped:

"There being no conductor, this (induced) E. M. F. will propel no current, but it will represent an electric force which was not there before, and the new force will be in a new direction; the direction of an induced electric force is perpendicular to the direction in which the growing magnetic lines are moving, which in the present case is outwards from the charge. Consequently the new or induced E. M. F. points in the direction of motion, though in a sense opposed to any change in it; and the effect of the superposition of this new E. M. F. upon the already existing field is to cause a certain small transmission of energy in a radial direction out and away from the accelerated charge."

A few arrows and a circle would have made all this so much more approachable. In fact the willingness to condescend to these courtesies for the reader's benefit is what gives J. J. Thomson's Silliman Lectures their peculiar charm.

Lodge's book is dedicated to the collaborators in the Cavendish laboratory, and is in a large measure a presentation of the great work done there. Much of this, as for instance the determination of the speed of cathode rays, their electrochemical equivalent, as Lodge calls *m/e* of the mass and charge of a corpuscle, the Zeeman contributions, etc., are to be found in many contemporary books. Lodge's presentations, which are here adequately illustrated, are characteristic of his earnestness as a writer, inasmuch as they make uncompromisingly for the difficulties involved. Much side light is thrown on the Zeeman effect. We miss the date of Wiechert's experiment on the speed of the cathode rays, which we believe to have been quite as early as the Cavendish determinations. We read on p. 84 that "Mr. Wilson tried to get an estimate of their size (fog particles are referred to) from the colours, but it was difficult and unsatisfactory." Such attempts were indeed made by J. J. Thomson (*Phil. Mag.*, 46, 529, 1898) and abandoned. C. T. R. Wilson, to our knowledge, merely assumed that fog particles in the large red coronas just above the violet are small as compared with the wave length of light,—a very different not to say hazardous thing (*Phil. Trans.*, 189, 301, 1897).

The chief burden of Lodge's summary is the electric theory of matter, and here the endeavor is to reproduce and interpret the very newest points of view. As a consequence, not only is the older Cavendish atom, with its globule of positive jelly in which revolving negative corpuscles are "sown," carefully discussed, but the very recent views of Thomson which virtually abandon the preceding theory and indicate that the number of electrons in an atom is comparable with its atomic weight, are systematically set forth. An appendix develops some of the mathematical equations used in the text. *Carl Barus*

Essais de Jean Rey, *Docteur en Médecine. Edition nouvelle avec Commentaire, publiée par Maurice Petit. 16 × 25 cm; pp. xxvii + 191. Paris: A. Hermann, 1907. Price: paper, 7 francs.*—*Quellenstudium* is by no means a lost art in Paris, judging from the number of excellent reprints and compilations which have issued from that center. A short time ago we reviewed what promises to be a monumental work by M. Duhem, on the early history of mechanics. In a similar category belongs the memoir of M. Brouillon, on the origins of electrical science. We have now before us a reprint of the chemical writings of Jean Rey, edited with copious notes by M. Gobet (originally), at present by M. Dezeimeris and in particular by M. Maurice Petit. Rey is nearly unknown to English readers; but he appears to have been the true discoverer (1630) of the fact that air is a ponderable medium. This conclusion is developed in an admirably logical series of essays on the basis of the increase of weight observed on calcining lead and tin. Not to have enshrined Rey with Torricelli (1643), Pascal (1648), and one might add Boyle, Mariotte, and Priestley, is regarded by M. Frémy as *une des grandes injustices commises dans l'histoire de la science.* The reader of this book cannot fail to voice the same sentiment. The new edition has been left in the old French text, adding no doubt much to its piquancy so far as Frenchmen are concerned; but the English student will find his progress hampered, at least at the outset. *Carl Barus*

Löslichkeit und Löslichkeitsbeeinflussung. *By V. Rothmund. (Handbuch der angewandten physikalischen Chemie. Herausgegeben von Prof. Dr. G. Bredig. Band VII.) 16 × 25 cm; pp. xi + 196. Leipzig: Johann Ambrosius Barth, 1907. Price: paper, 8 marks; bound, 9 marks.*—The subject is treated under the following heads: supersaturation; rate of solution; solubility determinations; effect of temperature on solubility; effect of pressure on solubility; change of solubility with changing state of solute; effect of third component on solubility; change of solubility due to chemical action. The general treatment is good, though the literature references are distinctly incomplete. On p. 6 a misprint makes the author say that small crystals are less soluble than large ones. On p. 39, Figs. 14 and 15 should either not have been given or should have been discussed properly. The reviewer doubts very much whether the Clausius-Clapeyron formula can be applied without modification to saturated solutions. While the author has limited himself rigidly to physical isomers, p. 105, it would have been well to have remembered the weakness of the flesh and to have pointed out explicitly under what circumstances the less stable modification may have the higher melting-point or the lesser solubility. *Wilder D. Bancroft*

A Text-Book of Electro-Chemistry. *By Max Le Blanc. Translated from the Fourth Enlarged German Edition, by Willis R. Whitney and John W. Brown. 15 × 23 cm; pp. xiv + 338. New York: The Macmillan Company, 1907. Price: $2.60 net.*—"The present work is a translation of the fourth German edition, and is essentially a revision and enlargement of that of the first German edition prepared by one of the present translators. Although in its preparation the earlier translation has been freely used, the changes and additions made by Professor Le Blanc, as well as minor additions introduced by the present translators, have either necessitated or rendered advisable the rewriting of a large part of the book." It has already been mentioned (11, 170) that the fourth German edition is a distinct improvement over the preceding three. There is one point which might well be changed in future editions. On p. 256 the single potential of hydrogen as a reducing agent is given as -0.311 volt while on p. 248 the single potential of hydrogen as a metal is given as -0.283 volt. Also, turf is not the equivalent for *Torf.* These things are confusing to students.
Wilder D. Bancroft

Deutsches Patentrecht für Chemiker. *By Julius Ephraim. (Monographien über angewandte Elektrochemie. XXV. Band.) 17 × 24 cm; pp. xxvii + 608. Halle: Wilhelm Knapp, 1907. Price: paper, 18 marks.*—The author has succeeded in writing an interesting book on what is apparently a hopelessly dry subject. Of course, the book has a practical value only for those who wish to take out or to overthrow German patents.
Wilder D. Bancroft

Elektrometallurgie des Eisens. *By Bernhard Neumann. (Monographien über angewandte Elektrochemie. XXVI. Band.) 17 × 24 cm; pp. x + 176. Halle: Wilhelm Knapp, 1907. Price: paper, 7 marks.*—The author discusses the processes, their actual results, the quality of the product, the power consumption, and the costs. Then he compares the electric furnace methods with the present methods. Finally there is a chapter on ferro-alloys. The author has done his work carefully and thoroughly, with the result that his book is an excellent one. The only weak point seems to be his ignorance as to the production of ferro-alloys in this country. In the comparison between electric furnace methods and chemical methods, the author's conclusions harmonize with those of practically everybody else. Under normal conditions the electric furnace cannot compete with the blast-furnace; but it will drive out the crucible process.
Wilder D. Bancroft

Über die elektrolytische Gewinnung von Brom und Jod. *By Max Schlötter. (Monographien über angewandte Elektrochemie. XXVII. Band.) 17 × 24 cm; pp. 50. Halle: Wilhelm Knapp, 1907. Price: paper, 2.40 marks.*—Under bromine the author takes up: chemical processes for manufacturing bromine; electrolytic processes; purification of bromine; analysis; uses and applications. Iodine is treated similarly though not at such length.
Wilder D. Bancroft

The Electrolytic Dissociation Theory. *By R. Abegg. Authorized Translation from the German, by Carl L. von Ende. 12 × 19 cm; pp. viii + 180. New York: John Wiley and Sons, 1907.*—The German edition appeared in 1903; so that it is not necessary to do more than call attention to the appearance of the English edition. The translator writes "cathion" throughout, but has otherwise done his work very satisfactorily.
Wilder D. Bancroft

Theoretical Electrochemistry and its Physico-Chemical Foundations. *By Heinrich Danneel. Translated from the Sammlung Göschen, by Edmund S. Merriam. 12 × 19 cm; pp. vii + 181. New York: John Wiley and Sons, 1907.*—The German edition has already been reviewed (10, 124). The translator has evidently not felt justified in correcting any of the errors, because they reappear in the same form. *Wilder D. Bancroft*

Van Nostrand's Chemical Annual. 1907. *A Handbook of Useful Data for Analytical, Manufacturing, and Investigating Chemists, and Chemical Students. Edited by John C. Olsen, with the Coöperation of Eminent Chemists. 12 × 19 cm; pp. iv + 496. New York: D. Van Nostrand Company, 1907. Price: $2.50 net.*—This is a book similar in scope to the corresponding German volume, though differing from it in some details. We are glad to see that the publishers consider that such a book has a chance for success when limited to English-speaking countries. It is much to be hoped that this volume will have the success that it deserves, and that it will be the first of a long series.

Wilder D. Bancroft

THE ELECTROLYTIC CORROSION OF BRASSES

BY AZARIAH THOMAS LINCOLN, DAVID KLEIN AND PAUL E. HOWE

Within recent years the increased demand for electrical energy in the industrial world has awakened renewed interest in the problem of corrosion of metallic structures by stray electric currents. We need only mention the work of certain classes of engineers upon the corrosion and consequent destruction of iron water mains, iron bridge foundations and possibly the foundations of the modern steel structure to show the great damage that electrolytic corrosion is doing yearly. Of equal technical interest is the corrosion of dissimilar metals in sea-water, such as the disintegration of the propellers on the ocean steamers, the rapid wearing out of hydraulic machinery. Within the last few years, scientific methods have been applied to the solution of the corrosion problem. Manifestly, it would require too much time to secure any data, if the experiments were to be performed under the same conditions as the metals corrode in actual usage. However, upon the basis that electrochemical and chemical action are identical, the same results may be secured by electrochemical means in a very much shorter period than by the chemical method. Such experiments have been performed by Mr. Curry[1] on the electrolytic corrosion of bronzes. In this paper, we present the results of a similar research on the electrolytic corrosion of brasses.

Our work has been confined primarily to the corrosion of the pure copper-zinc alloys, but a few experiments were made on the corrosion of copper-zinc-tin alloys containing a small percentage of tin. The constitution of alloys of copper and zinc has been a problem that has elicited the attention of a number of workers, but it was not until a few years ago that Shepherd[2] showed conclusively that there are no definite

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[1] Jour. Phys. Chem., 10, 474 (1906).

[2] Ibid., 8, 421 (1904).

compounds in the system copper-zinc He confirmed the work of Roberts-Austen that the liquidus consists of six branches and that there are six solid solutions, one in equilibrium with each branch of the freezing-point curve. The equilibrium curves, as worked out by Shepherd, are represented diagrammatically in Fig. 1.

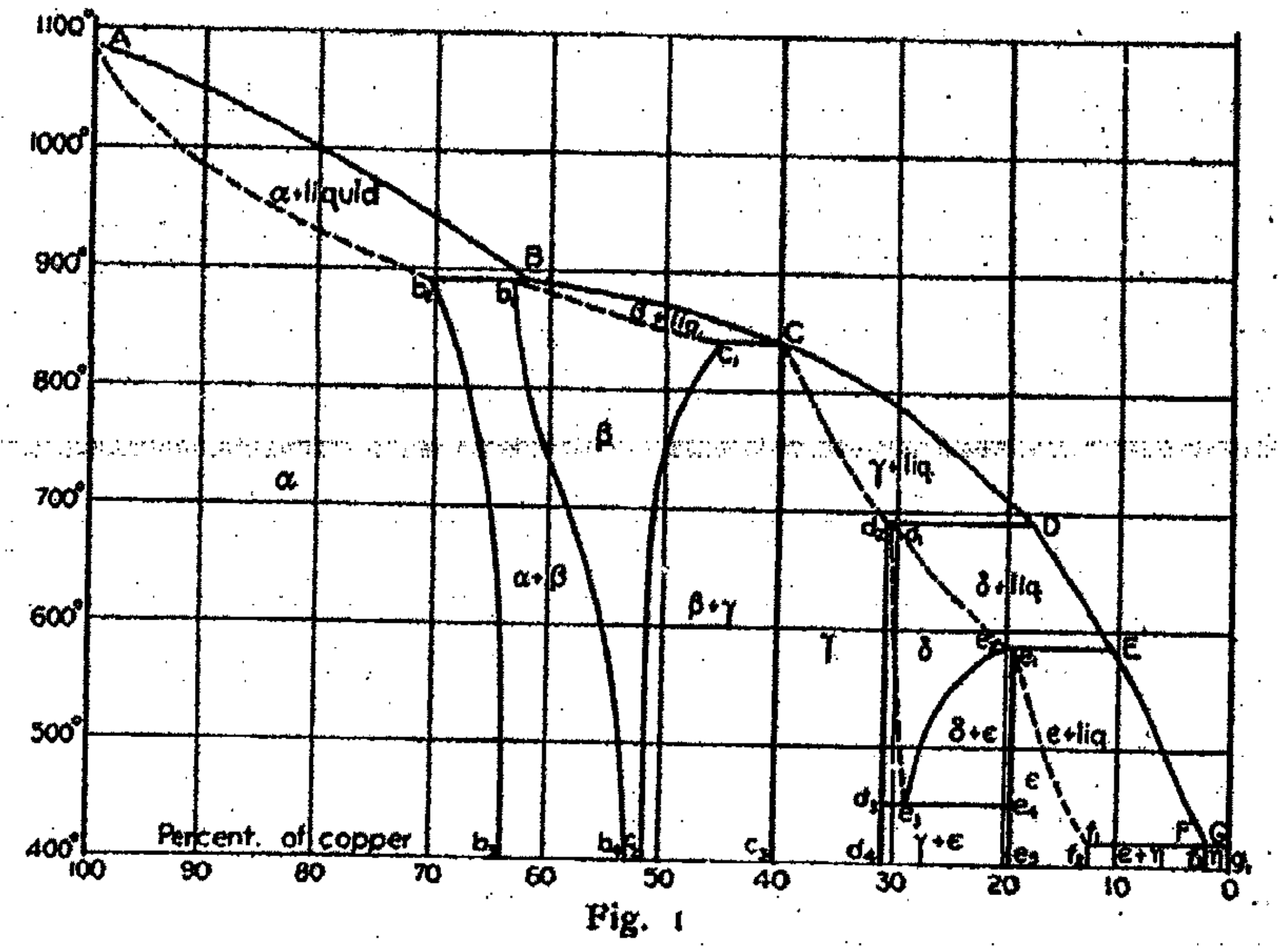

Fig. 1

The composition of the various solid solutions are represented, and the stable forms under various heat treatments. We shall only consider the solid solutions that constitute the alloys when they are annealed at 400° C, represented by the lowest horizontal line in the figure. From 100 percent to 64 percent copper, we have alloys of homogeneous α-crystals; from 64 to 53.5 percent, they consist of α-crystals scattered throughout the main mass of β, while from 53.5 to 51 percent, we have a solid solution of pure β. From 51 to 40 percent γ-crystals separate out from the β, and this sometimes results in forming large masses of the γ-crystals with a very marked decrease in the amount of β as the copper content decreases. From 40 to 31 percent copper, the alloy consists of homogeneous γ, and those containing from 31 to

20 percent are composed largely of the solid solution ε which contains a few γ-crystals, while between 20 and 12 percent, we have practically pure ε solid solutions. The annealed and cast samples of these alloys ranging in composition between 12 and 2.5 percent copper, are similar homogeneous mixtures of ε- and η-crystals. From 2.5 percent copper to pure zinc, the annealed samples are homogeneous, and all similar in structure consisting largely of η-crystals.

Brasses were prepared representing all of these stable forms at 400° C (except possibly the γ- and η-crystals) by melting pure electrolytic copper in a Battersea crucible under pulverized charcoal to prevent oxidation. When the copper was melted, the requisite amount of zinc was added in small quantities at a time and stirred with a graphite rod after each addition. When the melt was ready to be poured, the charcoal was skimmed off, the melt stirred very thoroughly with a graphite rod and poured quickly into a sand mould. Sand moulds were employed, as they were found much more satisfactory than moulds of graphite or iron which were worked with for a long time without obtaining good sound castings. The pattern was made of a seven inch brass rod, one-half inch in diameter, through which were drilled seven one-quarter inch holes, and into these were inserted one-quarter inch brass rods nine inches long, extending at equal distances on either side of the main rod. Great care was taken to have the center of all of these rods in the same plane. The mould was made in two parts, each receiving the impression of exactly one-half of the pattern. The upper half was then provided with a large "gate" and two "risers." The mould was thoroughly vented by perforating the sand by means of a large iron wire. With this form of sand mould very perfect and acceptable castings were readily obtained. The castings were removed as soon as they were solid enough to handle and cooled in water. The small one-quarter inch lateral rods were then removed by a hack saw. Two rods from different parts of the castings were filed and highly polished, and one piece was cut from the end of one near the "gate" and from the free end of the other. These pieces were selected for analysis, and 0.5 gram portions were taken and the copper determined electrolytically. From the numerous analyses made, there seemed to be no question but that the castings were of uniform composition, as the following data show.

No. of sample	Percent of copper	
	1	2
1	86.66	86.66
2	73.38	73.44
3	58.52	58.46
4	51.42	51.48

After having ascertained in this manner that the pieces from the castings were of the proper composition and would represent the desired phases, they were placed in a German silver resistance furnace, similar to the one described by Shepherd and annealed at 400° C for two weeks. They were then allowed to cool in the furnace. These pieces were then turned down by means of a three-sixteenth inch hollow tool and cut off to the required length, highly polished, numbered, and stored in glass stoppered bottles where they remained bright for months. The test pieces from some castings were too brittle to be worked, especially those for the γ-phase, so that we were compelled to omit these from the series. The series prepared represented all the solid solutions stable at 400° C with the exception of pure γ, and the test pieces employed in the corrosion had the following percentage composition of copper: 93.6, 86.6, 83.3, 76.3, 73.4, 66.5, 60.3, 56.8, 51.3, 47.6, 22.6, 10.5, 3.1.

The electrolytic corrosions were so arranged that the series of thirteen test pieces could be corroded simultaneously for the same electrolyte. A wooden frame standing about five inches above the desk was arranged to carry at a distance of five inches apart three-grooved wooden pulleys, each of which was attached to a three-sixteenth brass rod running in a brass sleeve. Each was provided at the lower end with an ordinary double connector by means of which the test piece was attached to the stirrer, while in the upper end of the rod was drilled a small hole into which mercury was placed to insure a good content with the wire conducting the current to the test piece. The apparatus consisted of two sections, one carrying six, and the other seven stirrers, and each set driven by its own motor, belted to one of the central pulleys which was two inches in diameter. Each pulley, one inch in diameter, was connected in series to the preceding one by a belt of round silk elastic. The fan motors used were of the same pattern and speed. Platinum wires were employed for the cathodes, and the current was conducted through the test pieces placed in series. Normal solutions were used, being approximately of the same strength Curry used in his work. Two hundred cc. of the electrolyte were used in each case. The experiments were conducted at room temperature and usually lasted for about eight hours. No attempt was made to have a current of exactly the same amperage in all exercises. The test pieces were immersed to the depth of two inches (5 cm.), exposing a surface of 1.2 square inches (7.7 sq. cm.). This was practically constant in all of the determinations and for all of the test pieces, except those which were used several times. In those cases, the surfaces were always filed and smoothed with emery cloth and then polished. The area of some of these would be slightly smaller than the new samples, but this slight change in the current density would make no material difference, as no attempt was made to employ exactly the same current in the corrosions in various liquids.

At the conclusion of the corrosion, each test piece was thoroughly cleaned by the aid of a rubber-tipped stirring rod. It was not always an easy matter to clean the test pieces in this manner, as frequently there was found a test piece on which there remained a copper-colored coating which could not be removed by scraping with a knife.

The precipitate resulting from the corrosion was dissolved in nitric acid, and the copper content of the corrosion product determined electrolytically. Cylindrical platinum gauze cathodes and a rotating spiral platinum anode were employed. This method, being practically the same as the one recently described by Perkins,[1] was in use by us for months before his description appeared. Most of the corrosion experiments were run in duplicate, and some of them more times. The results herein presented indicate simply the general trend of the corrosion of the brasses.

The following solutions were employed in the electrochemical tests: sodium chloride, sodium nitrate, sodium sulphate, sodium acetate, sodium carbonate, sodium phosphate, ammonium nitrate, ammonium oxalate, and acid ammonium oxalate.

In the experiments to test the chemical corrosion, the following solutions were used: sodium chloride, sodium nitrate, sodium persulphate and alkaline sodium persulphate. Air was bubbled through these solutions for several weeks.

As complex brasses are of great commercial importance, test pieces were prepared of copper-zinc-tin alloys, containing small percentages of tin. These were subjected to electrolytic corrosion in the same manner as the simple brasses in solutions of sodium chloride, sodium nitrate and sodium sulphate.

Corrosion in Sodium Chloride Solution

The data are given in Table 1 for the electrolytic corrosion in a normal sodium chloride solution. In the first column is given the composition of the test pieces expressed in percentage of copper; in the second column the number of grams the test pieces lost during corrosion, *i. e.*, the weight of the corrosion product; in the third column the number of grams of copper in the corrosion product; in the fourth column we have the percentage of copper in the corrosion product. In the last column is given the so-called current efficiency.

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[1] Trans. Faraday Soc., 2, 91 (1907).

TABLE I

Percentage of copper in test pieces	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	0.7204	0.6756	93.8	100.5
86.6	0.7165	0.6263	87.4	103.7
83.3	0.6935	0.5807	83.7	102.0
76.3	0.6519	0.4993	76.6	99.5
73.4	0.6460	0.5117	79.2	100.6
66.5	0.6056	0.4026	66.5	97.5
60.3	0.5773	0.3417	59.2	96.2
56.8	0.4576	0.1150	25.1	77.6
51.3	0.4618	0.0990	21.4	80.5
47.6	0.4077	0.0052	1.3	72.8
22.6	0.4042	0.0006	0.2	86.0
10.5	0.3975	0.0004	0.1	92.7
3.1	0.3972	0.0001	0.0	98.3

After the corrosion had been running for a few minutes in the sodium chloride, a light green flocculent precipitate appeared which soon changed to a dark yellow or orange color. This was present in all cases except the three lower brasses, where the precipitate remained almost pure white. No other electrolyte gave the same colored corrosion product. At the termination of the corrosion, the test pieces were found to be coated with a heavy red scale, in most cases easily removable while in one or two cases, not even scraping was efficacious. In observing the 51.3 percent brass a few days after running a corrosion test, it was noticed that the scale had become loosened and could be readily peeled off. This scale was removed, weighed and analyzed with the result that 0.3172 gram of the scale gave 0.3140 gram of copper, thus showing that the scale was about 99 percent pure copper.

The copper in the corrosion product was obtained by first depositing the copper electrolytically from an ammoniacal solution, dissolving in nitric acid and redepositing.

In Fig. 2 is represented diagrammatically the relation between the number of grams of the corrosion product and the composition of the brass. The boundaries of the different solid solutions are represented by the vertical dotted lines, and the areas are designated by the kind of stable crystals present. The percentages of copper are represented by the abscissae and the ordinates represent grams. The upper curve shows the variations in the amounts of corrosion with the change in concentration. There are no data for the γ-field, and the immediate regions of adjoining areas, so the values represented by this portion of the curve are interpolated. There is a rapid decrease in the amount of corrosion with the decrease in the copper content extending across the areas for α, $\alpha + \beta$ and β crystals when it drops very quickly in the $\beta + \gamma$ area to nearly 50 percent of the corrosion in the brasses of highest copper content. From about 50 percent brass to pure zinc, the amount of corrosion remains practically constant, the different crystalline forms, γ, ε and η do not seem to further affect the amount of corrosion. The lower curve represents the grams of copper in the corrosion product from which it is apparent that the amount of copper decreases very rapidly with the decrease in the copper content in the test piece, becoming practically zero for 50 percent brass and remaining that for all other brasses between this and pure zinc. The fact that practically no copper dissolves from brasses containing less than 60 percent copper, leaves

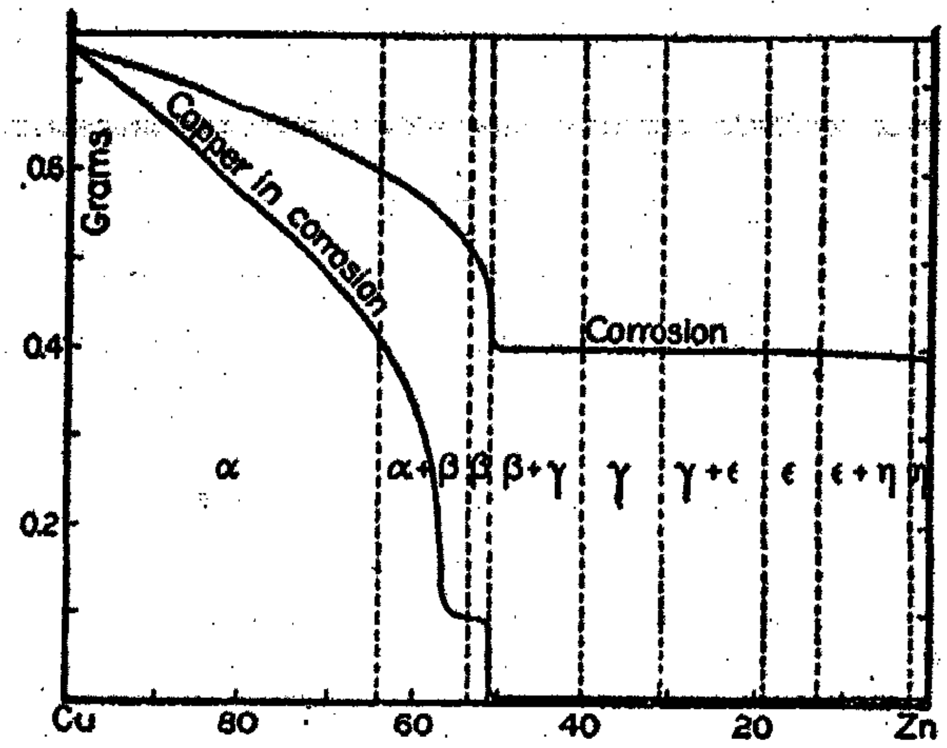

Fig. 2

the surface of higher copper content than the original form. This explains why the coating from the 51.3 percent brass mentioned above, was 99 percent copper. The apparent current efficiency expressed in the last column of Table 1 was calculated upon the basis of the electrochemical equivalents of pure copper and pure zinc, the copper dissolving as cuprous chloride. The corrosion of brass of any intermediate composition we assume would be equal to the sum of the copper and zinc corrosion of the same composition. It is perfectly apparent that such a state of affairs need not necessarily exist, for the copper and zinc may exist in brass in such a form as to yield a product much more readily corroded than pure copper and pure zinc. If this occurred, it would account for current efficiencies greater than 100 percent. The values given in the tables were obtained from the smoothed curves.

The brasses were examined microscopically after the corrosions with very interesting and surprising results. Any description of the appearance of the corroded test pieces would give an inadequate idea of their appearance. There seems to be a definite relation between the appearance of the test piece after corrosion and the crystalline phases in equilibrium. A number of photographs were taken of the various test pieces which had been corroded in the different solutions.

Corrosion in Sodium Nitrate Solution

The data obtained from the results of the corrosion in normal sodium nitrate solutions are given in Table 2. The headings of the columns have the same significance in this table as in Table 1, and the subsequent tables and are self-explanatory.

In sodium nitrate solution the corrosion products were apparently hydroxides of copper and of zinc in varying proportions. The corrosion product from the 3.1 percent brass was gray colored, due to metallic particles mixed with the zinc hydroxides. The test pieces were coated with a red scale easily removable and exposing the bright surface of the brass underneath.

TABLE 2

Percentage of copper in test pieces	Grams of corrosion	Grams of copper corrosion	Percentage copper corroded	Current efficiency
93.6	0.3091	0.2877	95.2	103.0
86.6	0.3191	0.2775	86.9	106.6
83.3	0.3173	0.2645	83.4	108.3
76.3	0.3308	0.2494	75.4	111.0
73.4	0.3375	0.2481	75.2	111.6
66.5	0.3398	0.2238	65.8	112.4
60.3	0.3452	0.2105	61.0	113.1
56.8	0.3355	0.1872	55.8	109.8
51.3	0.3375	0.1812	53.7	111.4
47.6	0.3504	0.1516	43.2	114.7
22.6	0.2352	0.0002	0.0	75.8
10.5	0.3316	0.0228	6.8	106.1
3.1	0.4804	0.0174	3.6	154.0

Fig. 3 represents diagrammatically, as does Fig. 2 and the subsequent figures, the relation of the grams of corrosion, the grams of copper in the corrosion product and the variation of these with the change in composition of the brass, while the vertical dotted lines represent the boundaries of the different solid solutions. The upper curve represents a gradual increase in the amount of the corrosion product with the decrease in the copper content of the brass until the $\beta + \gamma$ area is reached, while in the $\gamma + \varepsilon$ area the 22.6 per cent brass shows very much less corrosion, and with the further decrease in the copper content, there is a very marked

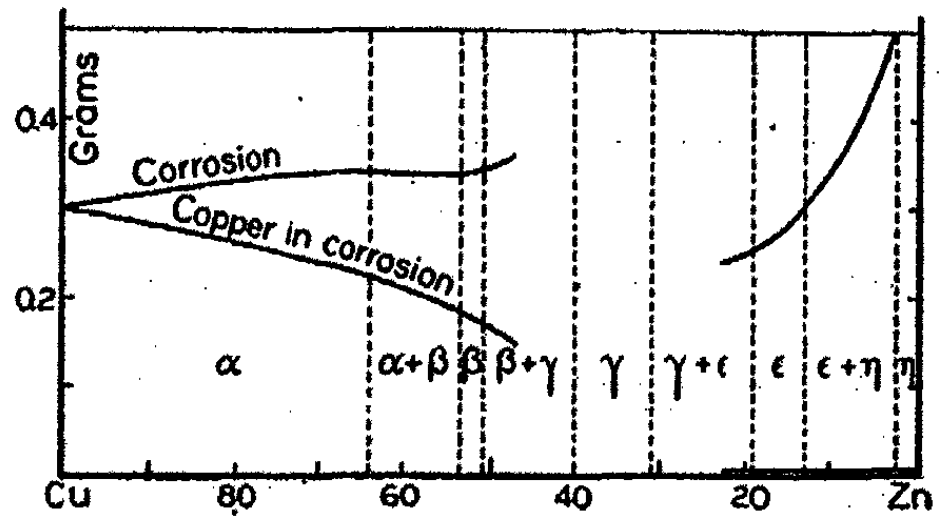

Fig. 3

increase in the amount of corrosion. A prolongation of this curve to the zinc axis would indicate the great corrosion of pure zinc, being about twice that for pure copper. Pieces of pure copper and pure zinc were corroded in normal sodium nitrate solution in series with a copper voltameter with the following results:

	1	2	
Copper	0.3922	0.3719	Grams corroded
Zinc	0.3656	0.3763	
Voltameter	0.3719	0.3497	Grams deposited

From these data it appears that practically the same amounts of copper and zinc are corroded from anodes of the pure metals. The large amount of corrosion obtained in the brasses low in copper is undoubtedly due to several factors, which are no doubt similar to those Mr. Curry had to deal with in the corrosion of bronzes in sodium nitrate solution. He showed that some of the crystals were dislodged by the matrix being dissolved away and these dropped from the test piece and remained undissolved in the nitrate solution. The high corrosion of the low copper bronzes he then attributed to disintegration, which no doubt accounts for the high corrosion in the case of the low copper brasses.

From the lower curve in Fig. 3, we observe the relation of the amount of copper in the corrosion product and the test piece. From a comparison of next to the last column in Table 2 and the second column, it is apparent that the corrosion product is of the same composition as the test piece until the γ-phase appears in the brasses when there is a marked difference. The amount of copper in the corrosion products from the brasses consisting of $\gamma + \varepsilon$ crystals is very small. For brasses of less copper content the amount of copper in the corrosion product increases at first and then decreases. The composition of the corrosion product from the brasses containing only a few percent of copper (the ε- and η-crystals) is virtually the same as the test piece.

The test pieces in sodium nitrate solutions become coated with an easily removable scale, and this was true of the pure copper in the experiment referred to above. When these scales are removed, a bright metallic surface is exposed. An effort was made to ascertain if any relation existed between the corrosion and this scale. A number of test pieces were corroded as usual in the normal nitrate solution, and an attempt was made to separate the scale which was formed from the remainder of the corrosion product by dissolving the hydroxides in very dilute sulphuric acid and immediately filtering the scale upon previously weighed filter-papers. The filter-papers and scale were dried and weighed and then the copper in the scale determined. In Table 3 these data are presented. In the first column is given the percentage of copper in the test piece; the grams of corrosion in the second; the total corrosion less the weight of the scale in the third; in the fourth, the weight of copper in the corrosion product; in the fifth, the weight of copper in the corrosion product less the weight of copper in the scale; the sixth, the percentage of copper in the corrosion product; while in the last column we have the percentage the copper in the hydroxide is of the total corrosion, *i. e.*, the percentage the fifth column is of the second.

From the data herein presented and also from its representation in Fig. 4, no apparent relation exists between the grams of corrosion and grams of scale which are designated "1" and "2" respectively by the upper curves. The lower curves "1" and "2" represent the grams of copper in the corrosion product, and the grams of copper in this after the amount in the scale has been deducted. These may indicate in a general way that for brasses containing chiefly γ-crystals or $\gamma + \varepsilon$ crystals, there may be no scale formation on the test pieces.

Photographs representing the corroded surfaces of 47.6 percent brass and 3.1 percent brass respectively in sodium nitrate solutions indicated very clearly the uneven corrosion of the surfaces, the marked way in which the crystals are

TABLE 3

Percentage of copper in test pieces	Grams of corrosion	Grams of corrosion-grams of scale	Grams of copper in total corrosion	Grams of copper in total corrosion-grams of copper in scale	Percentage of copper in total corrosion	Percentage copper in residue is of total corrosion
93.6	0.3479	0.2849	—	—	—	—
86.6	0.3538	0.3371	0.2964	0.2952	86.6	86.1
83.3	0.3428	0.3379	0.2943	0.2888	83.1	81.6
76.3	0.3596	0.3355	0.2690	0.2542	74.8	70.1
73.4	0.3616	0.3212	0.2671	0.2414	73.9	66.8
66.5	0.3549	0.3092	0.2290	0.2110	64.5	59.5
60.3	0.3621	0.3386	0.2157	0.2081	59.6	57.5
56.8	0.3616	0.3494	0.2038	0.1973	56.3	54.6
51.3	0.3750	0.3289	0.1987	0.1650	53.0	44.0
47.6	0.3866	0.3327	0.1840	0.1512	47.6	39.1
22.6	0.2697	0.2565	—	—	—	—
10.5	0.3649	0.3297	0.0258	0.0163	7.1	4.5
3.1	0.5520	0.4052	0.0202	0.0044	3.7	0.8

dissolved out, and the very deep pitting of the brasses of low copper content. Where such marked holes are produced there is not much doubt but that certain crystals are really loosened by having the material dissolved from around them and being more resistant to the solvent action, may become dislodged and drop from the test piece into the solution, there eventually to be considered a part of the corrosion product. Curry[1] has shown in his work on the bronzes that there are many such cases wherein the so-called corrosion product is the result of this disintegration and of the dissolving action of the electric current as well.

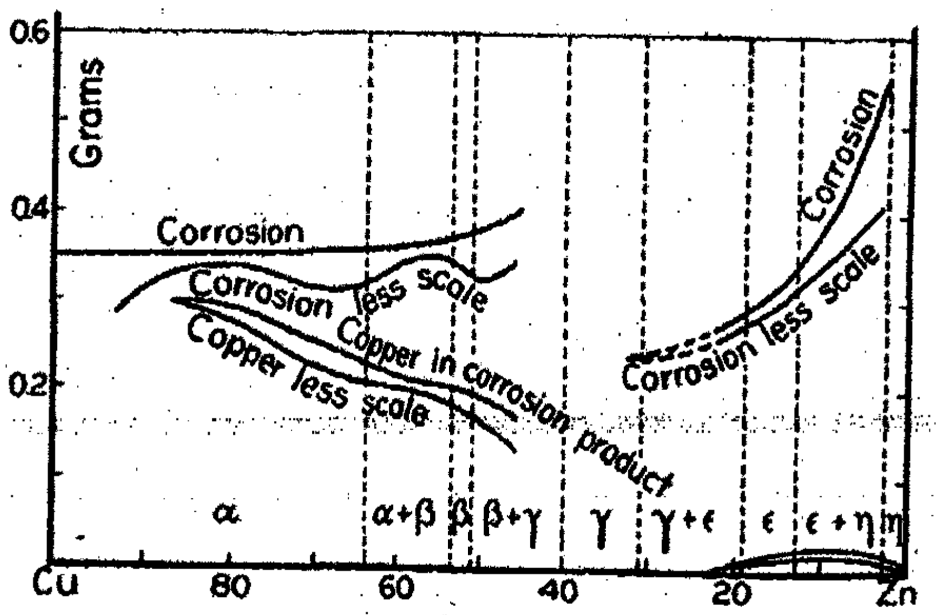

Fig. 4

Corrosion in Sodium Sulphate Solution

The data obtained from the results of the corrosion in normal sodium sulphate solutions are given in Table 4.

The test pieces were coated with a red scale, and the general character of the corrosion products was the same as in the sodium nitrate solution.

The amount of corrosion is practically the same for all the brasses, and this is clearly shown by the upper curve in Fig. 5. From a comparison of the first and last columns in Table 4, it is readily seen that the brasses containing less than about 70 percent copper become copper-rich on the surface. As shown by the lower curve in Fig. 5, the appearance of the

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[1] Loc. cit.

TABLE 4

Percentage of copper in test pieces	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	0.1184	0.1069	90.3	100.0
86.6	0.1184	0.1012	85.5	100.0
83.3	0.1177	0.0888	75.5	100.0
76.3	0.1192	0.0907	76.1	100.0
73.4	0.1188	0.0845	71.2	100.0
66.5	0.1192	0.0756	63.4	100.0
60.3	0.1214	0.0688	56.7	100.0
56.8	0.1172	0.0515	44.0	100.0
51.3	0.1136	0.0357	31.4	100.0
47.6	0.1132	0.0015	1.33	100.0
22.6	0.1031	0.0010	0.97	89.7
10.5	0.1094	0.0003	0.28	95.1
3.1	0.1116	0.0002	0.18	97.0

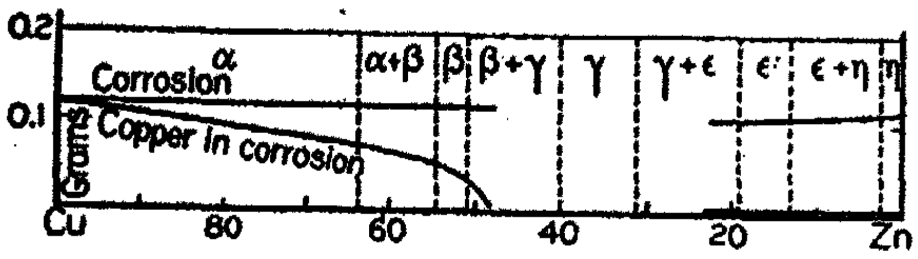

Fig. 5

γ-crystals again affect the amount of copper in the corrosion product. Brasses below 47.6 percent copper contain practically no copper in the corrosion product.

The set of test pieces used in the sodium sulphate solution were reduced in a current of hydrogen in order to ascertain the amount of oxide present and also to see whether there was present an invisible film on these test pieces that remained bright. The loss was insignificant. In a like manner the test pieces in other experiments which showed any indication of oxide present were reduced and the proper corrections made.

Corrosion in Sodium Acetate Solution

The data for the electrolytic corrosion in normal sodium acetate solution are given in Table 5.

TABLE 5

Percentage of copper in test pieces	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	0.1107	0.1036	93.6	46.0
86.6	0.2656	0.2311	87.0	90.8
83.3	0.2623	0.2139	81.5	103.0
76.3	0.3710	0.2785	75.1	116.6
73.4	0.3661	0.2719	74.3	119.3
66.5	0.4021	0.2668	66.3	121.7
60.3	0.4094	0.2397	58.5	118.1
56.8	0.4120	0.2247	54.5	118.1
51.3	0.4397	0.2249	51.1	114.7
47.6	0.4318	0.2043	47.3	113.0
22.6	0.3254	0.0015	0.0	71.8
10.5	0.3458	0.0022	0.0	70.0
3.1	0.4483	0.0147	3.3	86.5

From the second column it is apparent that the amount of corrosion increases very rapidly with the decrease in the copper content.

This is clearly seen from the upper curve in Fig. 6, the maximum value being reached with the appearance of the crystals, then from interpolation; the corrosion apparently decreases rapidly to about 22.6 percent brass, beyond which the amount of corrosion increases very rapidly. The values for the amount of corrosion of brasses of high copper were not obtained by extrapolation, because the exact nature of the curve is not known, but it undoubtedly ascends very rapidly and cuts the ordinate at about 0.23 gram, as is shown by the following experiment:

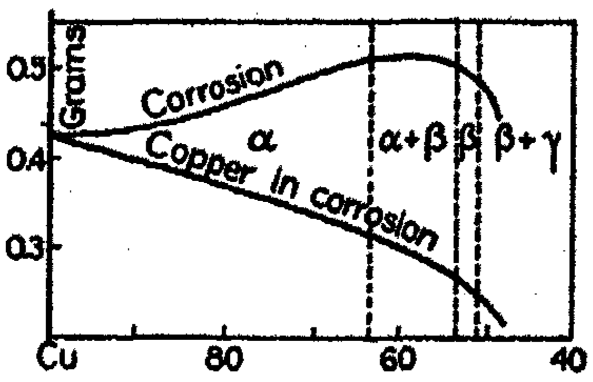

Fig. 6

A piece of pure copper in a normal sodium acetate solution was placed in series with a copper voltameter. The copper lost 0.1565 gram, while the voltameter registered a gain of 0.3719 gram, and 0.1491 against 0.3497 gram in the voltameter. The copper electrode remained perfectly clean and bright as did the 93.6 percent brass electrode. There was not the slightest trace of a scale. In the case of the brasses of high copper content, the corrosion product has practically the same composition as the test piece while for the test pieces which are least corroded, the corrosion product was virtually pure zinc. We have here again the marked influence of the γ-crystals on the corrosion.

Corrosion in Sodium Carbonate Solution

The data, as recorded in Table 6, represent the results of a determination of the corrosion of the test pieces in normal sodium carbonate solution.

TABLE 6

Percentage of copper in test pieces	Grams of corrosion
93.6	0.0022
86.6	0.0015
83.3	0.0019
76.3	0.0040
73.4	0.0018
66.5	0.0022
60.3	0.0046
56.8	0.0066
51.3	0.0158
47.6	0.0191
22.6	0.0032
10.5	0.0149
3.1	0.0095

It is apparent that there was but very little corrosion. There was experienced great difficulty in getting any current through the test pieces, due to the formation of insulating films. This was particularly true in the case of the 10.5 percent and 3.1 percent brasses, where white adherent coatings were formed. These test pieces were scraped off, washed free from the sodium carbonate solution and when tested with an acid solution gave a strong test for carbonates. These cleaned test pieces were replaced in the series, and the current went up rapidly to 0.15 ampere, but immediately dropped to almost nothing. At the end of the test the 51.3 percent and 47.6 percent brasses were covered with a green film, while the other test pieces were only slightly discolored.

Corrosion in Ammonium Nitrate Solution

The data for the results of electrolytic corrosion in normal ammonium solution are given in Table 7.

TABLE 7

Percentage of copper in test pieces	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	0.3976	0.3723	93.6	100.0
86.6	0.4032	0.3461	84.8	100.0
83.3	0.4158	0.3459	83.2	100.0
76.3	0.4162	0.3121	75.0	100.0
73.4	0.4306	0.3152	73.2	100.6
66.5	0.4332	0.2852	65.8	102.5
60.3	0.4202	0.2511	59.7	105.5
56.8	0.4471	0.2516	56.3	107.3
51.3	0.4424	0.2378	53.7	114.7
47.6	0.5014	0.2242	44.7	122.0
22.6	0.3908	0.0302	7.7	94.0
10.5	0.4707	0.0341	7.2	113.3
3.1	0.6582	0.0231	3.5	135.0

The corrosion is very similar to what takes place in the sodium nitrate solutions. The amount of corrosion remains practically constant for the brasses representing the α-crystals, and increases quite rapidly with further decrease in the copper content, showing that the β- and γ-crystals are more soluble than the α-crystals. With the appearance of the ε-crystals in the 22.6 percent brass, there is apparently a return to the normal corrosion as represented in the case of the α-crystals. With further decrease in the copper content, the amount of corrosion increases very rapidly.

This is graphically represented in Fig. 7. The copper content of the corrosion product is practically the same as that of the test piece with the exception of some of the brasses containing the ε-crystals. The change in the cation of the electrolyte does not seem to affect the corrosion, since the general character is the same in both the sodium and ammonium nitrate solutions.

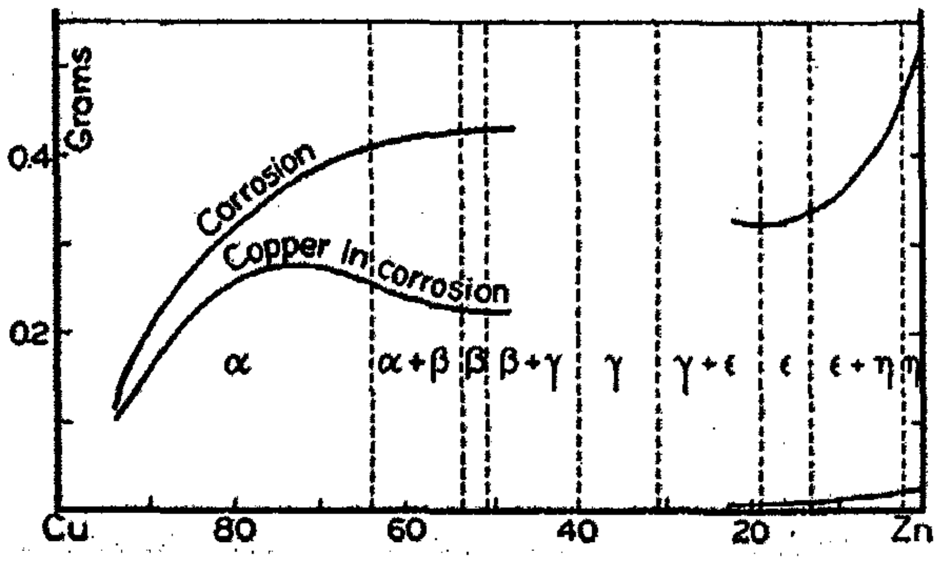

Fig. 7

Corrosion in Ammonium Oxalate Solution

The data for electrolytic corrosion in normal ammonium oxalate solution are given in Table 8.

TABLE 8

Percentage of copper in test pieces	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion	Current efficiency
93.6	0.4399	0.4095	93.1	103.3
86.6	0.4321	0.3712	85.9	101.2
83.3	0.4422	0.3624	81.9	103.3
76.3	0.4677	0.3542	75.7	108.7
73.4	0.4726	0.3459	73.2	109.9
66.5	0.4958	0.3219	64.9	115.0
60.3	0.4753	0.2818	59.3	109.8
56.8	0.5481	0.3114	56.8	126.0
51.3	0.4919	0.2447	49.7	112.8
47.6	0.4416	0.2139	48.4	101.5

In the first experiments with this solution, all of the test pieces were employed, and the current decreased to practically zero even when a pressure of 110 volts was employed. This is attributed to the fact that the test pieces low in copper developed insulating films, which did not break down even under high voltages. By the removal of the test pieces below 47.6 percent copper, the corrosion proceeded as in the other cases. The amount of corrosion increased with the decrease of the copper content, making a maximum in the brasses containing $\alpha + \beta$ crystals, and then decreasing very rapidly with the appearance of the γ-crystals in the brasses of lower copper content.

This is shown graphically in Fig. 8 and again indicates the marked effect of the presence of γ-crystals on the amount of corrosion. The copper in the corrosion product does not vary much from that in the test piece. The curve representing the grams of copper in the corrosion product shows a gradual decreasing amount of copper with the decrease in the copper of the test piece.

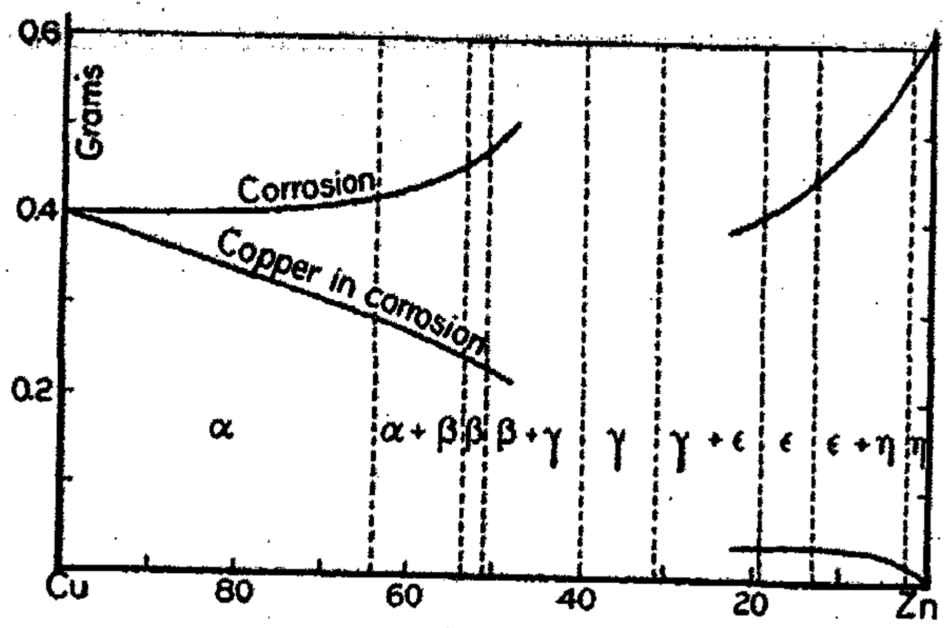

Fig. 8

Many efforts were made to determine the electrolytic corrosion of these brasses in a solution containing 3 percent ammonium oxalate and 3 percent oxalic acid. The results were very discordant and a detailed discussion of the corrosion in this solution will be deferred until more data have been obtained. As the corrosion continued, the current decreased very rapidly so that in a few minutes only a few milliamperes of current were flowing. Increasing the pressure to 110 volts produced only temporary increase in the current, and it soon decreased to its lower value. In order to ascertain where the drop in potential occurred, a few measurements were made. The drop at the 47.6 percent brass was found to be 40 volts, while at the 51.3 percent brass it was 20 volts. It is, therefore, evident that excellent insulating films were developed which even under very high impressed voltage would not break down.

The same condition of affairs was found to prevail in the corrosion of the brasses in a normal solution of the tertiary sodium orthophosphate. A number of series of corrosions were run with this solution as the electrolyte, but the current decreased very rapidly, and the results obtained from the various series were not concordant. The cause of the rapid decrease was due to the formation of the insulating films on the test pieces as is shown from the fact that the potential drop at the 10.5 percent brass was 60 volts, and the high pressure of 110 volts increased the current very little and then only temporarily. These are practically the same conditions that were found in the case of the corrosions in the solution of normal sodium carbonate. It will be necessary to redetermine the corrosions in all three of these solutions and collect the data very carefully in order to ascertain fully the nature of the corrosions.

By representing his data diagrammatically Mr. Curry[1] showed that the relation between the composition of the bronzes and the current efficiency brought out clearly the marked effect due to the phases in equilibrium. According to this idea then, theoretically, the brasses of intermediate composition should corrode in the proportion of their constituents. In the case of some bronzes of low copper content, Mr. Curry emphasizes the fact that the ε-crystals do not dissolve, but become loosened by the matrix around them dissolving and eventually dropping into the solution where they become a part of the corrosion product. He attributes

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[1] Loc. cit.

the fact that the current efficiency is over 100 percent to the presence of these disintegrated parts of the electrode in the corrosion product. He does not, however, emphasize the fact that in the bronzes of high copper content, the corrosion is in excess of the theoretical amount, but he does indicate it in the diagram illustrating the current efficiency in acidified ammonium oxalate solution. In attempting to represent the current efficiency of the corrosion of brasses, we were likewise confronted with the current efficiency of over 100 percent in the high percent copper brasses in solutions of sodium nitrate, ammonium nitrate, and ammonium oxalate, as well as of those low in copper. These high current efficiencies in the low copper brasses could be attributed to disintegration. In view of the fact that there are, no doubt, several factors entering into the production of the corrosion product and that at present we have no means of differentiating these, it would be fruitless to attempt to represent the current efficiency. We have, therefore, not presented any current efficiency diagrams, but have used other methods for showing the relation of the amount of corrosion and the phases in equilibrium as well as the crystals that are readily corroded.

For ready comparison the relation between the percentage of copper in the corrosion products and in the test pieces is represented diagrammatically in Fig. 9.

Curves are given for those six solvents in which the corrosion was found to be greatest. The abscissae represent the percentage of copper in the test pieces, and the ordinates the percentage of copper in the corrosion product. The similarity of the six curves is very marked. They show in general that the brasses of high copper content, from about 47.6 percent up, yield corrosion products of the same composition as the test pieces. Those below become copper-rich on the surface, and the corrosion product is nearly pure zinc, while the interpolated values for brasses between 47.6 percent and 22.6 percent copper indicate practically a pure zinc corrosion product, which would mean a copper-rich surface. In the case of the corrosion product from sodium and ammonium nitrate solutions, Curves 1 and 5, there is found a percentage of copper in the low copper brasses practically the same as in the test pieces, but this may be accounted for, owing to the deep pitting and great corrosion, by the

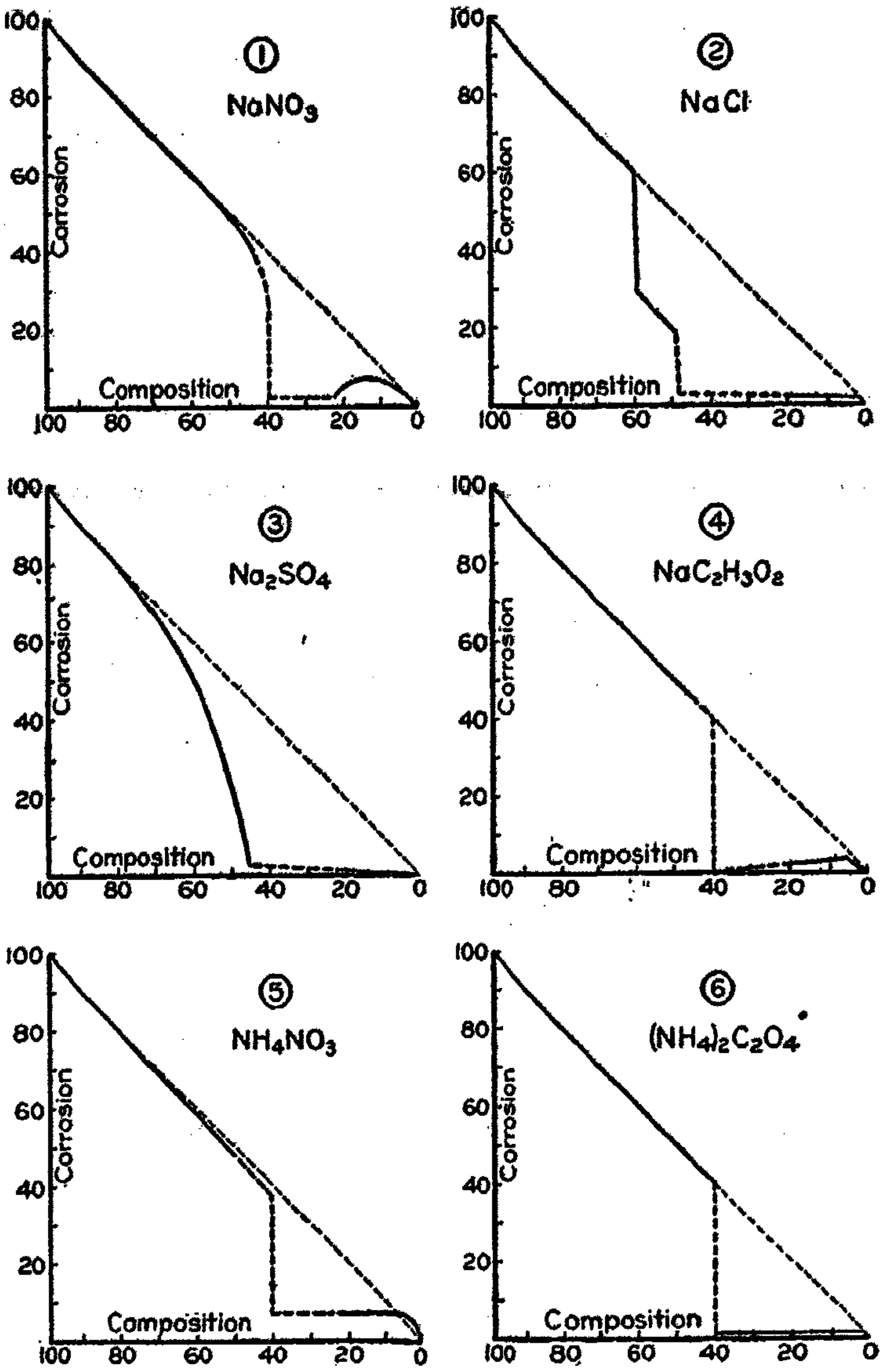

Fig. 9

disintegration of the test piece as indicated above. In the case of the corrosion in sodium chloride solution (Curve 2) there is a very rapid decrease in the amount of the copper corrosion of brasses whose copper content varies between about 60 and 50 percent of copper. These brasses become copper-rich and the corrosion is virtually pure zinc. This percentage represents closely the composition of Muntz's metal, and it is well known that Muntz's metal corrodes in sea-water. The corrosion product obtained from sodium sulphate solutions (Curve 3) has the same composition as the test piece for brasses of 70 percent copper up, while for brasses below this the percentage of copper decreases very rapidly, reaching practically 0 percent copper for 47.6 percent brasses and those to pure zinc.

Or stating it differently, the brasses consisting of α, $\alpha + \beta$ or pure β solid solutions yield corrosion products of practically the same percentage composition as the test pieces. The presence of γ-crystals decreases the percentage of copper in the corrosion product enormously, and the brasses consisting of γ, $\beta + \gamma$, $\gamma + \varepsilon$ or $\varepsilon + \eta$ crystals yield corrosion products which are virtually pure zinc.

Chemical Corrosion of Brasses

As it is generally held that chemical and electrochemical corrosion are identical, the same results should be obtained by both methods of corrosion. In order to ascertain this the test pieces were allowed to stand in the solutions through which air was bubbled for several weeks. The solutions used were normal solutions of sodium chloride, sodium nitrate, sodium persulphate and sodium persulphate containing 5 percent excess of sodium hydroxide.

The data from the results of the chemical corrosion in a normal sodium chloride solution are given in Table 9.

The test pieces in the sodium chloride solution became coated with a light deposit which was readily soluble in nitric acid without effervescence. From the table it is readily seen that the amount of the corrosion product decreases with the

TABLE 9

Percentage of copper in test pieces	Grams of corrosion	Grams of copper in corrosion	Percentage of copper in corrosion
93.6	0.0866	0.0713	82.2
86.6	0.0692	0.0565	81.6
83.3	0.0571	0.0456	79.9
76.3	0.0168	0.0126	75.0
73.4	0.0131	0.0095	72.5

decrease in the copper content of the test piece as occurred in the case of the electrical corrosion. A comparison of the last and first columns shows that the corrosion product contained less copper than the test piece.

In the sodium nitrate solutions the test pieces showed practically no corrosion.

The chemical corrosion in the alkaline persulphate solution was very unsatisfactory. In most cases the entire test piece was not immersed in the solution, but a part was exposed to the air. In these cases there was a very marked difference in the corrosion of the immersed part and that exposed to the air, it being slight on the former and extremely deep on the part in the air, and, therefore, the experiment was discontinued. Two days after the experiment was started the solutions containing brasses of less than 51.3 percent copper became perceptibly blue. Before discarding the brasses, they were examined carefully and the 93.6, 83.3 and 73.4 percent brasses were found to be badly corroded on the part of the test piece exposed to the air. The 22.6 percent brass, a silvery white alloy, was entirely coated with a bright layer of copper. The 10.5 and 3.1 percent brasses were coated with a black deposit apparently crystalline in character. The 60.3 and 76.3 percent brasses remained practically unchanged.

The chemical corrosion in the persulphate solution did not yield any more gratifying results than those obtained in the alkaline persulphate solution. Before the experiment was discontinued, the test pieces were carefully examined, and the brasses of high copper content were found to be very badly corroded. The 51.3 percent brass was coated with a layer of copper, while the portion of the test piece exposed to the air was scarcely affected. The 3.1 percent brass was coated with a very rough layer of copper. The solutions containing the brasses of low copper content remained practically colorless in contrast to those of the alkaline persulphate solutions which were colored blue. Much more experimental data on the chemical corrosion of brasses will have to be obtained before a satisfactory comparison can be made between chemical and electrochemical corrosion.

Electrolytic Corrosion of Copper-Zinc-Tin Brasses

Most of the commercial brasses contain besides copper and zinc, small quantities of one or more other metals. The use of tin as the third metal is very common, and the substitution of a small quantity of it for zinc affects the physical properties of the brass very much by increasing its hardness, strength, rigidity and elasticity. Thurston[1] has investigated the physical properties of these alloys of copper-zinc-tin which he termed "Kalchoids," and has showed that those containing about equal quantities of copper (58–54 percent) are the strongest "Kalchoids." Guillet[2] has recently investigated a few copper-zinc-tin alloys micrographically and states that "the introduction of tin has been shown by numerous experimenters to greatly increase the resistance to corrosion in sea-water."

In the study of the electrochemical corrosion of the "Kalchoids," it was our intention to prepare various series of alloys ranging in copper content from 50–100 percent and in tin content from 75–80 percent thus including the best and most valuable "Kalchoids." Only two series of castings were prepared in the time at our disposal. Nevertheless, these were employed in some corrosion tests. The following table gives the composition of the two series of test pieces.

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[1] Thurston: "Alloys, Brasses and Bronzes, Materials of Engineering," Part 3.

[2] Revue de Metallurgie, Feb., 1905, Iron and Steel Mag., 10, 21 (1905).

TABLE 10

Series I		Series II	
Percentage of copper	Percentage of tin	Percentage of copper.	Percentage of tin
81.0	0.78	86.9	0.98
77·1	0.78	77·2	0.94
73·3	0.76	74·8	0.90
64.0	0.77	71·4	1.02
58.0	0.79	66.7	1.07
54·8	0.75	63.0	1.05
54·7	0.65	..	..

These brasses were prepared in a manner similar to that used in the preparation of the simple brasses. The copper being first melted, the zinc and tin were then added, the melt thoroughly stirred, and then poured into the sand moulds. All test pieces were annealed at 400° C and then turned down to uniform size by the three-sixteenth inch hollow tool. The tin in the test pieces was determined as stannic oxide by ignition of the sulphide as described by Olsen.[1]

The copper was determined electrolytically in the filtrates from the tin determinations; usually 3–4 grams of the test piece were employed for analysis and duplicates taken. The amount of tin in the corrosion products was so very small that the data given in the tabulated results below must be considered merely as approximations, as much difficulty is experienced with the present methods in accurately determining small quantities of tin in presence of large quantities of copper and zinc.

Corrosion in Sodium Chloride Solution

The data from the determination of the electrolytic corrosion of two sets of test pieces in a normal sodium chloride solution are given in Tables 11A and 11B.

In both sets of brasses, those containing approximately 0.75 percent and 100 percent of tin, the amount of corrosion increases with the increase in the copper content of the test

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[1] Olsen: "Quantitative Analysis," p. 142.

TABLE 11A

Percentage of copper in test pieces.	Percentage of tin in test pieces	Grams of Corrosion	Grams of copper in corrosion	Grams of tin in corrosion	Percentage of copper in corrosion	Percentage of tin in corrosion
54.7	0.65	0.6941	0.3793	0.0040	54.5	0.57
54.8	0.75	0.6944	0.3809	0.0061	54.9	0.88
58.0	0.79	0.6861	0.4047	0.0036	59.0	0.93
64.0	0.77	0.7298	0.4719	0.0054	64.7	0.74
73.3	0.76	0.7599	0.5593	0.0047	73.6	0.83
77.1	0.78	0.7808	—	—	—	—
81.0	0.78	0.7895	0.6405	0.0040	81.1	0.52
63.0	1.05	0.7529	0.4751	0.0073	63.1	0.93
66.7	1.07	0.7545	0.5067	0.0078	67.2	0.49
71.4	1.02	0.7597	0.5445	0.0072	71.7	1.03
74.8	0.90	0.7464	0.5519	—	73.9	—
77.2	0.94	0.7808	0.6029	0.0061	77.2	0.78
86.9	0.98	0.8462	0.7324	0.0042	86.6	0.49

TABLE 11B

Percentage of copper in test pieces.	Percentage of tin in test pieces	Grams of Corrosion	Grams of copper in corrosion	Grams of tin in corrosion	Percentage of copper in corrosion	Percentage of tin in corrosion
54.7	0.65	0.5123	0.2779	0.0041	54.2	0.80
54.8	0.75	0.5167	0.2886	0.0041	55.8	0.79
58.0	0.79	0.5241	0.3033	0.0046	57.9	0.87
64.0	0.77	0.5447	0.3443	0.0042	63.2	0.77
73.3	0.76	0.5910	0.4350	0.0042	73.6	0.71
77.1	0.78	0.5906	0.4598	0.0059	77.9	1.00
81.0	0.78	0.6192	0.4977	0.0055	80.4	0.89
63.0	1.05	0.5519	0.3484	0.0043	63.1	0.79
66.7	1.07	0.5568	0.3678	0.0086	66.1	1.54
71.4	1.02	0.5674	—	—	—	—
74.8	0.90	0.5881	—	—	—	—
77.2	0.94	0.6076	0.4716	0.0055	77.6	0.91
86.9	0.98	0.6498	0.5707	0.0075	87.8	0.89

piece, and in the simple brasses the amount of corrosion increases. This is represented diagrammatically in Fig. 10, wherein the abscissae represent the grams of corrosion, and the ordinates the percentage of copper.

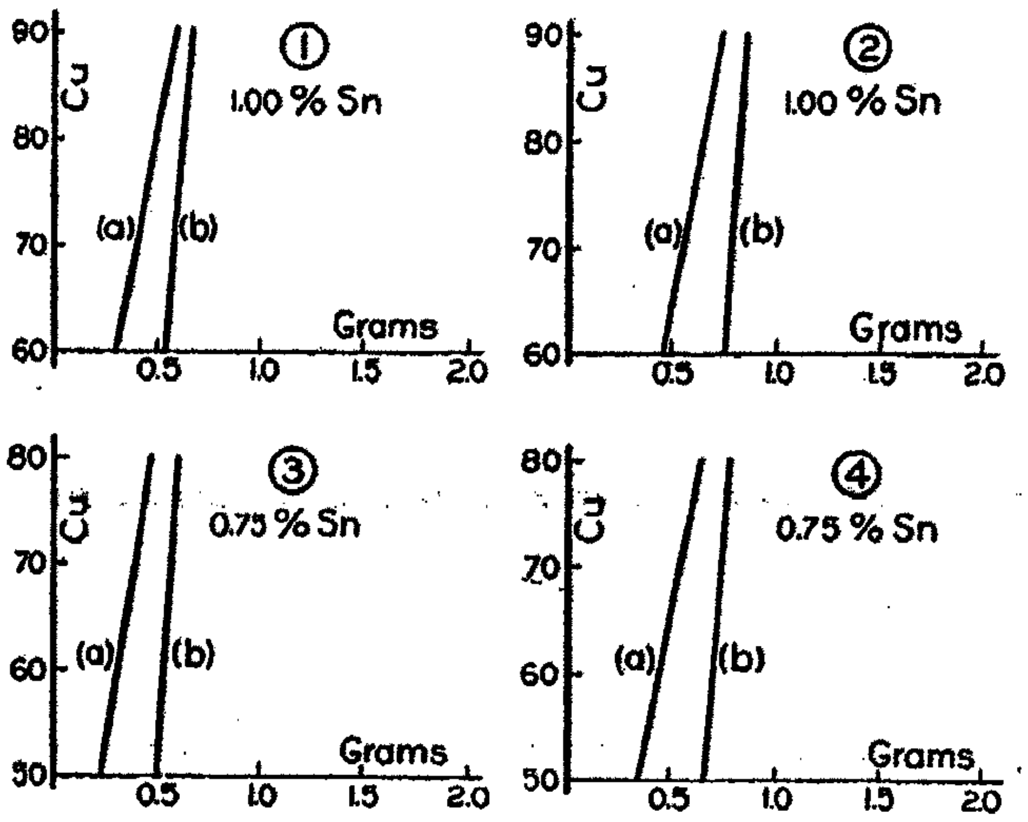

Fig. 10

Curve "*a*" refers to the weight of copper in the total weight of the corrosion product which is represented by curves marked "*b*." From a comparison of the data in the first and in the next to the last columns of the table, it is apparent that the copper content of the corrosion product is practically the same as that of the test piece, while the large variations in the tin content of the corrosion products can be readily attributed to errors in the analysis of the very small quantities of tin present. These corrosion determinations were made in duplicate, and from the two sets of curves "1" and "3" and "2" and "4," the general agreement is represented.

Corrosion in Sodium Nitrate Solution

The data presented in Table 12 were obtained in the electrolytic corrosion of the test pieces in a normal solution of sodium nitrate.

TABLE 12A

Percentage of copper in test pieces	Percentage of tin in test pieces	Grams of corrosion	Grams of copper in corrosion	Grams of tin in corrosion	Percentage of copper in corrosion	Percentage of tin in corrosion
54.7	0.65	1.3280	0.7262	0.0089	54.7	0.68
54.8	0.75	1.3633	0.7504	0.0147	55.0	1.08
58.0	0.79	1.3880	0.8124	0.0120	58.5	0.81
64.0	0.77	1.3768	0.8809	0.0155	64.0	1.13
73.3	0.76	1.4118	1.0404	0.0133	73.7	0.95
77.1	0.78	1.3708	1.0696	0.0123	78.0	0.90
81.0	0.78	1.3599	1.0982	0.0192	80.8	1.41
63.0	1.05	1.3767	0.8676	0.0141	63.0	1.03
66.7	1.07	1.4381	0.9570	0.0160	66.6	1.11
71.4	1.02	1.3577	0.9646	0.0144	71.1	1.06
74.8	0.90	1.3975	1.0524	0.0128	75.3	0.93
77.2	0.94	1.2989	0.9732	0.0135	75.0	1.04
86.9	0.98	1.3341	1.1682	0.0122	87.6	0.92

TABLE 12B

Percentage of copper in test pieces	Percentage of tin in test pieces	Grams of corrosion	Grams of copper in corrosion	Grams of tin in corrosion	Percentage of copper in corrosion	Percentage of tin in corrosion
54.7	0.65	1.6118	0.8878	0.0120	55.1	0.73
54.8	0.75	1.6030	0.8666	0.0151	54.0	0.94
58.0	0.79	1.6494	0.9546	0.0151	57.9	0.92
64.0	0.77	1.6471	1.0524	0.0119	64.0	0.72
73.3	0.76	1.5651	1.1492	0.0204	73.4	1.30
77.1	0.78	1.5850	1.1806	0.0155	74.5	0.98
81.0	0.78	1.5758	1.2669	0.0241	80.4	1.53
63.0	1.05	1.6520	1.0304	0.0128	62.4	0.77
66.7	1.07	1.6585	1.1162	0.0162	67.2	0.98
71.4	1.02	1.5640	1.1126	0.0198	71.1	1.26
74.8	0.90	1.5958	1.1958	0.0188	74.9	1.18
77.2	0.94	1.5155	1.1350	0.0183	74.9	1.21
86.9	0.98	1.5520	1.3312	0.0137	85.8	0.88

The amount of corrosion seems to decrease slightly with the increase in the copper percentage of the test piece for those containing approximately 1 percent tin. For those containing 0.75 percent tin the amount of corrosion is practically constant. This is represented in Fig. 11 wherein the curves for the duplicate determination are given, thus showing that practically the same general results were obtained in both series of experiments.

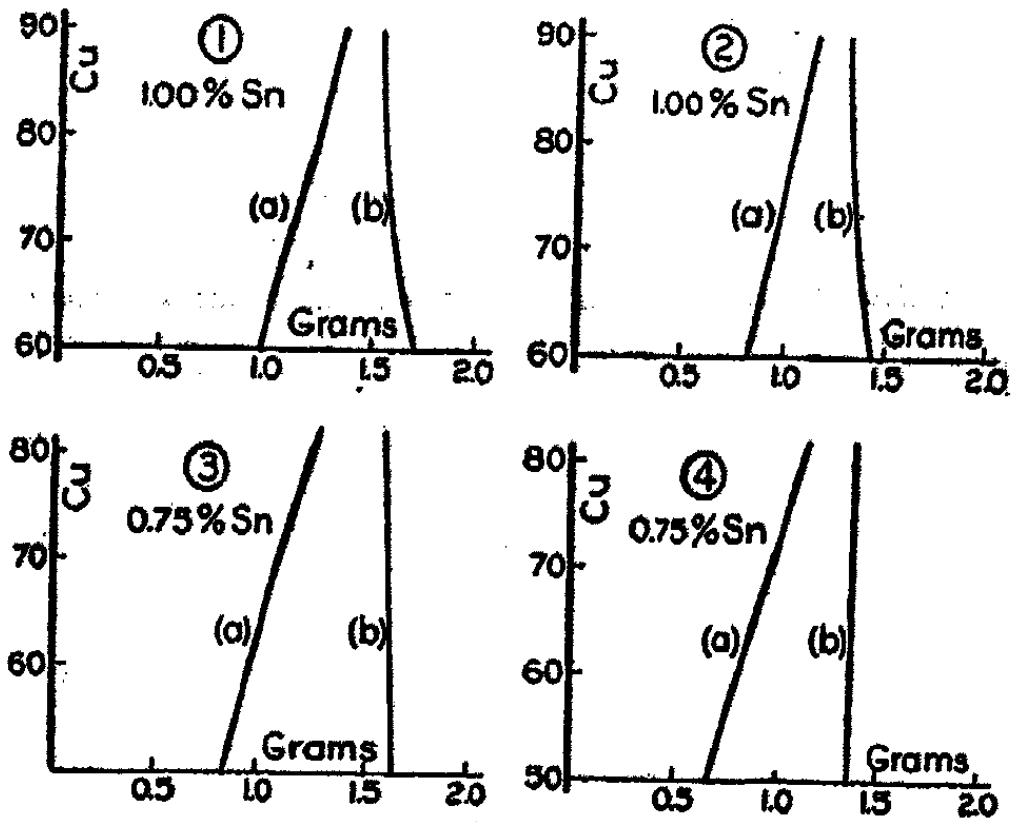

Fig. 11

The corrosion in these brasses is in general the same as in the pure brasses of high copper content, there being a slight increase in the amount of corrosion with the decrease in the copper content. The percentage of copper in the corrosion product is practically the same as in the test piece. The coating on the surface of the "Kalchoids" was not so heavy as on the simple brasses and was rather black.

Corrosion in Sodium Sulphate Solution

The data from the electrolytic corrosion of the test pieces in a normal sodium sulphate solution are given in Table 13.

The weight of the corrosion product obtained in the sodium sulphate solution is practically the same for all the brasses examined. Neither the variation in the percentage

TABLE 13A

Percentage of copper in test pieces	Percentage of tin in test pieces	Grams of corrosion	Grams of copper in corrosion	Grams of tin in corrosion	Percentage of copper in corrosion	Percentage of tin in corrosion
54.7	0.65	0.8564	0.4715	0.0041	55.1	0.49
54.8	0.75	0.8884	0.4788	0.0043	54.0	0.46
58.0	0.79	0.8458	0.4888	0.0063	57.8	0.75
64.0	0.77	0.8349	0.5209	0.0091	62.4	1.09
73.3	0.76	0.8347	0.6161	0.0093	73.8	1.12
77.1	0.78	0.8322	0.6425	0.0053	77.2	0.63
81.0	0.78	0.8317	0.6739	0.0117	81.0	1.40
63.0	1.05	0.8539	0.5367	0.0078	62.9	0.92
66.7	1.07	0.8412	0.5509	0.0112	65.5	1.33
71.4	1.02	0.8370	0.5967	0.0030	71.3	0.35
74.8	0.90	0.8342	0.6241	0.0114	74.8	1.37
77.2	0.94	0.8373	0.6466	0.0091	77.2	1.09
86.9	0.98	0.8316	0.7264	0.0118	87.4	1.42

TABLE 13B

Percentage of copper in test pieces	Percentage of tin in test pieces	Grams of corrosion	Grams of copper in corrosion	Grams of tin in corrosion	Percentage of copper in corrosion	Percentage of tin in corrosion
54.7	0.65	0.8812	0.4875	0.0036	55.3	0.41
54.8	0.75	0.8794	0.4802	—	54.6	—
58.0	0.79	0.8826	0.5194	0.0043	58.9	0.50
64.0	0.77	0.8796	0.5642	0.0071	64.1	0.81
73.3	0.76	0.8711	0.6250	0.0025	71.8	0.40
77.1	0.78	0.8706	0.6832	0.0077	78.5	0.89
81.0	0.78	0.8679	0.7014	0.0067	80.8	0.77
63.0	1.05	0.9097	0.5729	0.0095	63.0	1.04
66.7	1.07	0.8733	0.5841	0.0070	66.9	0.79
71.4	1.02	0.8662	0.6111	0.0096	70.6	1.10
74.8	0.90	0.8719	0.6591	—	75.6	—
77.2	0.94	0.8706	0.6678	0.0040	76.7	0.45
86.9	0.98	0.8664	0.7605	0.0056	87.8	0.65

of copper nor that of tin affects the amount of correction. This is the same thing found for the copper-zinc test pieces corroded in sodium sulphate solution. Duplicate determinations were made with practically the same results as shown clearly in Fig. 12, where the data from both series of experiments are represented, and emphasizes the constancy of the amount of the corrosion. The corrosion product contains apparently the same percentage of copper as the test piece. The corrosion surface of some of the test pieces was very characteristic. The same general type of corroded surface is obtained for the corrosions in the solutions of sodium nitrate and sodium chloride. The rough surfaces of the electrode is due to large golden rectangular crystals which give a most beautiful effect in sunlight.

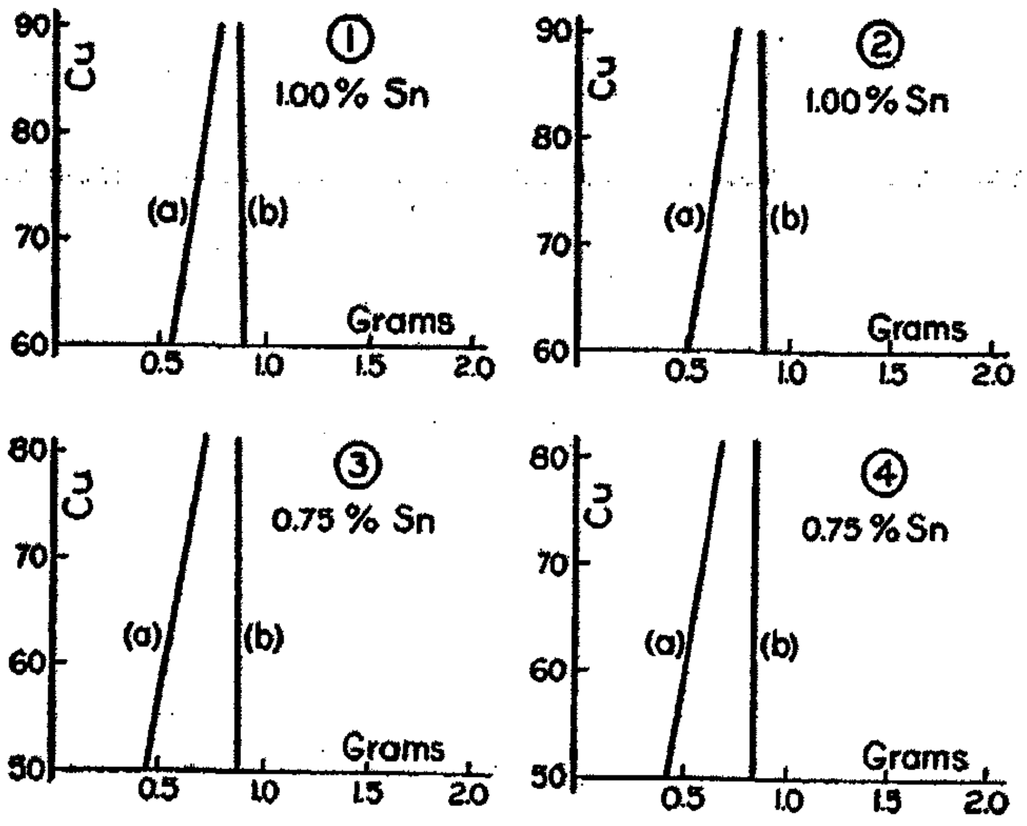

Fig. 12

In order to ascertain the relative amounts of corrosion in various solutions three brasses of practically the same copper content were selected, having different percentages of tin. These were corroded in normal solutions of sodium chloride, sodium nitrate and sodium sulphate, by passing the same current through them in series. The data are presented in Table 14.

TABLE 14

Percentage of copper in test piece	Percentage of tin in test piece	Grams of corrosion					
		NaCl		$NaNO_3$		Na_2SO_4	
		1	2	1	2	1	2
73.4	0.00	0.4509	0.9879	0.3108	0.7190	0.2876	0.6293
73.3	0.76	0.4486	0.9827	0.2992	0.6739[1]	0.2886	0.6307
74.8	0.90	0.4477	0.9636	0.2969	0.6815	0.2886	0.6304

[1] On this test-piece there remained some black patches which would increase the weight of the test piece, and thus indicate less corrosion than actually took place.

The experiment was stopped, the test pieces cleaned and weighed, the amount of corrosion being represented in the columns headed "1." The test pieces were replaced, and the experiment continued in order to obtain a larger amount of corrosion, the weights of which are recorded in the columns marked "2." The amount of corrosion for all three brasses is the greatest in the sodium chloride solution, the least in the sodium sulphate solution, and intermediate in the sodium nitrate solution. The brass containing the most tin corrodes in the sodium chloride solution a little less than brass containing no tin, while both of these corrode somewhat more than that brass containing 0.76 percent of tin. In the sodium nitrate solutions, the corrosion decreases with the increase of the tin content, while in the sodium sulphate all three test pieces are corroded the same amount. It might be interesting to inquire in which of these solutions does the normal theoretical corrosion occur? If we assume that copper dissolves in the cuprous form in the sodium chloride solution, then the corrosion in the other two solutions, on the assumption that the copper dissolves as bivalent copper, is very much in excess of what it should be, and we should say the current efficiency is over 100 percent. If we select either of the other two solutions as our standard of comparison, then we arrive at similar conclusions, for if pure copper anodes dissolve as bivalent copper, then sodium nitrate and sodium sulphate solutions corrode the same. It is a well-known fact, however, that the deposition of copper from a copper sulphate voltameter, is less than the theoretical amount, unless a little sulphuric acid is added. What should be selected as the theoretical amount of corrosion in any or all solutions in order to calculate the so-called current efficiency is a subject that requires further investigation.

Summary

A series of copper-zinc brasses was prepared representing most of the different solid solutions, and these were annealed for several weeks at 400° C to insure the presence of the stable forms at this temperature. These brasses were subjected to electrolytic corrosion in normal solutions of some of the more common sodium and ammonium salts.

In general, the electrolytic corrosion results in the formation of a corrosion product which is practically of the same composition as the test piece for the brasses of high copper content; *i. e.*, of 50 percent copper and up. The corrosion product of the low percentage copper brasses is practically pure zinc. The amount of corrosion in sodium chloride decreases with the increase in the copper content of the brass. In sodium nitrate, ammonium nitrate, ammonium oxalate and sodium acetate solutions, the amount of corrosion increases with the decrease of the copper content of the brass for the high copper brasses, and also for the very low ones. In sodium sulphate solutions, the amount of corrosion is practically constant over the whole range of concentration of the brasses.

The α, $\alpha + \beta$ or β brasses yield corrosion products of the same composition as the brass. The presence of γ-crystals seems to cause a marked decrease in the amount of corrosion, while the corrosion product from $\gamma + \varepsilon$ and $\varepsilon + \eta$ brasses is practically pure zinc.

A few copper-zinc-tin brasses containing small quantities of tin were subjected to electrolytic corrosion in normal solutions of sodium chloride, sodium nitrate and sodium sulphate with the same general results as in the case of the simple brasses.

Chemical corrosions were conducted in a few solutions, but the determinations were not satisfactory.

A portion of the expense of this research was met by an award granted by the American Electrochemical Society.

University of Illinois,
May, 1907.

ON THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS IN ETHYL AMINE

BY FREDERICK L. SHINN

Some years ago Kahlenberg and Ruhoff[1] published the results of some measurements of the electrical conductivity of solutions in amyl amine. The salts employed as solutes were silver nitrate, cadmium iodide, and ferric chloride. It was shown that these solutions afford striking examples of the phenomenon of the diminution of the so-called molecular conductivities upon increasing the dilution beyond a certain point. In all cases the molecular conductivities were small and attained extremely low values at dilutions ranging from fifth- to eightieth-normal.

More recently H. D. Gibbs,[2] in connection with a study of the solvent power of liquid methyl amine, has shown, in a qualitative way, that certain salts dissolved in that solvent yield very good conducting solutions, many of the solutions having specific resistances of less than 100 ohms. The specific conductivities, however, are much lower than for solutions in liquid ammonia,[3] of which methyl amine is the first homologue. On the other hand, solutions in liquid methyl amine are very much better conductors than solutions in amyl amine. It was therefore to be expected, in accordance with the general behavior of solvents which are members of a homologous series, that solutions in ethyl amine would show conductivities lying between those in liquid methyl amine and amyl amine. This was found to be the case.

The following salts were first rendered anhydrous and then examined as to their solubility in anhydrous ethyl amine. Many of them reacted with the solvent, forming insoluble or difficultly soluble residues. These precipitates were not

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[1] Jour. Phys. Chem., 7, 254 (1903).

[2] Jour. Am. Chem. Soc., 28, 1395 (1906).

[3] Franklin and Kraus: Am. Chem. Jour., 23, 277 (1900)

examined further, but they probably consist of addition products formed with ethyl amine.

NH_4Cl,	Very soluble with evolution of ammonia.
$LiCl$,	Soluble.
$FeCl_3$,	Slightly soluble.
$SnCl_2$,	Insoluble, unchanged.
$CoCl_2$,	Reacts with evolution of heat, forming greenish yellow precipitate.
$PbBr_2$,	Reacts, forming white precipitate which afterward dissolves.
KI,	Insoluble, unchanged.
CdI_2,	Slightly soluble.
PbI_2,	Reacts, forming white insoluble precipitate.
$AgCN$,	Slightly soluble.
$Hg(CN)_2$,	Slightly soluble.
$AgNO_3$,	Soluble, with evolution of much heat.
$NaNO_3$,	Insoluble, unchanged.
$Pb(NO_3)_2$,	Reacts, forming white insoluble precipitate.

The ethyl amine was Schuchardt's preparation. It was allowed to stand over potassium hydroxide and was then distilled. The portion passing over between 18.4° and 19.4° C at 747 mm was used in the conductivity measurements. Its specific conductivity was of the order of 4×10^{-7} at 0° C. The conductivity measurements were carried out at 0° C on account of the volatility of the solvent.

The simple resistance cell used and described by Kahlenberg and Ruhoff was employed in connection with the usual (Kohlrausch) method.

Few of the salts examined lent themselves well to conductivity measurements. Ferric chloride proved to be insufficiently soluble. The saturated solution possessed a specific conductivity of about 13.5×10^{-6} reciprocal ohms. Cadmium iodide is somewhat more soluble, but the specific conductivities of its solutions were less than 10×10^{-6} reciprocal ohms and did not appreciably change in passing from a concentration of fortieth- to seven hundred seventieth-normal. Silver nitrate, lithium chloride and ammonium chloride were sufficiently soluble in ethyl amine for the purpose in hand.

TABLE I

Volume	Specific conductivity × 10^4	Molecular conductivity
	$AgNO_3$ in Ethyl Amine	
0.9342	97.02	9.062
1.8467	43.13	7.965
2.9040	22.19	6.418
4.5245	10.74	4.858
6.884	4.937	3.399
9.672	2.891	2.796
12.573	1.842	2.315
75.15	0.307	2.310
	LiCl in Ethyl Amine	
0.511	37.58	1.920
0.622	35.67	2.217
0.867	27.49	2.384
1.284	16.81	2.158
2.189	6.592	1.437
3.846	1.936	0.745
8.563	0.3382	0.289
21.08	0.6676	0.134
95.67	0.0214	0.191
	NH_4Cl in Ethyl Amine	
0.9498	44.20	4.198
1.4233	21.35	3.039
2.303	6.887	1.596
3.709	2.156	0.800
7.013	0.5416	0.380
13.98	0.2255	0.315
18.24	0.1233	0.228
78.76	0.0451	0.255

The molecular conductivities of solutions of silver nitrate in ethyl amine are roughly ten times as large as in similar solutions in amyl amine. In the case of both solvents the silver nitrate solutions are found to conduct better than the other solutions examined. This behavior is in harmony with the presumption that stronger chemical affinities are brought into play in the solution of silver salts in amines than in the case of other salts. A correspondingly greater change in properties of both solvent and solute would therefore naturally be expected.

The tables indicate that the molecular conductivities decrease in all cases up to a dilution of about eightieth-normal, and at greater dilutions they appear to undergo a slight increase. However, the values at high dilution are attended with some uncertainty, owing to the limitations of the method when such high resistances are to be measured, and the slight increase is within the limits of experimental error.

The strongest solutions of lithium chloride in ethyl amine show at first increasing molecular conductivities with increasing dilution, which attain a maximum at a dilution of about 0.8 normal. The ammonium chloride solutions may perhaps be more properly regarded as solutions of ethyl amine hydrochloride in ethyl amine, the ammonia having been replaced by the stronger base. The conductivities fall off as dilution progresses, finally attaining a minimum value.

In passing from liquid ammonia to the homologous primary amines, using them as solvents, one observes a regular decrease in electrical conductivities of the solutions, and also a reversal of the parallelism between molecular conductivities and degree of dilution which obtains in the case of solutions in liquid ammonia.[1] The molecular conductivities in ethyl amine decrease with increasing dilution and appear to tend toward a minimum, while in the case of amyl amine the values continue to decrease as far as the dilutions could be carried. This last is true also for solutions in piperidine.[2] Solutions in pyridine[2] and its homologues, on the other hand, increase in molecular conductivity with increase of dilution.

The substitution of oxygen for two hydrogen equivalents in ethyl amine produces a marked increase in the solvent power, particularly toward the alkali salts and increases also the electrical conductivities of the solutions. But here again the tendency of the amido group to gain the ascendency in

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[1] Franklin and Kraus: Loc. cit.

[2] Lincoln: Jour. Phys. Chem., 3, 470 (1899).

bringing about a decrease of the conductivity manifests itself, for the molecular conductivities of solutions of potassium chloride, potassium iodide and potassium cyanide in acetamide,[1] although such solutions are very good electrolytes (molecular conductivities 25 to 40), reach maximum values and at further dilutions diminish.

From the standpoint of the theory of electrolytic dissociation the electrical behavior of solutions in primary and secondary amines and in amides, so far as such solutions have been studied, are inexplicable. The facts that for one and the same solute the molecular conductivities of solutions may not only be very large or very small, but may increase or decrease with dilution, or attain maximum or minimum values depending upon the specific nature of the solvent, suggest that the rôle of the solvent in the process of the transmission of an electric current through a solution is, in all probability, a very active rather than an indifferent one, and does not materially differ from that of the solute. In such event the prevalent conception of "molecular conductivity" becomes not only meaningless but misleading.

My acknowledgments are due Professor Kahlenberg for furnishing me with the ethyl amine which he has had on hand for some time with a view to making such measurements as are presented in this paper.

Laboratory of Physical Chemistry,
University of Wisconsin,
May 18, 1907.

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[1] Walker and Johnson: Jour. Chem. Soc., 87, 1597 (1905).

ON THE DISSOCIATION OF SOLUTIONS OF THE NEUTRAL CASEINATES OF SODIUM AND AMMONIUM.

BY T. BRAILSFORD ROBERTSON

(From the Rudolph Spreckels Physiological Laboratory of the University of California)

Introduction

In a previous paper I have shown that in considering the electrolytic and hydrolytic dissociation of the salts of ampholytes we cannot, in general, neglect the acid while measuring the basic function and vice versa.[1] For instance in the case of serum globulin in acid solution we cannot regard the protein as being purely a base or the protein ions as being entirely cations, for on applying the formulae for the dissociation of an ampholyte to this particular case we find that at quite considerable hydrion concentrations a measurable percentage of the protein ions are still anions. At the same time it was found that in a protein, such as serum globulin, in which the acid function is of considerably greater magnitude than the basic function, the protein *in the presence of an excess of a base* may be regarded, as far as dissociation is concerned, as a weak non-amphoteric acid.

Nevertheless, it was also pointed out that this fact did not suffice to enable us to directly determine the acid affinity constant without the additional assumption (not generally warranted by facts) that the salt of the protein is practically completely dissociated into ions, and attention was drawn to the fact that improbable as this assumption may seem (when ampholytes are under consideration) it has nevertheless been frequently made by previous investigators on the affinity constants of ampholytes.

In this paper I will describe experiments tending to show

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[1] T. Brailsford Robertson: Jour. Phys. Chem., 11, 437 (1907).

that casein,[1] like serum globulin, can, in the presence of bases, even in neutral solution, be treated, in estimating its dissociation constants, as if it were a non-amphoteric acid.

Experimental

In a previous paper[2] I have shown that the maximum amount of casein which a given concentration of a base will keep in solution is that with which it will combine to form the neutral caseinate of the base (1 gram = 5.6 cc N/10) and that solutions of neutral caseinates formed by shaking up an excess of casein in a solution of a base are neutral to litmus and to cyanin.

Excess of casein (25 percent in excess of the amount which would be necessary to neutralize the base) was shaken up in N/50 NaOH and the solution filtered through rapid-filtering ash-free paper. The solution thus obtained was diluted to various concentrations and the conductivity of the solutions measured at 25°. The following were the results obtained:

The conductivity of the water employed (8×10^{-6}) is subtracted from each of the tabulated conductivities.

TABLE I

Concentration NaOH "saturated" with casein	x = conductivity in reciprocal ohms	$\lambda = x \times 1.037 \times 10^{-2}$
0.02 N	751×10^{-6}	779×10^{-8}
0.01 N	417 "	432 "
0.0068 N	297 "	308 "
0.005 N	232 "	241 "
0.004 N	195 "	202 "
0.0028 N	140 "	145 "
0.002 N	105 "	109 "
0.001 N	84 "	87 "

A similar excess of casein was shaken up in N/50 $NH_4(OH)$ and the solution filtered through rapid-filtering ash-free paper

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[1] I employ the nomenclature of Schultz and Röse, the term "casein" being applied to the substance present in milk and unaltered by rennet. The casein used in these experiments was Eimer and Amend's C. P., prepared according to Hammarsten's method.

[2] T. Brailsford Robertson: Journ. Biol. Chem., 2, 337 (1907).

and diluted to various concentrations. The solutions were neutral to litmus; their conductivities were measured at 25°.

The following were the results obtained, the conductivity (8×10^{-6}) of the water employed having been subtracted from each of the measured conductivities.

TABLE II

Concentration $NH_4(OH)$ "saturated" with casein	x = conductivity in reciprocal ohms	$\lambda = x \times 1.037 \times 10^{-2}$
0.02 N	914×10^{-6}	948×10^{-8}
0.01 N	508 "	527 "
0.0068 N	361 "	374 "
0.005 N	278 "	288 "
0.004 N	228 "	236 "
0.0028 N	171.5 "	178 "
0.002 N	142 "	147 "
0.001 N	67 "	69.5 "

A tendency was observed in both solutions for the casein to be precipitated at the electrodes[1] but by making the determinations as soon as possible after the conductivity vessel and its contents had arrived at the temperature of the bath the error due to this could be minimized. Since the solutions were neutral the error due to the hydrolysis of the protein, which assumes large proportions in solutions of higher hyroxidion content,[2] could be neglected; as a matter of fact it was found that constant readings were readily obtained.

Theoretical

Let the concentration of the protein anion XOH^- be represented by c, while that of the sodium ion is β, then assuming that the casein under these conditions behaves essentially as a monobasic acid we have:

$$c\beta = GT \qquad (1)$$

where G is constant and T is the concentration of the salt formed.

Let m be the concentration of OH^- which has been neutralized by the casein, then the amount of sodium which is bound

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[1] W. B. Hardy: Journ. of Physiol., 33, 273 (1905).

[2] T. Brailsford Robertson: Jour. Phys. Chem., 11, 437 (1907).

by the protein (=T) is $m-c$, assuming that all the natrion is derived from the casein salt and that no sodium is bound in complex ions or in basic ampho-salts.

Hence:

$$c\beta = G(m-c) \qquad (2)$$

Now equating the sum of the concentrations of the negative ions to the sum of the concentrations of the positive ions, assuming that the protein cation HX^+ is only present in negligible concentration; since the hydrion and hydroxidion concentrations are also negligible (the solution being neutral), we have:

$$\beta = c \qquad (3)$$

Hence, substituting in (2) we have

$$c^2 = G(m-c) \qquad (4)$$

Now if x be the specific conductivity of the solution in reciprocal ohms, and if $\lambda = 1.037 \times 10^{-2} x$, we have

$$\lambda = U\beta + vc \qquad (5)$$

where U is the specific migration-velocity of the sodium ion and v that of the protein ion; but $\beta = c$ so that we have

$$c = \frac{\lambda}{U+v}, \qquad (6)$$

and substituting in (4) we have

$$m = \frac{\lambda}{U+v} + \frac{\lambda^2}{G(U+v)^2}. \qquad (7)^1$$

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[1] It may be as well to point out how this formula, which assumes that the casein is acting simply as a non-amphoteric acid, can be derived directly from Ostwald's dilution-law for a binary electrolyte.

We have

$$K = \frac{\left(\frac{\mu_v}{\mu_\infty}\right)^2}{\left(1 - \frac{\mu_v}{\mu_\infty}\right) V},$$

where K is the dissociation-constant, μ_v is the molecular conductivity at dilution, V and μ_∞ is the molecular conductivity at infinite dilution, that is: $96.44\,(U+v)$. Now $\mu_v = \frac{x}{m}$ where x is the specific conductivity in reciprocal ohms and m is the equivalent concentration, hence from the above equation we have

$$1 - \frac{1.037 \times 10^{-2} x}{m(U+v)} = \frac{1}{KV} \left\{ \frac{1.037 \times 10^{-2} x}{m(U+v)} \right\}^2;$$

putting λ for $1.037 \times 10^{-2} x$ and m for $\frac{1}{V}$ this reduces to equation (7).

If we apply this equation to the first two observations in Table I and, inserting the constants thus obtained, calculate the values of m for the remaining observations, we find that the actual and the calculated values agree fairly well except in the last observation ($m = .001$) which is probably an experimental error. Omitting this observation and applying the method of least squares to the remainder, we obtain:

$$m = 1881\,\lambda + 0.894 \times 10^{-8}\lambda^2$$

In the subjoined table the actual and calculated values of m are compared:

TABLE III

$m \times 10^4$ actual	$m \times 10^4$ calculated
200	201
100	98
68	66.4^6
50	50.5
40	41.6
28	29.2
20	21.6
10	13

The agreement is such as to enable us to state that the assumptions which lead to this formula are in all probability correct, namely, that casein in combination with sodium, forming the neutral caseinate, behaves essentially as if it were a weak non-amphoteric monobasic acid.

Thus we find that for sodium caseinate $\frac{1}{U + v} = 1881$, hence $U + v = 53.2 \times 10^{-5}$. Now U for Na^+ at 18° is 44.4×10^{-5};[1] at 25° it will be about 14 percent higher, that is, 50.6×10^{-5}; hence, the velocity of the casein ion at 25° would be $53.2 \times 10^{-5} - 50.6 \times 10^{-5} = 2.6 \times 10^{-5}$. This velocity is somewhat low as compared with other determinations of the mobilities of protein ions. By a direct (boundary) method Hardy obtained values of the order of 10×10^{-5} cm per sec

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[1] Kohlrausch und Holborn: Leitvermögen der Elektrolyte, S: 200. It is clear from the above derivation of equation (7) that it is the ionic mobilities *at infinite dilution* which actually enter into the equation.

for the velocity of the serum globulin ion.[1] In my previous investigation I found *v* for the serum globulin cation to be 7×10^{-5}.

It will be observed that no account has been taken of the possible influence of the *viscosity* of the solutions upon the velocities of the ions; the effect of this would be to lower the value of U and thus to enhance the determined value of *v*. However, this effect would not be constant, it would be much greater in the concentrated than in the more dilute solutions; hence, if the effect were of measurable magnitude it could hardly fail to influence the *form* of equation (7), and the agreement between observed and calculated values of *m* as shown in Table III could not be obtained. Hence we must conclude that the effect of viscosity is negligible in these measurements; this agrees, also, with the work of previous observers.[2]

The results so far considered do not appear to indicate the presence in the solutions of basic ampho-salts ($NaX^+ + OH^-$),[3] but it can be shown that under certain conditions the presence of the basic ampho-salt in this system would not alter the *form* of equation (7).

Taking into consideration the basic ampho-salt we have the following equations:

$$NH_4^+ + XOH^- \rightleftarrows NH_4XOH \qquad \text{I}$$
$$NH_4^+ + XOH^- \rightleftarrows NH_4X^+ + OH^- \qquad \text{II}$$
$$NH_4X^+ + XOH^- \rightleftarrows NH_4XXOH \qquad \text{III}$$
$$NH_4X^+ + OH^- \rightleftarrows NH_4XOH \qquad \text{IV}$$

For I we have the following equilibrium-equation:

$$\beta c = GT \tag{8}$$

For III we have:

$$d'c = HT \tag{9}$$

And for IV:

$$d'b = rT \tag{10}$$

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[1] W. B. Hardy: l. c.

[2] Graham: Phil. Trans. Roy. Soc., 151, 183 (1861). Voigtländer: Zeit. Physik. Chem., 3, 36 (1889). Whetham: Phil. Trans. Roy. Soc., 186A, 507 (1895). Bayliss: Arch. d. sci. Biol., II Suppl., p. 261 (1904). W. B. Hardy: l. c.

[3] Cf. T. Brailsford Robertson: Jour. Phys. Chem., 10, 524, et seq (1906).

Equating the sum of the positive to that of the negative ions and neglecting b we have

$$\beta = c - d'. \tag{11}$$

From (11), (10) and (8) we have

$$d' = \frac{rc^2}{Gb + rc}. \tag{12}$$

Hence, from (10),

$$T = \frac{bc^2}{Gb + rc}, \tag{13}$$

and from (8),

$$\beta = \frac{Gbc}{Gb + rc}. \tag{14}$$

Now we obviously have the relation,

$$T + T' = m - \beta; \tag{15}$$

hence, from (13) and (14),

$$T' = m - \frac{Gbc}{Gb + rc} - \frac{bc^2}{Gb + rc}. \tag{16}$$

But from (9) and (12) we have,

$$T' = \frac{rc^2}{H(Gb + rc)}. \tag{17}$$

Hence, from (16) and (17),

$$m = \frac{Gbc}{Gb + rc} + \frac{bc^2}{Gb + rc} + \frac{rc^2}{H(Gb + rc)}. \tag{18}$$

Now from equation (12) it is obvious that if r be large, that is, *if the major part of the protein is present as ampho-salt,* so that bG can be neglected in comparison with rc, then $d' = c$ and equation (18) becomes

$$m = \frac{b}{r}c + \frac{c^2}{H}. \tag{19}$$

Now $\lambda = U\ (c - d') + vc + v'd'$, where v' is the specific velocity of the ampho-salt cation. Hence, since $d' = c$ we have

$$c = \frac{\lambda}{v + v'}, \tag{20}$$

and, substituting in (19) we have

$$m = \frac{b}{r} \cdot \frac{\lambda}{v + v'} + \frac{\lambda^2}{H(v + v')^2}. \tag{21}$$

Hence the effect of the presence of the ampho-salt would, in such a case (b being constant), be merely to multiply the value of U + v as determined from equation (7) by a value, in general *less* than unity, departing more or less widely from unity according to the relative values of U, v, v', b and the dissociation-constant of the ampho-salt. If r and b were of such values that rc were commensurate with bC, equation (7) could not possibly be found to hold good, while if r were still smaller so that the concentration of d' would be negligible, equation (7) would again be found to hold good. The experimental data in the case of sodium caseinate allow us the choice of either the first or the last of these three alternatives but obviously, if we adopt the last alternative, we have a possible explanation of the apparently unusually low velocity of the casein ion (as compared with globulin) as determined from these experiments. Evidently, however, if r were sufficiently large one might obtain, on applying equation (7), an apparent value of U + v *less* than the value of U itself.

This theoretical possibility is experimentally realized in the case of the neutral caseinate of ammonium.

If we apply the least squares method to all the observations in Table II and, inserting in equation (7) the constants thus obtained, we find that the actual and calculated values of m agree well except in the case of the penultimate observation (m = .002N), which is probably an experimental error. Omitting this observation and applying the least squares method to the remainder, we obtain:

$$m = 1569\lambda + 0.5756 \times 10^{-8}\lambda^2$$

In the subjoined table the actual and calculated values of m are compared:

TABLE IV

$m \times 10^4$ actual	$m \times 10^4$ calculated
200	200.5
100	98.7
68	66.7
50	50
40	40.25
28	29.8
20	24.3
10	11.2

The agreement between the observed and calculated values is excellent; nevertheless, we see that in this case $\frac{1}{U + v} = 1569$, hence, for ammonium caseinate at 25° $U + v = 63.7 \times 10^{-5}$, but U for NH^+_4 at 18° is 64.2×10^{-5} and at 25° is about 14 per cent higher, namely, 73.2×10^{-5}, so that the apparent value of $U + v$ is considerably less than the actual value of U for the ammonium ion; this, it appears to me, can only be interpreted as indicating the presence in the solution of complex ions containing ammonium. Even if we consider that the viscosity of the solutions under investigation may retard the sodium and ammonium ions, or if we suppose that the temperature-coefficients of the sodium and ammonium ions are, under these circumstances, lower than usual, there will still be a large difference between the apparent velocities of the casein ions in the two cases. In addition, it should be noted that almost all the possible experimental errors in this investigation would only tend to *obscure* the peculiar relations which we have found. The alteration of the protein at the electrodes, hydrolysis of the protein and the presence of saline impurities in the casein employed would all tend to *raise* the observed conductivities and thus to enhance the apparent values of $U + v$. Then it may be inquired why phenomena such as these were not observed in the experiments upon serum globulin of which an account was previously published in my previous paper,[1] but it should be observed that not only does the occurrence of ampho-salts in all probability depend upon a specific relation between the protein and the non-amphoteric bodies with which it combines, but in all the experiments described in my previous paper the hydrion or hydroxidion concentrations were from 1000 to 100,000 times as great as in the experiments herein described; the effect of multiplying b a thousand-fold might readily be to entirely reverse the relative values of bG and rc in equation (12) and to reduce it to the form $d' = \frac{rc^2}{Gb}$ from which, bG being large as compared with rc, d' would be

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[1] T. Brailsford Robertson: Jour. Phys. Chem., 11, 437 (1907).

a very small fraction of *c*. Hence to detect the presence of ampho-salts, it is advisable to employ, as in these experiments, very nearly neutral solutions.

As Loeb has pointed out,[1] it is necessary to assume the existence in living tissues of two types of ion-proteid compounds, the one containing the non-protein ion in a form dissociable as such, and the other containing the non-protein ion in a non-dissociable form. Even the salts of the alkalies and alkaline earths, which do not, as a rule, form insoluble compounds with proteins nevertheless stand in a double relation towards tissues. On the one hand, they induce properties which are readily modified or reversed by other salts, on the other hand, in some instances, they undoubtedly form compounds of a more stable type and not nearly so easily converted, by substitution, into other compounds. I refer to the well-known power possessed by certain living tissues of "selecting" or storing up certain salts in a much greater concentration than the medium in which they live. For example, the muscles of animals contain a much higher percentage of potassium than the blood which bathes them. Obviously if the potassium existed in the muscle in a dissociable, readily replaceable form, if, in fact, it were present *as* the potassium ion, it would speedily diffuse out into the blood and its place would be taken by some other substance, probably sodium; hence a large proportion of the potassium must be present in such a form that it is not dissociated as such. It is possible that these complexes are ampho-salts such as we have just found to be formed by the interaction of casein and ammonium, or that they are complexes derived from such ampho-salts. From the second constant in equation (7) and from the value of the first, it is possible to compute the dissociation-constants of the casein salts. In this way we find the dissociation-constants for sodium caseinate and for ammonium caseinate, respectively, to be .0395 and .0428; these salts are therefore fairly highly dissociated.

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[1] J. Loeb: Dynamics of Living Matter, p. 72 (1906).

Conclusions

1. It has been shown that under certain circumstances it is theoretically possible to detect from the conductivity of neutral solutions of proteins the presence of ampho-salts of the type $CX^+ + OH^-$ or $CX^+ + XOH^-$; while in the case of sodium caseinate no certain evidence was obtained of the existence of such complexes, they were found to be present solutions of ammonium caseinate.

2. So far as I am aware, this constitutes the first direct experimental indication of the actual existence, in vitro, of the compounds of proteins with alkalies and alkaline earths in which the non-protein ion is not dissociable as such, the existence of which, in living tissues, has been pointed out by Loeb.

3. Assuming that in sodium caseinate no ampho-salts are formed, the specific velocity of the casein ion is found to be 2.6×10^{-5}.

4. The dissociation-constants of the neutral sodium and ammonium caseinates are, respectively, .0395 and .0428.

EXPERIMENTAL DETERMINATION OF THE HEAT OF VOLATILIZATION OF LIQUID AMMONIA AT ITS BOILING-POINT AT ATMOSPHERIC PRESSURE

BY EDWARD C. FRANKLIN AND CHARLES A. KRAUS

Several years ago the authors[1] announced that they had made preliminary measurements of the heat of volatilization of liquid ammonia at its boiling-point and accompanied their statement with a promise to publish their final values together with a description of the method used. For various reasons, further work along this line had not been prosecuted up to the present time. Furthermore in view of the improbability of either of us being able to take up this work again, it is deemed worth while to publish a short account of our preliminary results.

At the time our work was done, there were four determinations of the heat of volatilization of ammonia on record, three earlier ones by Regnault,[2] who obtained the values 294.21, 291.32 and 297.38 at 7.8°, 11.04° and 16° respectively, and a later one by von Strombeck,[3] whose measurements carried on at 14° to 18° gave him a value of 292.4 calories. Since that time, however, Dieterici[4] has made experimental determinations of the heat of volatilization at 0° and 20°, and de Forcrand[5] and Brill[6] have calculated the heat of volatilization of the liquid at its boiling-point. De Forcrand obtained 338, and Brill 321 small calories for 1 gram.

Apparatus and Method of Manipulation

The scheme adopted by the authors was a modification of that described by Marshall and Ramsay in a paper on

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[1] Am. Chem. Jour., 21, 12 (1899).

[2] Ann. Chim. Phys. [4], 24, 423, 438 (1871).

[3] Jour. Franklin Inst., 130, 472 (1900).

[4] Referred to by Brill: Drude's Ann., 21, 179 (1906).

[5] Ann. Chim. Phys. [7], 28, 539 (1903).

[6] Drude's Ann., 21, 179 (1906).

"A Method of Comparing Directly the Heats of Evaporation of Different Liquids at their Boiling-Points."[1] The amount of electrical energy consumed in converting a known weight of the liquid at its boiling-point into vapor at the same temperature was determined by measuring the quantity of electricity passed through a coil of platinum wire immersed in the liquid, and the difference of potential between its two ends.

Since the measurements given in this paper were made, the same general method has been used by Shearer,[2] Estreicher,[3] and by Brown[4] for the determination of the heats of volatilization of liquid air and its constituents, sulfur dioxide, and a long list of alcohols, organic acids and esters.

The accompanying figure shows the apparatus used by us: A is a vacuum-jacketed tube fitted with a stopper carrying the boiling cell B, together with the tube C, for introducing liquid ammonia into the bath in A, and tube D for the escape of ammonia gas. The evaporation of a known quantity of liquid between the glass pointers *b′* and *b″* was effected by passing a current of electricity through the coil of fine platinum wire E, which was soldered with gold to the heavy lead wires FF. These in turn were connected to the exterior by means of metallic mercury contained in the tubes GG. A copper voltameter and a Westinghouse ammeter were included in the circuit, the former for the purpose of measuring the amount of electricity passed in an experiment, the latter for facilitating the control of the current. The potential difference between the two ends of the coil E was measured by means of a Weston voltmeter connected through the mercury in the tubes GG. With the apparatus thus assembled, liquid ammonia was run into the bath through C, and into the boiling cell through H, until the surface of the liquid in the latter stood a short distance above the pointer

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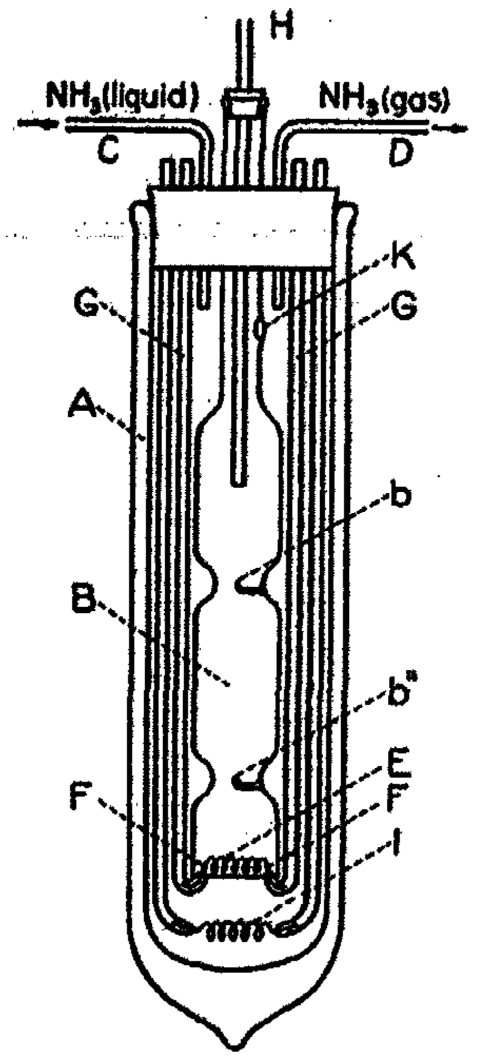
[1] Phil. Mag. [5], 41, 38 (1896).

[2] Phys. Rev., 15, 188 (1902); 17, 469 (1903).

[3] Zeit. phys. Chem., 49, 597 (1904).

[4] Jour. Chem. Soc., 83, 987 (1903).

b'. Current was then turned through the coil I, to bring the bath to constant temperature, when, without including the voltameter, the circuit through the coil E was closed and the liquid in the cell boiled away until its surface just touched the tip of the pointer *b'*. Successive momentary breaking of the current gave the necessary quiet surface of the liquid for making this setting. The voltameter was then included in the circuit and the boiling of the liquid continued until the surface approached the lower pointer *b''*, when a repetition of the process described above enabled the operator to adjust the surface to this latter pointer. During the boiling, readings of the voltmeter were made each minute, and the mean of these readings, which were found to vary but slightly, was used in the calculations. The constrictions in the cell at the two pointers were for the purpose of realizing more accurate determinations of the volume of the liquid boiled, away. The opening K was for the purpose of allowing the ammonia gas from the boiling cell to escape along



with that from the bath, thus insuring equal pressure and consequently the same temperature within and without the cell.

Constants of the Cell and Calculation of Results

The volume of the cell, determined by weighing the amount of water required to fill the volume between the two pointers, was 19.68 cc, which, since the specific gravity of liquid ammonia at —33.5° is 0.674,[1] gives 13.27 grams as the amount of ammonia evaporated during each experiment. The resistance of the coil of platinum wire at —33.5° was 4.15 ohms. From 1.7 to 2.5 amperes were used.

The calculation of the heat of volatilization was accomplished by means of the formula, $\lambda = \frac{0.239\,\pi\,W}{0.000328\,g}$, in which λ is the heat of volatilization, 0.239 is the heat equivalent of the joule, π the reading of the voltmeter, W the weight of copper deposited in the voltmeter, 0.000328 the electrochemical equivalent of copper, and g the weight of ammonia evaporated. The results thus calculated, diminished by one calorie, the correction for the current diverted by the voltmeter, are given below.

After a considerable number of experiments, giving results ranging from 344 to 362 calories, had been made while getting the apparatus into final shape, three determinations yielded the following data:

Mean reading of voltmeter	Copper deposited	λ
10.31	0.6065	343.0
7.69	0.8029	338.0
7.71	0.8050	340.0

A mean value of 341 calories was thus obtained as the specific heat of volatilization of liquid ammonia at its boiling-point.

Remarks

The values mentioned in our earlier paper[2] were the re-

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[1] A. Lange: Zeit. gesammt. Kalte-Ind., 5, 18.

[2] Loc. cit.

sult of diminishing the above observed results by from 2 to 4 percent which corrections were made for the reason that determinations of the heat of volatilization of water in a similar apparatus gave results too high by this amount. However, a reconsideration of the method as applied to the two substances leads us to conclude that such a correction of the results for ammonia was unjustified. In the arrangement of the apparatus used for water there was always some condensation in the neck of the boiling cell and, as was observed in at least one instance, some of this water drained back into the body of the cell, thus introducing a plus error in the result. Furthermore, as a result of the action of the water on the glass cell, the liquid became, to some extent, a conductor as was evident from an observed marked electrolysis between the heavy platinum leads. A portion of the energy supplied was therefore not used in evaporating the water. No electrolysis was observable during the experiments on ammonia and, furthermore, because of the fact that the boiling-point of ammonia is well below that of the laboratory, a possible error, due to heat exchange with the exterior, would have the effect of diminishing rather than increasing the observed values of the heat of volatilization of this solvent.

The result we have obtained is seen to agree fairly well with the value, 337 calories, calculated by de Forcrand, but to differ rather widely from 321 calories, the value calculated by Brill.

More important, however, as it seems to the authors, is the agreement of our experimentally determined value with that calculated by means of the well-known formula of van't Hoff, $0.02T^2/k = \lambda$, when the experimentally determined value of k, the molecular elevation of the boiling-point, and the recently carefully determined boiling-point[1] of ammonia are introduced into the equation. Franklin and Kraus,[2]

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[1] Jour. Am. Chem. Soc., 27, 858 (1905).

[2] Am. Chem. Jour., 20, 841 (1898).

using water and ethyl alcohol as solutes, obtained 3.40 as a mean value of the constant *k*. One series of measurements on water gave a mean value of 3.46, another 3.37, while for a series in which alcohol was used a mean of 3.38 was obtained. Substituting 239.5, the temperature of ebullition of ammonia at atmospheric pressure, for T and 3.40, 3.37 or 3.46 for *k* in van't Hoff's equation, the values 337, 341 and 332, respectively, are obtained for the heat of volatilization of ammonia at its boiling-point, values which agree very well with the experimental results.

It may be noted, furthermore, that the substitution of 341 calories in the formula of Trouton, $\lambda M/T = \text{const.}$, gives the constant 24.2, which places ammonia along with water and the alcohols in the class of associated liquids as its other properties[1] seem to require.

Stanford University,
California, June, 1907.

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[1] Cf. Franklin and Kraus: Am. Chem. Jour., 21, 8 (1899).

OPTICAL ROTARY POWER OF LIQUID AMMONIA, METHYLAMINE, AND SULFUR DIOXIDE SOLUTIONS[1]

BY RALPH H. SHERRY

Introduction

The striking properties exhibited by liquid ammonia as a solvent for both salts and non-electrolytic carbon compounds which have been brought to light by the researches of Professor Franklin and his co-workers[2] make a study of the rotary power of optically active substances in this solvent desirable. In view of the fact that no important general relations have yet been discovered connecting the optical rotation of various solutions with the nature of the solvent, it was not expected that any very important results would be reached. It seemed, however, worth while to have measurements of the rotation of solutions of optically active substances in ammonia on record, to note whether or not such solutions show any considerable temperature coefficient, to observe the dependence of activity on concentration, to discover whether or not the conspicuous phenomenon of multi-rotation characteristic of aqueous solutions of certain sugars, is also exhibited by ammonia solutions, and to determine whether ammonium salts, which in ammonia solutions behave in many ways in a manner similar to the corresponding acids in aqueous solutions, show any of the effects on ammonia solutions of active substances such as are familiar in the case of acids in water solutions.

It may be said at once that the phenomenon of multirotation was not observed, nor does the presence of ammonium

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[1] From the author's thesis submitted, in May 1905, to the Department of Chemistry of the Leland Stanford Junior University for the degree of Master of Arts. Prepared for publication by E. C. Franklin.

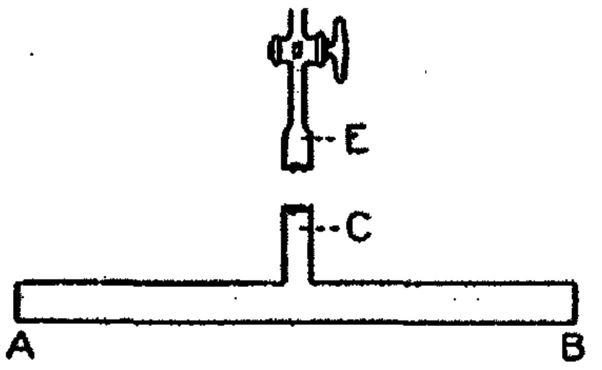
[2] Am. Chem. Jour., 20, 820, 836 (1898); 21, 1, 8 (1899); 23, 277 (1900); 24, 83 (1900); 28, 83 (1902). Jour. Am. Chem. Soc., 26, 499 (1904); 27, 191, 820, 851 (1905).

salts have any effect on the rotary power of active substances in ammonia solution.

Apparatus and Method of Manipulation

As the nature of the solvent necessitates certain modifications of the ordinary method of making measurements of optical rotation it seems desirable to describe briefly the procedure whereby the results given in this paper were obtained.

After ineffectual attempts to obtain glass tubes closed at one end by plane parallel ground windows from professional glass-blowers, polarization tubes after the manner of the figure were made in this laboratory by sealing glass discs cut from microscope slides to the ends of the tube at A and B. It was not possible with the skill of a non-professional to get the windows into a position such that their planes are accurately parallel, nor was it possible to seal in the ends without leaving them more or less deformed. However, tubes were prepared through which fairly good images could be obtained in the polariscope. In consequence of these imperfections in the windows, no special precautions were taken in measuring the lengths of the tubes, nor in adjusting the volumes of the solutions. The lengths given are accurate to within something less than 0.5 mm, while the volumes are in error by not more than 0.05 cc.



The procedure followed in making a measurement is as follows: With the polarization tube and the stop-cock separated at E, a weighed quantity of the solute was introduced into the former. The stop-cock was then sealed to the polarization tube before the blowpipe, after which ammonia was distilled into the tube, after the manner described by Franklin,[1] until it reached or slightly passed the calibration mark C. After thorough mixing and adjustment of the surface of the solution to the calibration mark, the volume of the solution becomes known. The measurements were made by means of a Wild polariscope using sodium light and, excepting when otherwise noted, at the ordinary laboratory temperature, 20° to 23°.

It was not considered feasible to weigh the tubes with their contents of liquid ammonia solution because of the danger to the balance from possible explosions. Determinations of the densities of the solutions were therefore dispensed with and the calculations of the specific rotation were made by means of the formula $[\alpha]_D = \frac{V\alpha}{Lg}$, in which $[\alpha]_D$ represents the specific rotation for sodium light, V the volume of the solution in cubic centimeters, α the observed rotation, L the length of the tube in decimeters, and g the weight of the solute in grams. In the tables the concentrations in grams per 100 cc of the solution, are given under the superscription *c*. The following experimental results have been obtained.

Cane-Sugar

Sugar is very soluble in liquid ammonia, forming, in high concentrations, very viscous, syrupy solutions. No changes in the readings of the polariscope were observable between 0° and 23°, nor does the presence of ammonium chloride in the solution have any effect on the rotation.

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[1] Jour. Am. Chem. Soc., 27, 831 (1905).

L = 230 mm. V = 16.4 cc.

g	c	α	$[\alpha]_D$
0.5	4.1	6.4	78.0[1]
1.0	8.2	12.45	76.0[1]
2.0	12.2	21.3	75.9
2.0	14.3	25.0	76.1[2]
2.0	16.4	24.7	75.3[1]
2.0	16.4	24.9	76.0[1]
2.0	16.4	24.9	76.0[1]
3.0	18.3	31.9	75.9
4.0	24.4	42.7	76.1
4.0	24.7	43.5	76.2[3]
4.1	25.0	43.3	75.5
4.1	25.0	43.25	75.2
4.2	25.6	44.2	75.0
4.0	27.0	46.7	75.3[4]
4.5	27.4	47.25	74.8
5.0	30.5	52.3	74.6
4.0	32.8	48.8	74.5[1]
4.0	32.8	51.0	77.8[1]
6.0	36.6	62.5	74.4
7.0	42.7	72.5	73.8
8.0	48.8	82.6	73.6

Cane-sugar in Mixtures of Water and Ammonia

It was believed that data of some importance might be obtained by measuring the rotation of sugar in water ammonia mixtures.[5] Accordingly, solutions containing per 100 cc of the solution, 24.4 grams sugar and the respective quantities of water indicated in the table, were made up and measured

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[1] These earlier measurements were made on ordinary granulated sugar, which because of impurities gave colored solutions. For the remaining measurements pure sugar, which gave entirely clear, colorless solutions, was used. The observation tube used for the measurements marked (1) was 200 mm long and had a capacity of 12.2 cc.

[2] V = 14.0 cc.

[3] V = 14.84 cc.

[4] V = 16.12 cc.

[5] Ost (Neue Zeitschr. Rübenz. Ind., 9, 42) has shown that strong aqua ammonia solutions of sugar give a higher specific rotation than do aqueous solutions, while Wilcox (Jour. Phys. Chem., 6, 341 (1902)) has found the specific rotation of a 10 percent solution of sugar in 25 percent ammonia to be 69.1° at 25°.

with the results given. The solutions were made by introducing 4 grams of sugar into an observation tube 230 mm long and of 16.4 cc capacity followed by the requisite quantity of water, after which ammonia was distilled in until the solution filled the tube to the calibration mark. In column C is given the concentration with respect to water; the superscriptions of the remaining columns are self-explanatory.

C	α	$[\alpha]_D$	C	α	$[\alpha]_D$
0	42.7	76.1	50	38.0	67.8
3	42.7	76.1	60	37.5	66.9
6	42.6	75.9	70	37.4	66.7
10	42.3	75.4	dil. NH_3	37.3	66.6
20	41.3	73.7	100	37.2	66.5
30	40.0	71.4	100	37.2	66.5
40	39.0	69.6	—	—	—

Asparagine

In water solution asparagine has a specific rotation of —5.95° to —5.30°,[1] decreasing with increasing concentration. In solutions to which strong acids have been added the rotation becomes strongly positive. The strong left-handed rotation in ammonia is not affected by the presence of ammonium chloride. The asparagine used was twice recrystallized before use.

$L = 200$ mm. $V = 12.2$ cc.

g	c	α	$[\alpha]_D$
1	8.2	— 4.4	—26.9
1	8.2	— 4.4	—26.9
2	16.4	— 8.9	—27.1
4	32.8	—17.3	—26.4
4	32.8	—16.8	—25.6
1	6.1	— 3.7	—26.4[2]

Amygdaline

The laboratory specimen was used without further purification.

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[1] Ber. Chem. Ges. Berlin, 14, 1030 (1881).

[2] Length of observation tube, 230 mm. Capacity, 16.4 cc.

In aqueous solution, amygdaline has a specific rotation of —35.5°.[1]

L = 200 mm. V = 12.2 cc.

g	c	α	$[\alpha]_D$
0.5	4.1	— 4.4	—53.7
1.0	8.2	— 8.8	—53.7
2.0	16.4	—17.6	—53.7
4.0	24.3	—30.0	—53.5[2]

Coniine Hydrochloride

In water coniine hydrochloride has a specific rotation of 0.27°.[3] A laboratory specimen was used without further purification. As ammonia is distilled into the tube containing the salt, the base separates before going into solution.

L = 200 mm. V = 12.2 cc.

g	c	α	$[\alpha]_D$
0.5	4.1	0.84	10.25
1.0	8.2	1.65	10.06

Raffinose

The material used in these determinations was made by Kahlbaum and was not further purified. In water solution raffinose shows a specific rotation of 104.5°.[4]

L = 200 mm. V = 12.2 cc.

g	c	α	$[\alpha]_D$
0.5	4.1	8.4	102.5
1.0	8.2	16.8	102.5
2.0	16.4	33.6	102.5

Lactose

For these measurements anhydrous milk sugar was prepared by recrystallizing the commercial product from hot

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[1] Bouchardat: Comptes rendus, 19, 1174.

[2] L = 230 mm. V = 16.4 cc.

[3] Landolt: "Optische Drehungsvermögen organischer Substanzen," 2te Aufl. p. 617.

[4] Tollens: Liebig's Ann., 232, 169 (1886).

water and drying in the air bath at 98°. The solutions were allowed to stand over night, one of them for several days, for the purpose of determining whether or not multirotation effects might be shown. None were observable. The specific rotation of lactose in water changes with time from 83° to 52.5°.[1]

L = 200 mm. V = 14.4 cc.

g	*c*	*α*	$[\alpha]_D$
1.0	6.95	4.6	33.2
2.0	13.9	9.3	33.5
4.0	27.8	18.0	32.5

Glucose

Solutions of *d*-glucose, made from the specially crystallized material of Kahlbaum, were allowed to stand from 5 to 40 hours without any change in the rotation manifesting itself. In aqueous solution the specific rotation changes with time from 105.2° to 52.5°.[2]

L = 200 mm. V = 14.4 cc.

g	*c*	*α*	$[\alpha]_D$
0.5	3.47	3.9	56.1
1.0	6.94	7.6	54.7
1.0	6.94	7.7	55.5
2.0	13.9	15.2	54.8
4.0	27.8	30.7	55.3

Galactose

A preparation by Kahlbaum was used. The specific rotary power of galactose in water changes with the time from 117.3° to 80.3°.[3] In ammonia no multirotation effects were observed.

L = 200 mm. V = 14.4 cc.

g	*c*	*α*	$[\alpha]_D$
1.0	6.94	1.7	12.2
1.0	6.94	1.7	12.2

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[1] Parcus and Tollens: Liebig's Ann., 257, 170 (1890).

[2] Parcus and Tollens: *Ibid.*, 257, 164 (1890).

[3] Parcus and Tollens: *Ibid.*, 257, 168 (1890).

Cocaine

Cocaine from Kahlbaum was used. The specific rotation of cocaine in chloroform is —16.3°.[1]

L = 200 mm. V = 14.4 cc.

g	c	α	$[\alpha]_D$
0.5	3.47	—1.66	—24.0
1.0	6.94	—3.33	—24.0
0.5	4.1	—1.97	—24.0[2]

Fructose

No one of several specimens of *d*-fructose gave an observable rotation in ammonia, nor was any effect produced by the presence of ammonium chloride in the solution.

Rotation in Liquid Sulfur Dioxide

The following active substances were found to be insoluble in sulphur dioxide: Cane-sugar, *d*-fructose, tartaric acid, malic acid, glucosazone, asparagine, amygdaline, and morphine.

The following are soluble: Strychnine (very), cinchonine (slightly), cocaine, brucine, quinine, nicotine, coniine, atropine, coniine hydrochloride, hyoscyamine, codeine, aconitine, and veratrine.

Such of these substances as were tested for their optical activity in sulfur dioxide solution gave the results indicated in the tables which follow.

Strychnine

It is interesting to note that in sulfur dioxide strychnine gives a right-handed rotation, while in all other solvents so far studied, it shows strong laevoactivity.[3]

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[1] Antrick: Ber. chem. Ges. Berlin, 20, 321 (1887).

[2] V = 12.2 cc.

[3] Oudemans: Liebig's Ann., 166, 76 (1873). Tykocjner: Rec. Trav. chim. Pays-Bas, 1, 146 (1882).

L = 200 mm. V = 13.9 cc.

g	c	α	$[\alpha]_D$
1.0	7.2	9.8	68.2
2.0	14.4	20.0	69.5
0.5	3.05	4.85	69.3[1]

Quinine

Solutions of quinine in sulfur dioxide are rather strongly colored. In absolute alcohol quinine has a specific rotation varying with the conditions of temperature and concentration between —171.4° and —159.8°.[2] A marked temperature coefficient, of opposite sign, however, also characterizes sulfur dioxide solutions of quinine.

L = 200 mm. V = 13.86 cc.

g	c	$\alpha_{23°}$	$[\alpha]_D^{23°}$	$\alpha_{4°}$	$[\alpha]_D^{4°}$
0.5	3.6	—14.7	203.0	—15.8	—219.0
0.5	3.6	—15.0	208.0	—16.0	—222.0
1.0	7.2	—29.0	201.0	—30.01	—208.0

Coniine Hydrochloride

L = 200 mm. V = 13.0 cc.

g	c	α	$[\alpha]_D$
1.0	7.7	1.1	7.2
2.0	15.4	1.7	5.5

Aconitine

Specific rotation in alcohol 11.0°.[3]

L = 200 mm. V = 13.0 cc.

g	c	α	$[\alpha]_D$
1.0	7.7	2.6	16.9

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[1] L = 230 mm. V = 16.4 cc.

[2] Lenz: Fresenius' Zeit. anal. Chem., 27, 549 (1888).

[3] Dunstan, Ince: J. Chem. Soc., 59, 281 (1891).

Other Solutes

A solution of cocaine in sulfur dioxide showed no measurable rotary power. Even freshly distilled nicotine gave a solution so strongly colored that it was impossible to measure the rotation.

Rotation in Methylamine Solutions

As in liquid ammonia, so also in methylamine and in ethylamine, *d*-fructose is without measurable action on a beam of polarized light.

Sucrose

L = 230 mm. V = 16.4 cc.

g	*c*	*α*	$[\alpha]_D$
2.0	12.2	20.8	74.2[1]
2.0	12.6	20.6	75.8[2]

This work was done under the direction of Professor E. C. Franklin in the chemical laboratories of the Leland Stanford Junior University.

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[1] At 0°.

[2] At 20°. The volume, 16.4 cc., of the solution at 0° increased to 17.0 cc. at 20°. This solution and another which was made, were so strongly colored by the cement used for making connection with the lead tube and with the lubricant used on the stop-cock, both of which are rapidly attacked by methylamine, that further work with these solutions was abandoned.

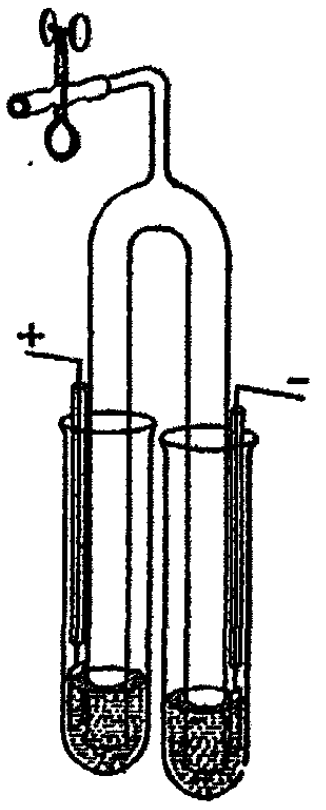
THE EFFECT OF ACETONE ON THE TRANSPORT NUMBERS OF SODIUM AND POTASSIUM CHLORIDES IN AQUEOUS SOLUTION

BY HENRY F. LEWIS

The migration of a number of salts has been studied in solutions in alcohol, glycerine, methyl alcohol, etc., and in every case the transport number was found to be within a few percent of that in pure water. Salts dissolved in mixtures of alcohol and water have also been studied from this point of view with the same result.[1] The following experiments which show that the ratio *u/v* for the ions of potassium chloride and sodium chloride in aqueous solution is more than halved by addition of acetone are therefore of considerable interest, and must be taken into account in all attempts to interpret the electrical conductivities of these solutions.

The Apparatus

The apparatus with which I worked is not adapted to give results of a very high order of accuracy; as will be seen from the table the results of individual experiments differed by as much as 4 units in the second decimal place. The accuracy was, however, sufficient for the purpose in view, which was to make sure that the transport number is really affected by the presence of acetone; and as the apparatus is easily put together, and determinations may be made with it rapidly, I have thought it worthy of being described, and have detailed a number of test experiments made with it which show that the results of my measurements were not affected by errors due to diffusion or mixing.



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[1] An index to the literature of migration determinations in solvents other than water is contained in J. W. McBain's. "Experimental data of the quantitative determinations of electrolytic migration." Trans. Wash. Ac. Sci., 9, 1 (1907).

About 200 cc of solution were used in each experiment. The U-tube was filled by suction, and the pinch-cock closed; the electrodes were then inserted, and connected with a silver voltameter and the source of current. In one experiment a Weston millammeter was used as well as the voltameter; readings were made at one minute intervals during the hour and a half that the electrolysis lasted, and the number of coulombs so obtained agreed within 0.5 percent with that given by the voltameter.

When the electrolysis was at an end, about 12 cc were withdrawn for analysis from the tube *m* ("middle portion"). The pinch-cock on *m* was then slightly opened, and the liquid in the U-tube allowed to run slowly into the electrode tubes, the U-tube being raised so that it never dipped deeply into the liquids in the electrode tubes; the cathode was removed and rinsed into the cathode tube with a little unelectrolyzed solution; these solutions were then removed, cooled, and analyzed.

Thus the anode and cathode portions were easily separated without the use of diaphragms or taps; the legs of the U-tube were rinsed out with the unaltered middle portion of the electrolyte; a middle portion was readily obtained for analysis, and gas bubbles or changes in density at the electrodes could not produce harmful stirring.

The following experiments were made to test the reliability of the apparatus; a decinormal solution of sodium chloride in 50 percent acetone was used.

1. *Diffusion of Alkali from the Cathode.*—A little litmus was added to the solution and turned pink by a trace of acid. After electrolyzing for an hour and a half the blue zone at the cathode extended less than a centimeter into the upright tube.

2. *Diffusion of Acid from the Anode.*—Methyl orange and a little alkali added to the electrolyte gave a yellow solution, which after a quarter of an hour was quite red at the anode. In another hour the solution in the anode glass

was bleached, the red remained in the upright tube about a centimeter above the liquid in the glass.

3. *Diffusion of Chlorine.*—Indigo added to the electrolyte was bleached at the anode, but at the end of an hour and a quarter the bleaching had not extended appreciably into the upright tube.

4. *Evaporation of Acetone from the Electrode Glasses.*—A tube was set up in the usual manner, but no electricity was passed through. A Bunsen burner was set near the apparatus so that it might be as warm as during an electrolysis. After two hours the liquid was removed from one side, made up to 100 cc, and analyzed in the usual way; 93.18 cc of the silver solution were required instead of 92.74 cc.

The Method of Analysis

Fifty cc of the unelectrolyzed solution, or 10 cc of the middle portion, were evaporated to dryness on the water-bath to remove acetone; the residue was dissolved in water, 1 cc of a neutral solution of potassium chromate added, and the chlorine determined by decinormal silver nitrate. The cathode solution after electrolysis was made up to 100 cc with unelectrolyzed solution and evaporated as before; the alkali was then neutralized with decinormal sulphuric acid, using methyl orange as indicator, and before titrating with silver a drop of decinormal alkali was added to restore the yellow color. Blank analyses showed that the method was reliable.

The chlorides and the acetone were C. P. preparations of Merck; all measuring vessels and burettes were calibrated.

Results of the Measurements

All the solutions experimented with were approximately decinormal with respect to the salt. The first column of the table gives the parts by volume of acetone in one of the solution. The second, the weight of silver (W) deposited in the voltameter. The third, the duration of the electrolysis in minutes. The fourth, the amount of decinormal silver nitrate required to precipitate the chlorine in 100 cc of the unelectro-

TABLE I

Salt	Parts of acetone	Grams of silver W	Time. Minutes	Analyses		Difference L	Change in middle	H
				Before	After			
NaCl	0	0.1875	45	90.94	79.66	10.28	—	0.59
	$\frac{1}{8}$	0.1662	60	89.08	80.66	8.42	0.00	0.55
					80.48	8.60	−0.05	
	$\frac{1}{4}$	0.1342	60	95.20	89.08	6.12	0.02	0.52
					88.35	6.85	−0.03	
	$\frac{1}{2}$	0.1006	65	93.32	89.69	3.63	−0.04	0.38
					89.89	3.43	0.02	
	$\frac{3}{4}$	0.0622	60	89.68	87.43	2.25	0.04	0.38
					87.52	2.16	0.08	
KCl	0	0.1586	40	98.02	90.91	7.11	0.14	0.49
					90.64	7.38	0.09	
	0	0.1928	60	95.12	86.52	8.60	0.12	0.48
	0	0.1232	45	95.12	89.43	5.69	0.03	0.49
	0	0.2020	55	93.31	84.28	9.03	0.18	0.48
	$\frac{1}{8}$	0.1942	60	96.78	88.94	7.84	−0.10	0.44
	$\frac{1}{4}$	0.1844	65	93.20	86.93	6.27	0.00	0.37
					86.69	6.51	0.03	
	$\frac{1}{4}$	0.2020	55	101.14	93.22	7.92	−0.17	0.42
	$\frac{1}{2}$	0.1154	60	99.90	95.65	4.25	0.03	0.39
					95.87	4.03	0.05	
	$\frac{1}{2}$	0.1232	45	96.22	92.22	4.00	0.02	0.35
	$\frac{3}{4}$	0.0832	75	96.70	94.01	2.69	0.02	0.32
					94.38	2.32	−0.03	
	$\frac{3}{4}$	0.0768	60	100.16	97.98	2.18	−0.04	0.29
					98.24	1.92	−0.03	

lyzed solution; and the fifth, the silver required by the 100 cc of solution obtained by adding unelectrolyzed solution to the cathode solution as explained on page 571. Column six gives the difference between the last two, that is, the loss (L) of chlorine from the cathode compartment. The seventh column gives the loss or gain in the 10 cc middle portion, expressed as cubic centimeters of the decinormal silver. The last column gives the transport number (H) of the chlorine, computed by the formula

$$H = 0.0108\ L/W.$$

When two tubes were electrolyzed in series with the same solution in each, the numbers in the first four columns are the same for each, and are not repeated in the table. The fourth and twelfth electrolyses in the KCl series were carried out in series with each other; likewise the fifth and ninth.

These results show clearly that the transport numbers of the salts investigated are much lower in solutions containing acetone than in pure water, although they do not agree well enough among themselves to fix definitely the amount of the decrease.

In conclusion, I desire to express my thanks to Professor W. Lash Miller at whose suggestion these measurements were undertaken in the Spring of 1906, and to the authorities of the University of Toronto for the use of the electrochemical laboratory.

The University of Toronto,
May, 1907.

NEW BOOKS

Vorlesungen über theoretische Physik von H. von Helmholtz. Band IV. Vorlesungen über Elektrodynamik und Theorie des Magnetismus. *Herausgegeben von Otto Krigar-Menzel und Max Lane. 17 × 26 cm; pp. 406. Leipzig: Johann Ambrosius Barth, 1907. Price: paper, 16 marks; bound, 17 marks.*— This is the last of the six great volumes of von Helmholtz's lectures to make its appearance, the companion volume, V, on the electromagnetic theory of light, issued in 1897, having been one of the first. We now have, in readable and admirably consecutive form, all that the great master gave to his classes, inasmuch as not only Helmholtz's own notes, which were liable to be incomplete, but the note-books of his more gifted students have been used as sources of information. The editors are to be congratulated on the completion of so handsome and memorable a piece of work.

If we glance over the pages of the volume before us, in comparison with other notable modern treatises like that of Abraham and Föppl, 1905, the first impression gained suggests a remarkable change of front in modern physics. In fact Helmholtz's pages, written in Cartesian geometry with their solid phalanx of equations, already look antiquated and the computations labored when contrasted with those works in which the vector calculus is used. True, the disciples of the modern method usually know the answers and state their cases in such a way that the demonstrations run with peculiar smoothness along their own particular lines. Nevertheless there can be no doubt that the character of physics is such that the vector calculus is more and more irresistibly forced upon the modern writer, because of its immediate adaptation, and the simplicity and clearness of the demonstrations attainable by its use.

These lectures were given by Helmholtz as long ago as 1888 to 1889, and for this reason begin with Coulomb's law, a method of exposition which is not now customary. The first two chapters, on electrostatics, are self-contained and very complete. The doctrine of the potential is treated in full, and the beautiful method of electrical images is given extended application. The essentials of spherical harmonics follow in the third chapter.

The second part contains the remaining phenomena which may be derived from a potential, including the treatments of dielectric and magnetic bodies and of steady currents. In all these cases the important problems are entered into deliberately.

The third part of the work discusses the phenomena of the electromagnetic field, successive sections being devoted to steady currents and to oscillating currents.

The advanced student will particularly value this work as a commentary on von Helmholtz's original contributions, as for instance his well-known interpretation of *Doppelschichten*, the profound contribution of a field of vortex lines which grew out of his hydrodynamic researches, etc.; or we may wish to consult the original solutions of classical problems in which the book abounds, as for instance the comprehensive treatment of Stokes's theorem, etc. Von Helmholtz's own equations of the electromagnetic field, derived from Coulomb's law by pure induction, are broad enough to include Maxwell's equations, but they are receiving little attention at a time when the obtrusiveness of the medium is daily becoming more unmistakable.

The general student will find this an excellent work of reference, though here his labors would have been greatly facilitated, if the editors had appended a synopsis of the notation peculiar to von Helmholtz. *Carl Barus*

Modern Chemistry, Theoretical and Systematic. *By William Ramsay. 10 × 15 cm; pp. 329. New York: The Macmillan Company, 1907. Price:* $.70 net.—This little book is of course not adapted as a beginner's book in chemistry; its purpose is rather to give an account of systematic chemistry in such a form as could be followed intelligently by a mature reader, but the work would also be a most useful review book for students, and would provide good reading for many who have all examinations behind them.

The amount of information conveyed in these 300 pages is astonishing; the first 125 pages are taken up with a brief account of theoretical and historical developments, and the remainder of the book is given over to systematic chemistry, *i. e.*, to a systematic study of the elements and their properties, the whole of the material being handled in a way that is quite novel and interesting.

It would have been an improvement if the index to both parts had been placed at the end of the book; as it is, the index to the first part occurs quite casually in the middle of the volume. *A. P. Saunders*

Practical Physical Chemistry. *By Alex. Findlay. 13 × 20 cm; pp. xii + 282. New York: Longmans, Green and Co., 1906. Price: $1.20.*—One of the needs of physical chemistry is a good laboratory guide. Teachers of physical chemistry have hitherto relied on the works of Ostwald, Ostwald-Luther, Traube, and Getman in outlining their courses. These books are admirable for reference. They are, however, of little assistance to the student who is beginning a study of physical chemistry because they deal too exclusively with methods and do not pay enough attention to the description of experiments which illustrate physical chemical principles. Findlay's book is a long step in the right direction. It was written with an understanding that the beginner needs a book which gives not only typical methods but also directions for experiments. This general idea is very well worked out. Moreover, the method of instruction set forth in the book has worked satisfactorily in the author's laboratory at the University of Birmingham.

Besides containing the conventional physical chemical experiments on the density of liquids and gases, viscosity, molecular weight of substances in solution, conductivity, transport numbers, solubility and distribution, it contains interesting and instructive experiments in reaction velocity, thermochemistry and the determination of transition points.

The book will be a great help in laboratory instruction and will do much toward realizing the author's hope that it will "promote the more general introduction of physical chemistry into the courses of study in other universities."
G. R. White

Die Kathodenstrahlen. *By G. C. Schmidt. (Die Wissenschaft. Sammlung naturwissenschaftlicher und mathematischer Monographien. Heft 2.) Zweite verbesserte und vermehrte Auflage. 14 × 22 cm; pp. vi + 127. Braunschweig: Friedrich Vieweg und Sohn, 1907. Price: paper, 3.00 marks; linen, 3.60 marks.* —The second edition of Professor Schmidt's work (the first edition of which was fully reviewed in these columns) is a slight enlargement (about seven pages) of the original book, the new development of the last three years having been conscientiously added. Professor Schmidt's pages contain a clear-cut treatment of a definite series of phenomena, written almost without mathematics in a way to accentuate the experimental side. The book concludes with a set of references to the original sources from which the text has been compiled, and there are excellent figures throughout. Since the appearance of Lodge's summary of the work leading up to the modern theory of matter, Schmidt's monograph has been ably and perhaps more seriously paralleled, but the two books may be read together with advantage. *Carl Barus*

An Elementary Study of Chemistry. *By William McPherson and William Henderson. Revised Edition. 13 × 19 cm; Boston: Ginn and Company, 1906.*—No claim for originality is made in this book; it is frankly admitted to be "a textbook constructed along lines which have become recognized as best suited to an elementary treatment of the subjects." But there is always a touch of originality in excellence, and this volume is excellent. It provides a feasible, comprehensible, and suitable course for the beginner whose time is limited and whose intelligence is not superhuman. Theoretical chapters appear at intervals through the text and are not gathered together in awful array at the beginning. Thus, the student, after becoming acquainted with oxygen, hydrogen, and water, is introduced to the laws of chemical combination, and then to the atomic theory; this chapter is followed by one on chemical equation and calculations; nitrogen and the rare elements of the atmosphere come next, and so on. The theory of electrolytic dissociation claims attention early in the work, but very little use is made of it in the general consideration of reactions, and the equations throughout are given in the older form.

There is always room for differences of opinion as to the arrangement of a course in chemistry, but all teachers who have elementary classes will be interested in examining a work which is so carefully adapted to the needs of the beginner as is this one. *A. P. Saunders*

Exercises in Chemistry. *By William McPherson and William Henderson. 13 × 19 cm. Boston: Ginn and Company, 1906.*—These experiments are intended to accompany the text by the same authors. The course is perhaps cut down too far for college use, being based on the assumption that the student spends only an hour and a half twice weekly in the laboratory. The general lines of the book are the same as those of the reading text, and the experiments are selected with the same good judgment there manifest. *A. P. Saunders*

Erinnerungen an Johannes Wislicenus aus den Jahren 1876-1881. *By Wilhelm Sonne. Mit einem Vorworte von Max Conrad. 15 × 22 cm; pp. 36. Leipzig: Wilhelm Engelmann, 1907. Price: paper, 1.20 marks.*—This little pamphlet of 36 pages offers an account of the activities of the Wurzburg laboratory under Wislicenus during the years 1876–1881. The glimpses of the personality of Wislicenus are of considerable interest, and the whole narrative, though rather slender in material, is not unentertaining. *A. P. Saunders*

THE SOLUBILITY OF CALCIUM CARBONATE IN AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE AND POTASSIUM SULPHATE AT 25°[1]

BY F. K. CAMERON AND W. O. ROBINSON

The solubility of calcium carbonate in various aqueous solutions of electrolytes has been investigated in this laboratory.[2]

In this paper are given results obtained for the solubility of calcium carbonate in aqueous solutions of potassium chloride and of potassium sulphate; first, where carbon dioxide has been excluded from the atmosphere, and secondly, where carbon dioxide alone formed the gas phase under a pressure equal to that of the atmosphere.

For the experimental part of this work, bottles were filled with solutions of the chloride or the sulphate of potassium of varying concentrations, using distilled water recently boiled. To each solution an excess of calcium carbonate was added and the bottles were then shaken in a thermostat at 25° for a period of ten weeks.

At the end of this time the contents of the bottles were allowed to settle and 25 cc portions of the supernatant solution were analyzed for calcium. The sulphates or chlorides were estimated in the usual manner. Tables I and II contain the data obtained for these systems.

The figures obtained for potassium chloride solutions may be compared with the results of Cantoni and Goguelia.[3] They found that after 98 days at 12°–18° solutions containing 7.45, 10 and 20 percent potassium chloride had dissolved 0.00748, 0.00742 and 0.00828 gram of calcium carbonate, respectively, to 100 cc of solution.

Carbon dioxide was forced into the previously prepared solutions at one and one-half atmospheres pressure at a

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[1] Published by permission of the Secretary of Agriculture.

[2] Cameron and Seidell: Jour. Phys. Chem., 6, 50 (1902).

[3] Bull. Soc. Chim., Paris [3], 33, 13 (1905).

TABLE I

The solubility of calcium carbonate in aqueous solutions of potassium chloride at 25°

Specific gravity, $\frac{25^\circ}{25^\circ}$	KCl	$CaCO_3$
	Percent	Percent
1.000	0.00	0.0013
1.024	3.90	0.0078
1.046	7.23	0.0078
1.072	11.10	0.0076
1.092	13.82	0.0072
1.101	15.49	0.0076
1.122	18.21	0.0070
1.133	19.84	0.0072
1.179	26.00	0.0060

TABLE II

The solubility of calcium carbonate in aqueous solutions of potassium sulphate at 25°

Specific gravity, $\frac{25^\circ}{25^\circ}$	K_2SO_4	$CaCO_3$
	Percent	Percent
1.010	1.60	0.0104
1.021	3.15	0.0116
1.033	4.73	0.0132
1.048	6.06	0.0148
1.061	7.85	0.0168
1.069	8.88	0.0192
1.083	10.18	0.0192
1.084	10.48	0.0188

temperature slightly above 0°. As soon as these solutions were saturated with carbon dioxide under the conditions imposed, they were removed to the constant temperature bath 25°. After shaking for a week the stoppers were occasionally removed, for a moment only, allowing the pressure of the gas phase to adjust itself to that of the atmosphere, but not at the same time displacing the carbon dioxide with the atmosphere.

It was observed that the solutions of potassium sulphate of higher concentrations were capable of dissolving much more carbon dioxide than the corresponding solutions of potassium chloride and that in such solutions there was a change in the solid phase.

After the bottles had shaken for eight days at constant pressure of the carbon dioxide, they were allowed to settle and the clear solutions analyzed for the same constituents as before. The data are presented in Tables III and IV.

TABLE III

The solubility of calcium carbonate in aqueous solutions of potassium chloride at 25° saturated with carbon dioxide at atmospheric pressure

KCl	$CaCO_3$
Percent	Percent
3.90	0.145
7.23	0.150
11.10	0.166
13.82	0.165
15.49	0.167
18.21	0.154
19.84	0.140
26.00	0.126

TABLE IV

Solubility of calcium carbonate and syngenite in aqueous solutions of potassium sulphate at 25° saturated with carbon dioxide at atmospheric pressure

SO_3	CaO
Percent	Percent
0.0	0.062
0.69	0.69
1.37	0.69
1.67	0.47
2.18	0.30
2.99	0.24

From these figures it can be seen that there is a change in the solid phase. This change occurs at a concentration of

1.37 percent sulphuric anhydride. In solutions more concentrated than this the solid is composed of fine acicular crystals. When washed with water they are decomposed, yielding gypsum and a solution of potassium sulphate, thus showing them to be syngenite.

To confirm this conclusion a solution was prepared containing 7.5284 grams potassium sulphate to 100 grams water. To this solution 0.4318 gram calcium carbonate was added. Carbon dioxide was then forced into the system till the carbonate had changed into the double salt and the supernatant solution was analyzed for calcium oxide, sulphuric acid, and potash. Table V gives the composition of the solution before and after the precipitation.

TABLE V

The composition of a solution of potassium sulphate before and after precipitating with a weighed amount of calcium carbonate in the presence of an excess of carbon dioxide

	Before precipitation	After precipitation
Grams K_2O	4.0728 to 100 gm. H_2O	3.6988 to 100 gm. H_2O
" SO_3	3.4556 " " "	2.8406 " " "
" CaO	0.2418 added	0.0188 found in solution

These figures show that the precipitate was composed of 0.223 gram calcium oxide, 0.374 gram potash, and 0.615 gram sulphuric anhydride, corresponding in reacting weights to $1CaO : 1K_2O : 1.94\ SO_3$.

In this paper we have shown that calcium carbonate is much more soluble in aqueous solutions of potassium sulphate than of potassium chloride; that the solubility curve for calcium carbonate in potassium chloride solutions passes through a maximum; and in potassium sulphate solutions above 1.37 percent sulphuric anhydride, or 2.98 percent potassium sulphate, syngenite is formed.

Bureau of Soils,
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Washington, D. C.

THE DISTRIBUTION OF SOLUTE BETWEEN WATER AND SOIL[1]

F. K. CAMERON AND H. E. PATTEN

In studying the distribution of an added solute between an absorbent and solvent there is difficulty in obtaining accurate data when the absorbent already contains the solute in question. There is no method of determining absolutely the quantity of any soluble material in a soil, which has already been absorbed on the soil grains, and the total amount present as absorbent material cannot be ascertained, although the amount of solute present in the water added to the soil be measured exactly.

To determine the character of this distribution readily, water-soluble bodies have been used which are not contained in the soil naturally, and which are not appreciably changed by contact with the soil. Thus, there is known the quantity of solute, that of the soil and of the water; and there are obtained a series of systems in equilibrium in which the distribution of solute between water and soil can be examined quantitatively.

Soil, Gentian Violet, Water

The dye gentian violet has been found particularly well adapted to studying distribution, because it is very slightly changed, if at all, by contact with the soils used or with quartz flour, and because it can be readily estimated colorimetrically to within a fraction of a part in a million of solution. It is a basic dye (gentianin), represented by the formula $(CH_3)_2N.C_6H_3:SClN.:C_6H_3.NH_2$, analogous to ammonia bases in general. The solubility of the dye in water at 25° is approximately 6.8 percent by weight.

One hundred gram portions of each soil were placed in strong glass bottles of some 300 cc capacity, with 150 cc of dye solution, agitated in a shaker for several days, placed in a

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[1] Published by permission of the Secretary of Agriculture.

centrifuge and whirled for several hours, and a small portion of the liquid withdrawn from each and the dye content estimated colorimetrically. The bottles were then replaced in the shaker, again centrifuged, and the dye in solution again determined. This was repeated till equilibrium had been reached, which usually required about a week's time.

It was found that the necessity of centrifuging these bottles at room temperature for hours to insure settlement after complete mingling of soil and solution had finally been secured, rendered a thermostat useless for the present purpose. The experiments presented here were accordingly carried out at room temperature, which varied but little from 25°.

By a separate experiment it was found that 100 grams of Marshall silt loam[1] absorb 4 cc of water from a saturated atmosphere at 29°. This was taken as representing the volume of water which is extracted from the solution when brought into contact with this soil. So, in effect, the volume of solution for which the concentration of dye is determined is not 150 cc—the volume of the liquid added—but 146 cc.

Similarly 100 grams of Hagerstown loam[1] absorb 4.5 cc of water from a saturated atmosphere at 29°, and accordingly this value was used in calculating the concentration of the solutions after absorption. The quartz flour used absorbed 0.8 cc water under the same conditions, but as this correction affects the distribution curve by less than 1 percent, it is neglected.

Table I gives the experimental data for the distribution of gentian violet between soil and water. The first column shows the concentration of dye solution added; the weight of dye withdrawn from solution per kilo of soil is shown in the second column for Marshall silt loam, a representative fertile soil; and the grams of dye remaining in a liter of solution, in the third column. The distribution for Hagerstown loam, another fertile soil, is given similarly in the fourth and fifth

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[1] For a description of these soils see, Soil Survey Field Book, Bureau of Soils, U. S. Dept. Agr., Field Season, 1906, pp. 48, 126, 144.

columns; and for fine quartz flour in the sixth and seventh columns.

TABLE I

Soils and gentian violet

Dye added per liter	Distribution					
	Marshall silt loam		Hagerstown loam		Quartz flour	
	Dye per kilo soil	Dye per liter solution	Dye per kilo soil	Dye per liter solution	Dye per kilo quartz	Dye per liter solution
Grams	Grams	Grams	Grams	Grams	Grams	Grams
0.04	—	—	—	—	0.06	trace
0.10	—	—	—	—	0.14	0.0001
0.5	—	—	—	—	0.743	0.0040
0.67	—	—	—	—	1.984	0.0108
1.33	—	—	1.9996	0.00023	1.901	0.066
2.00	3.00	trace	—	—	2.66	0.224
2.66	—	—	3.9998	0.00140	2.89	0.740
3.33	4.999	0.0001	4.9996	0.00250	2.95	1.370
4.66	—	—	—	—	2.97	2.668
6.67	9.999	0.00083	9.9825	0.0120	2.93	4.710
10.00	—	—	14.95	0.0325	—	—
13.33	19.99	0.006	19.817	0.1250	—	—
16.66	24.97	0.020	—	—	2.90	14.75
20.00	29.91	0.060	20.45	6.525	—	—
21.33	31.89	0.070	—	—	—	—
26.67	37.00	2.050	20.25	13.500	—	—

In Fig. 1 are charted the distribution curves for the three soils given in Table I. Since the purpose is to compare the *form* of the curves at greatest curvature, the curves are given on the same chart but necessarily to widely different scales. The concentration of dye in solution is taken as abscissa, and the concentration of the soil as ordinate. The curves thus obtained appear to be parabolic in form. By extrapolating the curve in Fig. 1, when drawn to scale, the maximum absorptive capacity of the soil for gentian violet is found to be approximately 38 grams of dye per kilogram of soil for Marshall silt loam, when the solution is saturated with respect to the dye. For Hagerstown loam the maximum absorptive capacity is 20.45 grams dye per kilogram of soil; and for quartz flour, 2.97 grams dye per kilogram quartz. These absorptive capacities are in the ratio of 113 : 61 : 1, and show that each soil has its own specific absorptive power. The soil grain area of Marshall silt loam is probably about the same as that of Hagerstown loam, as a comparison of their mechanical analyses shows, and yet the Marshall soil absorbs nearly twice the amount of dye taken up by the Hagerstown soil. Again, both of these soils have an area presented by their grains probably twice as great as the surface offered by the same weight of the quartz flour used, and yet the quartz has by no means half the absorptive capacity of either of the soils. The presence of organic matter is undoubtedly a very important factor in determining the magnitude of the absorption. But it is certain that the mineral constituents of a soil, as well as the organic matter it contains, are a factor in determining its absorptive capacity, and that mineral constituents other than gelatinized products of hydrolysis are capable of absorbing soluble bodies from the soil solution to a marked extent.

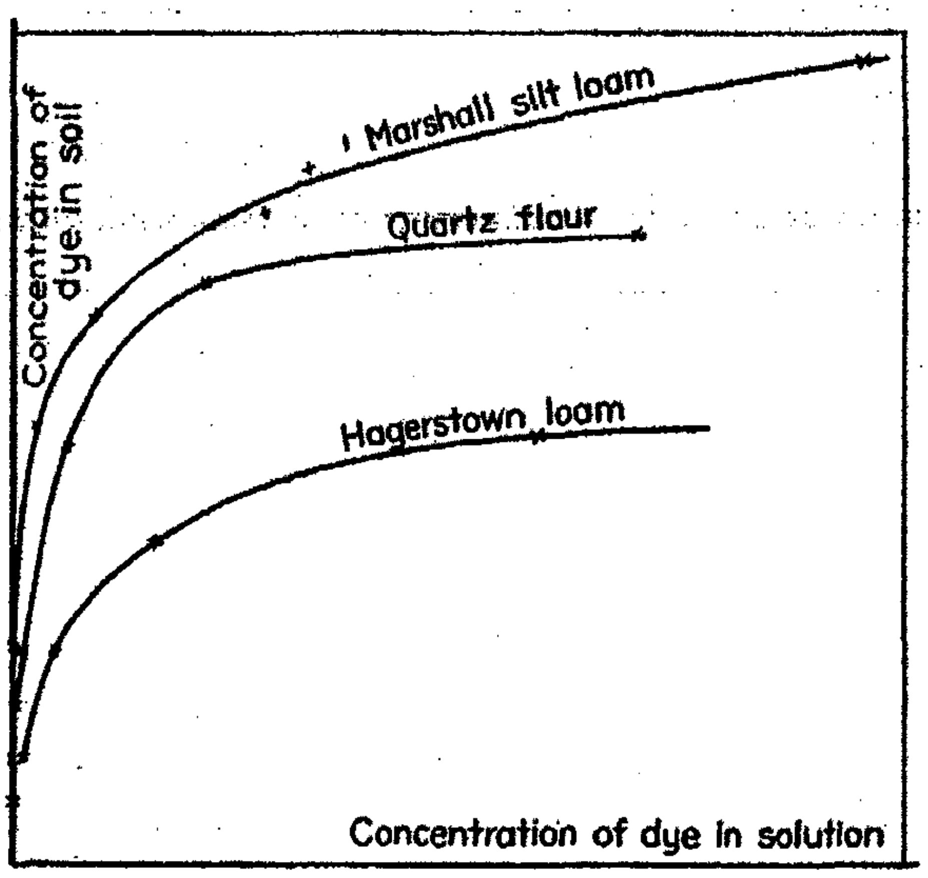

Fig. 1

Considering the concentrations of dye when the soil has nearly reached its maximum absorption capacity a computation from the data in Table I shows that Marshall silt loam abstracted from solution 92.5 percent of the total dye added; the Hagerstown loam, 51.1 percent; and the quartz flour, 59 percent. At lower concentrations of dye in solution the soils absorb relatively more dye, and although the dye is truly distributed between soil and solution, the soil holds so large a portion of dye that for practical purposes the dye is all absorbed. Thus, for 0.5 gram dye added, the Marshall silt loam absorbed 97 percent, the Hagerstown loam 99.99 percent, and the quartz flour 59 percent of dye. When only 0.075 gram dye was added the quartz flour absorbed 99 percent, leaving but 1 percent in solution. Consequently, it is clear that absorption experiments carried on over a limited range of concentrations may lead to false conclusions regarding the distribution. Further, these experiments emphasize the fact that a soil may hold a relatively large quantity of water-soluble material even in contact with a very dilute aqueous solution.

Quartz Flour, Eosine, Water

Table II gives the data for the distribution of sodium eosine between quartz flour and water. Here the absorptive capacity of the quartz for eosine does not tend to a limiting value, as it does for gentian violet, but the absorption of eosine increases almost proportionally with the quantity of

TABLE II
Quartz Flour and Eosine

Dye added per liter solution	Distribution	
	Dye absorbed per kilo quartz	Dye per liter solution
Grams	Grams	Grams
0.0331	0.009	0.027
0.1000	0.0135	0.091
0.3351	0.084	0.274
1.0000	0.348	0.768
10.0000	4.200	7.200

eosine in solution. The distribution is therefore represented by a rather flat parabolic curve, which bends rather toward the axis of concentration in quartz than toward the axis of concentration in solution as in the cases considered above.

Manure Extract, Soil, Water

Several concentrations of a well fermented and matured manure extract were allowed to stand in contact with soils, with frequent shaking, for two weeks at room temperature. Then the supernatant liquid was poured off, centrifuged, evaporated to dryness, and the organic matter determined by weighing before and after ignition. The quantity of organic matter in the original manure extract solution was determined similarly.

Table III

Soil and manure extract

Organic matter in added extract per liter	Distribution					
	Hagerstown loam		Marshall silt loam		Norfolk sand	
	Organic matter per kilo soil	Organic matter per liter solution	Organic matter per kilo soil	Organic matter per liter solution	Organic matter per kilo soil	Organic matter per liter solution
Grams	Grams	Gram	Gram	Gram	Gram	Grams
0.147	0.056	0.133	—	—	(—)0.129	0.179
0.294	0.364	0.203	—0.109	0.321	(—)0.100	0.319
0.588	0.740	0.403	0.354	0.500	0.077	0.569
1.175	1.180	0.880	0.885	0.954	0.440	1.065

Table III contains data for Hagerstown loam, Marshall silt loam, and Norfolk sand. A correction for the volume of water absorbed on the soil grains was not applied here as it amounts to less than 1 percent, and the data serve to show merely the general trend of the distribution. As there is some organic matter already present in the soil, the absorption appears negative for low concentrations of manure extract, since the organic matter comes out of the soil and increases the total amount present in solution. For Hagerstown loam the maximum absorptive capacity was found, by extrapolation of the distribution curve, to be approximately 1,700 parts per million. This means that with very great concentration of manure in solution, one kilo of this soil would absorb 1.7 grams of this soluble manure from the extract and no more. The data do not admit of calculating the maximum absorptive capacity for the other two soils, but a comparison of the soils on the basis of the highest quantity of manure absorbed by each gives a ratio of 2.7 : 2 : 1, in the order, Hagerstown loam, Marshall silt loam, and Norfolk sand respectively. Here the order of the absorption capacities is the reverse of that found for gentian violet as shown in Table I, where Marshall silt loam had nearly twice the absorptive power found for the Hagerstown loam.

This experiment is important in showing that absorption is dependent as much on the nature of the solute as on that of the absorbent. It further indicates the probable futility of attempting to select empirically a dye with which quantitative measurements might be made to determine the absorptive power of a soil for manures or fertilizers, or to determine its relative crop-producing power.

Selective Absorption

The effect of fine powder or other absorbing media in selectively absorbing the base and leaving the solution acid has been considered in a previous paper,[1] but the distribution of the solute is particularly interesting in this connection. For this purpose Peters'[2] results on the absorption of potassium chloride by a soil have been recalculated for Table IV and Fig. 2, so that they might be compared with the data given above.

The similarity between this curve and the previous curves in Fig. 1 shows that selective absorption proceeds in the same manner as absorption which is not accompanied by a marked chemical reaction.

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[1] Bull. No. 30, p. 60, Bureau of Soils, U. S. Dept. Agr., 1905; see also, Bell and Cameron: Jour. Phys. Chem., 10, 658 (1906).

[2] Landw. Vers.-Stat., 2, 129 (1860).

TABLE IV

The distribution of potassium between soil and solution of potassium chloride, according to Peters

Potassium per kilo soil	Potassium per liter solution
Grams	Grams
1 011	0.0648
1.096	0.0628
1.168	0.0677
1.238	0.0797
1.328	0.089
1.390	0.127
1.453	0.203
1.511	0.361
1.579	0.679
1.610	1.310

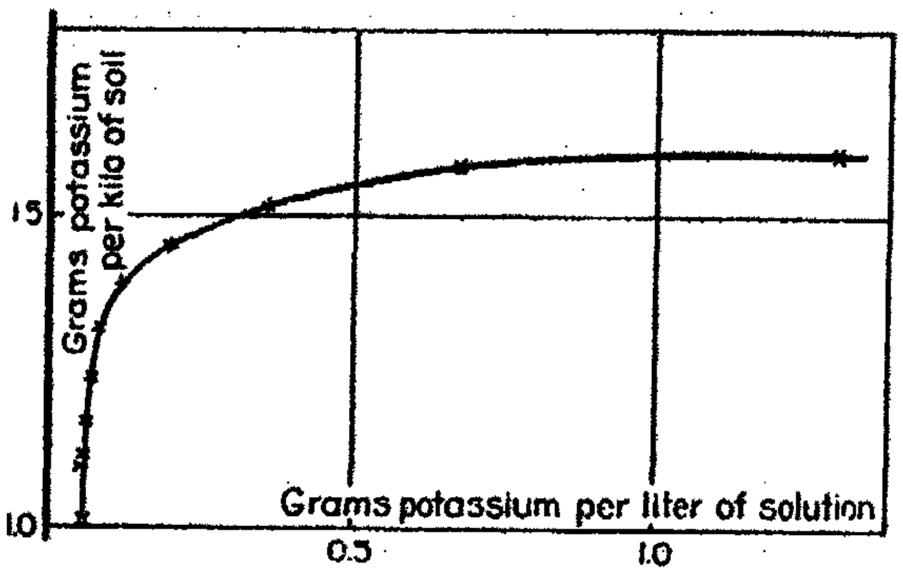

Fig. 2

The magnitude of the absorption effect by which a soil withdraws a salt from solution is well illustrated by these measurements of Peters'. With his most dilute solution, 67 percent of the total potassium added was absorbed; and in the case of his most concentrated solution (originally 16 times as concentrated as the most dilute one), 20 percent of the base was absorbed. But it should also be kept in mind that the *percentage* of solute absorbed is dependent upon the relative mass of solution and solvent, and in the case of a soil in the field the proportion of soil to soil solution is so large that the percentage of solute absorbed must be very great indeed at such concentrations of the soil solution as normally exist in humid areas.

Peters determined also the calcium extracted from the soil by these same solutions which were being studied mainly with respect to the absorption of potassium. He found that the calcium is distributed in a manner entirely analogous to potassium, and that the curve for the distribution of the calcium between soil and water has apparently the same form as that for potassium. This observation indicates that the selective absorption of two solutes or of two radicles may proceed simultaneously but in a very nearly independent manner at least when the concentrations of both are low.

But little of the extant work on absorption is available for such considerations. For example, Lagergren[1] has pointed out that van Bemmelen's work involves such striking chemical changes in many cases that it is out of the question to consider the systems of which he treats as types of "adsorption" phenomenon, and equally of course as typical absorption effects. Nevertheless, some of van Bemmelen's data furnish most important and interesting cases, as, for instance, his results for the distribution of hydrochloric acid (HCl), and potassium chloride (KCl), between stannic oxide and water,[2] which are plotted in Figs. 3 and 4. In Fig. 3 only his values calculated for stannic oxide ($SnO_2.2.2H_2O$) are used. Ordinates are in milligram molecules of hydrogen chloride in 1 gram molecule of water, and abscissas in milligram molecules of hydrogen chloride in 1 gram molecule of stannic oxide. The dotted portion of the curve indicates the probable direction if no solution of stannic oxide in hydrochloric acid had taken place. The curve in reality changes its trend entirely owing to this solution of tin oxide in hydrochloric acid solution, and to the change in the composition of the solution as well as to the consequent decrease in effective absorbent material and surface.

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[1] Bihang till K. Sv. Vet.-Akad. Handl., 24, Afd. II, No. 5 (1898).

[2] Zeit. anorg. Chem., 23, 112 (1900).

Comparing the curves in Figs. 3 and 4, it is seen that the distribution of potassium chloride between hydrated stannic oxide and water is a linear function, but this same absorbing material shows an entirely different distribution curve when hydrochloric acid is used. Thus it will be seen that the same several types of distribution curves are obtained whether the solute be absorbed as a whole or whether there be a selective absorption of some constituent of the solute or mixture of solutes.

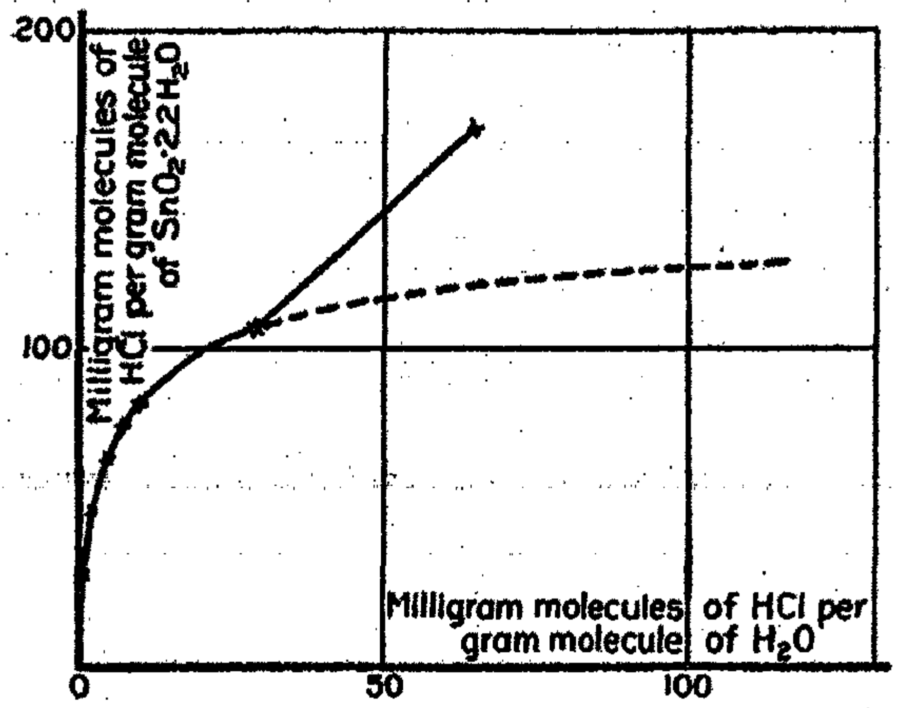

Fig. 3

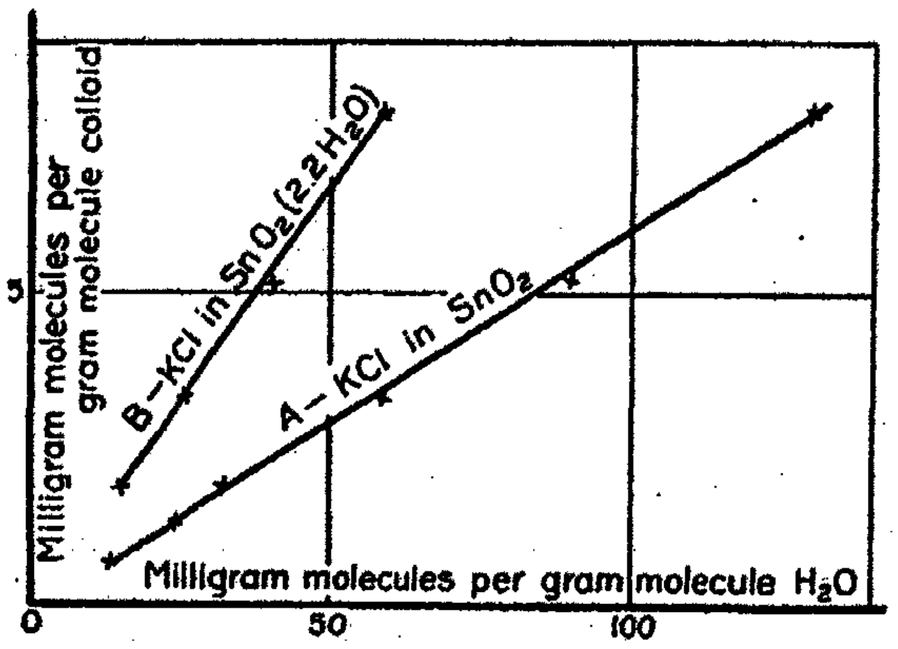

Fig. 4

Distribution Formula

A number of investigators have advanced formulas to express the distribution of a solute between a solvent and an absorbing medium. These expressions have been generally suggested by the apparent analogy to the distribution of the solute between two non-consolute solvents, for which two general equations have been proposed.

If C be the concentration of the solute in one solvent and C_1 the concentration in the other, then, when there is no association of solute in either solvent, the distribution is described by the formula $C/C_1 = K$, but if there be association of solute in either solvent the formula becomes $C''/C_1 = K$; K is a constant for any standard conditions.

Examples of linear distribution between a solid and liquid are known. For instance Gaubert[1] observed it for the absorption of methylene blue by crystals of phthalic acid deposited from solution in the dye, when the solution is cooled; and for the absorption of the same dye by crystals of nitrate of urea. And van Bemmelen[2] has studied an interesting case in the absorption of potassium chloride by stannic oxide, as shown in Fig. 3.

The exponential formula has been found to hold more or less well for a number of cases of absorption of which a few will be cited. Thus Schmidt[3] found it held for the absorption of iodine and several acids by charcoal, but it did not hold for the absorption of picric acid by cellulose or of eosine or malachite green by silk. Küster[4] found such a relation held for the absorption of iodine by starch. Walker and Appleyard[5] studied a case of unusual interest, finding that the distribution of picric acid between water and silk was described by the formula, $\frac{S}{W^{\frac{1}{2.7}}} = 35.5$, where S represented concentration

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[1] Comptes rendus, 142, 936 (1906).

[2] Zeit. anorg. Chem., 23, 113 (1900).

[3] Zeit. phys. Chem., 15, 60 (1894).

[4] Liebig's Ann., 283, 360 (1894).

[5] Jour. Chem. Soc., 69, 1334 (1896).

of the dye in the silk, and W the concentration in water. This would indicate that, in the concentration studied, the molecule of picric acid in the water solution is 2.7 times as large as that represented by the formula $C_6H_2(NO_2)_3OH$, but this is negatived by the cryoscopic measurements of the osmotic pressure, and of the conductivities of aqueous solutions of picric acid.

Biltz[1] has studied several similar cases. An especially interesting one is the absorption of alizarin by ferric oxide, the distribution being described by an exponential formula. But the curve representing it does not go through the origin. That is, the concentration of the solution must be above a certain value before any absorption on the solid could take place. Similar cases, as for instance, in the absorption of phosphates from solution by soils, have been observed in this laboratory.

The data given above for the distribution of a solute between water and soil do not accord well with the equation $C''/C_1 = K$, but with equations of a more complex form. As these complex equations are different for each particular case and are purely empirical they are not given here. A reason for the deviations from the simpler form of the distribution equation was apparent in the marked changes in the state of aggregation or "flocculation"[2] of the soil particles induced by different concentrations of the solute in the aqueous solutions. In the absorption of eosine by quartz, where the distribution curve was very flat and approached a straight line there was no flocculation of the absorbing grains which could be observed readily. But the same quartz flour was decidedly flocculated when absorbing gentian violet and very differently at different concentrations of dye. Moreover, the extent of the flocculation, with increasing amount of dye,

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[1] Ber. d. chem. Ges. Berlin, 37, 1766, 3138 (1904); 38, 2963, 2973, 4143 (1905); Biltz und Utescher: Nachr. K. Ges. Wiss. Göttingen, Math.-Physik. Klasse, 18 (1904); 46, 271 (1905).

[2] Patten: Trans. Am. Electrochem. Soc., 10, 66 (1906).

went through a maximum, so that no simple formula could be expected to hold for the distribution curve.[1] The soils studied showed similar flocculation phenomena.

Conclusions

The foregoing data and considerations lead to the following conclusions:

(1) The distribution of solute between solvent and absorbent, presents, in general, the same characteristics with soils as with other absorbents.

(2) For any series of soils or other absorbents, the order of the absorptive capacities for one solute may be entirely different from the order for another solute.

(3) The distribution of a solute between solvent and absorbent appears to be represented by the formula $C^n/C_1 = K$, where n may be less than, equal to, or greater than unity. Generally, when soils are the absorbents, the change of surface or "flocculation" introduces a modifying factor and the form of the distribution equation becomes more complex.

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[1] In an article which has come to our attention since writing the above, Pelet and Grand (Rev. Gen. Mat. Col., 11, 255 (1907) abstract Jour. Soc. Chem. Ind., 26, 1920 (1907)) describe a curve for silica, methylene-blue and water for which they give the formula $\frac{x}{m} = \beta C^{1/p}$, where x is the quantity of dye absorbed, m the weight of silica, C the end concentration of the dye solution, and β and p are constants.

MOLECULAR ATTRACTION, VII. AN EXAMINATION OF SEVEN ESTERS

BY J. E. MILLS

In previous papers[1] we derived and discussed the equation:

1. $$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant} = \mu'.$$

Here L is the heat of vaporization of a liquid, E_1 is the energy spent in overcoming external pressure, $L - E_1$ is, therefore, the internal heat of vaporization, d and D are the density of liquid and vapor respectively, and the constant we have called μ'.

For a more complete discussion of the ideas underlying this equation, and its limitations, the reader is referred to the second and sixth papers to which references are given above. It is sufficient to repeat here that the equation was deduced upon the assumption that the molecular attraction varied inversely as the square of the distance apart of the molecules. If the equation is finally proved true it will indicate that the molecular attraction varies according to the same law as does the gravitational attraction so far as the variation with the distance is concerned, and will also show that this attraction alone is sufficient to account for, and is a measure of, the cohesion between the molecules of a liquid.

In the second paper above cited, the equation is applied to twenty-one substances, in most cases over a range of temperature extending from near the freezing-point of the liquid nearly to the critical temperature itself, the excellent measurements of Drs. Ramsay and Young, and of Dr. Young, being used. In the fifth paper the equation was applied to ten additional substances, three of these ten being esters which had been measured by Prof. Young and Mr. Thomas. The results obtained from the thirty-one substances previously

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[1] Jour. Phys. Chem., 6, 209 (1902); 8, 383 (1904); 8, 593 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132 (1907).

examined and reported upon have confirmed in the most satisfactory manner the truth of the equation above cited. The present paper deals with seven esters measured by Prof. Young and Mr. Thomas and therefore concludes the examination of the ten esters measured by them. We may add further, that so far as we are aware, the present paper concludes the study of all of the liquids for which the necessary measurements are available.

In the work which follows the heat of vaporization was calculated by using the well-known thermodynamical equation:

2. $$L = \frac{T}{J}\frac{dP}{dT}(V - v) = 0.0_4 31833\, T\frac{dP}{dT}(V - v).$$

The $\frac{dP}{dT}$ was obtained by first calculating the constants for an equation of the form proposed by Biot, *viz.*:

3. $$\log P = A + b\,\alpha^t + c\,\beta^t.$$

The smoothed pressures as observed by Young and Thomas were used for the calculation. If now we let,

4. $$A = 168.775\,(b.\ \log.\ \alpha.\ \alpha^t + c.\ \log\beta.\ \beta^t),\ \text{then,}$$

5. $$\frac{dP}{dT} = 0.031414\ PA,\ \text{and}$$

6. $$L = \frac{P(V - v)T}{10^6}.\ A.$$

For calculating E_1 we used, as in previous papers, the formula,

7. $$E_1 = 0.0_4 31833\ P(V - v).$$

The density (volume) of the liquid up to the critical temperature is in every case obtained from the measurements of Prof. Young and Mr. Thomas[1] as is also the density of the vapor, except at 0° C where it was calculated from the formula,

8. $$D = 0.0_4 16014\frac{Pm}{T}.$$

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[1] Jour. Chem. Soc., 63, 1191 (1893).

The data at the critical temperature was taken from a paper by Dr. Young.[1]

The constants for the Biot formula, equation 3, are given below in Table 1.

The observed vapor pressures, and the calculated vapor pressures making use of the above constants, are given below, Tables 2 to 5 inclusive. We have already shown[2] that Biot's formula does not, and cannot by any recalculation of the constants be made to, fit the vapor pressure curve exactly, in the neighborhood of the critical temperature. As will be seen, the comparison given below is further evidence upon this point, the divergence being even more marked in the case of the esters than with the ordinary substances. Hence the $\frac{dP}{dT}$ and consequently the heat of vaporization calculated with its aid, will both be too small in the neighborhood of the critical temperature. This will make the constant found for equation 1, that is μ', decrease as the critical temperature is approached, a result not wholly, if at all, due to an actual departure of the substance from the law, but merely to the error thus introduced by the Biot formula. Needless to say, were a perfect formula for representing the vapor pressure curve known to us, we would use it, but as the error in the Biot formula does not appear appreciably large until within 20°, or less, of the critical temperature, and elsewhere its behavior seems perfect, we have thought it best to continue the use of the formula. As a check upon the results in the immediate neighborhood of the critical temperature, we have obtained the $\frac{dP}{dT}$ directly from the observations, and also by another method from the theory of Crompton alluded to later in this paper. These results in most cases confirm the belief that the entire divergence near the critical temperature is introduced by the Biot formula. But with the ten esters there seems usually to be a greater divergence than can be

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[1] Phil. Mag. [5], 50, 291 (1900).

[2] Jour. Phys. Chem., 9, 402 (1905).

TABLE I

	Propyl formate	Ethyl acetate	Methyl propionate	Propyl acetate	Ethyl propionate	Methyl butyrate	Methyl isobutyrate
A	2.581860	10.435035	11.274048	—7.999050	—2.285598	12.741658	11.396715
log α . .	0.000774195	$\bar{1}$.99964446	$\bar{1}$.99969907	0.00014984	0.000282082	$\bar{1}$.99974894	$\bar{1}$.99970733
log β . .	$\bar{1}$.99607821	$\bar{1}$.99533526	$\bar{1}$.99547189	$\bar{1}$.9958014	$\bar{1}$.99572535	$\bar{1}$.99543458	$\bar{1}$.99544792
log b . .	0.1328519	0.8560404	0.9012080	1.0566077	0.7564249	0.9875800	0.9148635
b . .	1.357850	—7.178610	—7.965407	11.392200	5.707224	—9.718070	—8.219842
log c . .	0.3732144	0.2720318	0.2940685	0.4510098	0.4493506	0.3932874	0.3206232
c . .	—2.361644	—1.870819	—1.968197	—2.824944	—2.814171	—2.473360	—2.092297
t =	T° — C 10	T° C	T° C	T° C + 10	T° C + 10	T° C + 10	T° C

accounted for as above. We hope during the coming year to be able to investigate the $\frac{dP}{dT}$ at the critical temperature experimentally, and therefore will not give here the detailed data upon this subject.

The calculations involved in all of the tables given in this paper were checked and were carried to that degree of accuracy warranted by the measurements.

We give below the equations for calculating A, and also the detailed results of the calculations, Tables 6 to 12, inclusive.

For propyl formate,

$$A = \text{antilog}\,(\bar{1}.2490105 + 0.000774195\,t) + \text{antilog}\,(0.1940070 - 0.00392179\,t),\ t = T^\circ\,C - 10.$$

For ethyl acetate,

$$A = \text{antilog}\,(\bar{1}.6342371 - 0.00035554\,t) + \text{antilog}\,(0.1681675 - 0.00466474\,t),\ t = T^\circ\,C.$$

For methyl propionate,

$$A = \text{antilog}\,(\bar{1}.6069817 - 0.00030093\,t) + \text{antilog}\,(0.1772937 - 0.00452811\,t),\ t = T^\circ\,C.$$

For propyl acetate,

$$A = \text{antilog}\,(\bar{1}.4610421 + 0.00014984\,t) + \text{antilog}\,(0.2594356 - 0.00419859\,t),\ t = T^\circ\,C.$$

For ethyl propionate,

$$A = \text{antilog}\,(\bar{1}.4369301 + 0.000282082\,t) + \text{antilog}\,(0.2648128 - 0.00427465\,t),\ t = T^\circ\,C.$$

For methyl butyrate,

$$A = \text{antilog}\,(\bar{1}.6121551 - 0.00025106\,t) + \text{antilog}\,(0.2344221 - 0.00456542\,t),\ t = T^\circ\,C.$$

For methyl isobutyrate,

$$A = \text{antilog}\,(\bar{1}.6085499 - 0.00029267\,t) + \text{antilog}\,(0.2061414 - 0.00455208\,t),\ t = T^\circ\,C.$$

TABLE 2

Temperature	Propyl formate		Δ	Ethyl acetate		Δ
	Pressure calculated	Pressure observed		Pressure calculated	Pressure observed	
—20° C	—	—	—	6.59	6.55	0.04
—10	11.56	11.40	0.16	13.02	12.95	0.07
0	21.42	21.40	0.02	24.30	24.3	0.0
10	37.85	37.85	0.0	43.12	42.7	0.42
20	64.03	63.9	0.13	73.09	72.8	0.29
30	104.13	104.1	0.03	118.88	118.7	0.18
40	163.34	163.6	— 0.26	186.33	186.2	0.13
50	247.97	249.4	— 1.43	282.42	282.2	0.22
60	365.37	364.9	0.47	415.37	415.4	— 0.03
70	523.9	523.9	0.0	594.53	596.3	— 1.77
80	732.9	734.5	— 1.6	830.37	832.7	— 2.33
90	1002.5	1004	— 1.5	1134.4	1130	4.4
100	1343.6	1345	— 1.4	1519.2	1517	2.2
110	1767.7	1770	— 2.3	1998.1	2001.5	— 3.4
120	2286.9	2288	— 1.1	2585.7	2586	— 0.3
130	2914.0	2915	— 1.0	3297.0	3298	— 1.0
140	3662.1	3676	—13.9	4148.6	4166	— 17.4
150	4545.4	4558	—12.6	5157.5	5168	— 10.5
160	5578.4	5605	—26.6	6342.4	6369	— 26.6
170	6777.1	6797	—19.9	7722.6	7742	— 19.4
180	8158.3	8177	—18.7	9319.1	9318	1.1
190	9740.9	9734	6.9	11154	11125	29
200	11545	11560	—15	13253	13200	53
210	13594	13575	19	15539	15565	74
220	15912	15870	42	18343	18255	88
230	18529	18465	64	21393	21270	123
240	21477	21425	52	24825	24807.5	17.5
245	—	—	—	26693	26740	— 47
247	—	—	—	27471	27535	— 64
249	—	—	—	28266	28370	—104
250	24792	24693	99	28671	28800	—129
250.1	—	—	—	28711	28877.5	—166.5
260	28519	28520	— 1	—	—	—
264.85	30488	30553	—65	—	—	—

TABLE 3

Temperature	Methyl propionate		Δ	Propyl acetate[1]		Δ
	Pressure calculated	Pressure observed		Pressure calculated	Pressure observed	
—20° C	5.93	5.65	0.28	—	—	—
—10	11.72	11.55	0.17	3.70	3.60	0.1
0	21.90	21.9	0.0	7.38	7.4	—0.02
10	38.93	38.85	0.08	13.92	13.9	0.02
20	66.15	66.2	—0.05	25.00	25.1	—0.1
30	107.89	107.8	0.09	42.71	42.7	0.01
40	169.58	169.3	0.28	70.67	70.8	—0.13
50	257.8	256.7	1.1	112.2	112.2	0.0
60	380.3	380,3	0.0	172.1	171.8	0.3
70	545.94	548.0	—2.06	255.9	257.3	—1.4
80	764.65	771.0	—6.35	370.7	372.8	—2.1
90	1047.4	1045	2.4	523.2	524.8	—1.6
100	1406.2	1406	0.2	721.9	723.6	—1.7
110	1853.8	1854	—0.2	975.5	976	—0.5
120	2404.0	2406	—2.0	1294	1293	1
130	3071.2	3071	0.2	1687	1685	2
140	3871.1	3888	—16.9	2166	2171	—5
150	4819.6	4830	—10.4	2743	2747	—4
160	5934.5	5957	—22.5	3432	3441	—9
170	7233.7	7245	—11.3	4240	4269	—29
180	8737.0	8737	0.0	5190	5189	1
190	10465	10420	45	6287	6275	12
200	12441	12380	61	7556	7543	13
210	14687	14625	62	9011	8973	38
220	17231	17160	71	10673	10620	53
230	20101	20000	101	12563	12505	58
240	23325	23325	0.0	14704	14675	29
245	25080	25115	—35	—	—	—
250	26937	26997.5	—60.5	17123	17090	33
253	28102	28205	—103	—	—	—
255	28900	29055	—155	—	—	—
256	29306	29445	—139	—	—	—
257.4	29882	30032.5	—150.5	—	—	—
260	—	—	—	19849	19855	—6
266	—	—	—	21645	21685	—40
270	—	—	—	22913	22980	—67
273	—	—	—	23903	24060	—157
275	—	—	—	24584	24750	—166
276.2	—	—	—	24998	25227.5	—229.5

TABLE 4

Temperature	Ethyl propionate		Δ	Methyl butyrate		Δ
	Pressure calculated	Pressure observed		Pressure calculated	Pressure observed	
—10° C	4.05	4.05	0.0	3.55	3.55	0.0
0	8.10	8.30	— 0.2	7.13	7.3	— 0.17
10	15.31	15.55	— 0.24	13.52	13.8	— 0.28
20	27.50	27.75	— 0.25	24.34	24.55	— 0.21
30	47.16	47.75	— 0.59	41.82	41.95	— 0.13
40	77.58	77.9	— 0.32	68.90	69.2	— 0.30
50	122.8	123.0	— 0.2	109.28	109.65	— 0.37
60	188.0	188.0	0.0	167.5	167.5	0.0
70	279.0	279.9	— 0.9	248.9	250.3	— 1.4
80	402.5	403.6	— 1.1	359.7	361.4	— 1.7
90	566.2	569.5	— 3.3	507.0	507.0	0.0
100	778.4	785.0	— 6.6	698.4	700.7	— 2.3
110	1048	1048	0.0	942.6	941	1.6
120	1386	1386	0.0	1249	1248	1
130	1801	1801	0.0	1627	1627	0.0
140	2305	2316	— 11	2088	2100	— 12
150	2911	2920	— 9	2643	2657	— 14
160	3630	3657	— 27	3304	3328	— 24
170	4476	4505	— 29	4085	4111	— 26
180	5465	5487	— 22	4998	5020	— 22
190	6611	6619	— 8	6061	6063	— 2
200	7934	7934	0.0	7287	7287	0.0
210	9452	9456	— 4	8696	8684	12
220	11186	11195	— 9	10306	10285	21
230	13161	13145	16	12137	12105	32
240	15402	15425	— 23	14213	14230	— 17
250	17941	17970	— 29	16557	16550	7
260	20811	20825	— 14	19197	19185	12
265	22381	22400	— 19	—	—	—
268	23370	23415	— 45	—	—	—
270	24050	24105	— 55	22161	22160	1
271.5	24570	24660	— 90	—	—	—
272.9	25064	25217.5	—153	—	—	—
275	—	—	—	23774	23795	— 21
278	—	—	—	24787	24820	— 33
280	—	—	—	25482	25560	— 78
281.3	—	—	—	25942	26055	—113

TABLE 5

Temperature	Methyl isobutyrate		Δ
	Pressure calculated	Pressure observed	
—10° C.	6.28	6.22	0.06
0	12.15	12.15	0.0
10	22.28	22.4	— 0.12
20	38.93	38.9	0.03
30	65.10	65.45	— 0.35
40	104.6	104.7	— 0.1
50	162.3	162.0	0.3
60	243.8	243.8	0.0
70	355.7	355.2	0.5
80	505.5	505.0	0.5
90	701.5	707.0	— 5.5
100	952.8	952	0.8
110	1269	1270	— 1.0
120	1662	1662	0.0
130	2141.6	2142.5	— 0.9
140	2720	2733	— 13
150	3411	3418	— 7
160	4226	4248	— 22
170	5180	5196	— 16
180	6291	6291	0.0
190	7571	7557	14
200	9040	9011	29
210	10715	10690	25
220	12617	12570	47
230	14768	14700	— 2
240	17190	17190	0.0
250	19910	19925	— 15
256	21695	21740	— 45
260	22954	23030	— 76
263	23935	24080	—145
265	24608	24780	—172
266.5	25121	25345	—224
267.55	25486	25740	—254

TABLE 6

Propyl formate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P. \Delta V. T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0° C	21.42	0.9287	$0.0_3 1106$	52.85	1.88519	99.63	6.16	93.47	0.9276	100.8
80	732.91	0.8341	0.003077	83.76	1.03177	86.42	7.55	78.87	0.7959	99.1
90	1002.5	0.8214	0.004115	87.99	0.96366	84.79	7.72	77.07	0.7763	99.3
100	1343.6	0.8080	0.005435	91.61	0.90180	82.61	7.82	74.79	0.7556	99.0
110	1767.7	0.7947	0.007018	95.60	0.84567	80.85	7.94	72.91	0.7348	99.2
120	2286.9	0.7811	0.008969	99.04	0.79477	78.71	8.02	70.69	0.7131	99.1
130	2914.0	0.7670	0.01135	101.92	0.74866	76.30	8.05	68.25	0.6907	98.8
140	3662.1	0.7523	0.01420	104.45	0.70694	73.84	8.05	65.79	0.6673	98.6
150	4545.4	0.7369	0.01767	106.21	0.66925	71.08	7.99	63.09	0.6427	98.2
160	5578.4	0.7209	0.02179	107.51	0.63521	68.29	7.90	60.39	0.6174	97.8
170	6777.1	0.7045	0.02667	108.31	0.60455	65.48	7.78	57.70	0.5910	97.6
180	8158.3	0.6873	0.03236	108.85	0.57698	62.80	7.65	55.15	0.5638	97.8
190	9740.9	0.6691	0.03891	109.17	0.55222	60.28	7.51	52.77	0.5357	98.5
200	11545	0.6487	0.04717	107.37	0.53005	56.91	7.23	49.68	0.5044	98.5
210	13594	0.6259	0.05698	104.71	0.51026	53.43	6.90	46.53	0.4729	98.4
220	15912	0.6024	0.06897	100.72	0.49264	49.62	6.50	43.12	0.4345	99.2
230	18529	0.5757	0.08403	94.71	0.47701	45.18	5.99	39.19	0.3939	99.5
240	21477	0.5438	0.1045	85.16	0.46323	39.45	5.28	34.17	0.3452	99.0
250	24792	0.5025	0.1340	70.91	0.45113	31.99	4.32	27.67	0.2833	97.6
260	28519	0.4404	0.1848	47.72	0.44056	21.02	2.85	18.17	0.1912	95.0*

TABLE 7

Ethyl acetate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P.\Delta V.T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d}-\sqrt[3]{D}$	$\frac{L-E_1}{\sqrt[3]{d}-\sqrt[3]{D}}$
0° C	24.30	0.9244	$0.0_3 1255$	52.85	1.90364	100.61	6.16	94.45	0.9240	102.2
80	830.37	0.8245	0.003509	83.19	1.02717	85.45	7.50	77.95	0.7857	99.2
90	1134.4	0.8112	0.004673	87.62	0.96036	84.15	7.68	76.47	0.7654	99.9
100	1519.2	0.7972	0.006173	91.05	0.90005	81.95	7.77	74.18	0.7438	99.7
110	1998.1	0.7831	0.008000	94.68	0.84556	80.06	7.87	72.19	0.7217	100.0
120	2585.7	0.7683	0.01031	97.26	0.79634	77.45	7.88	69.57	0.6982	99.6
130	3297.0	0.7533	0.01312	99.48	0.75182	74.79	7.86	66.93	0.6740	99.2
140	4148.6	0.7378	0.01650	101.52	0.71154	72.24	7.82	64.42	0.6490	99.2
150	5157.5	0.7210	0.02062	102.79	0.67505	69.39	7.73	61.66	0.6225	99.0
160	6342.4	0.7033	0.02577	102.66	0.64200	65.91	7.55	58.36	0.5939	98.2
170	7722.6	0.6848	0.03165	103.13	0.61203	63.12	7.41	55.71	0.5651	98.6
180	9319.1	0.6653	0.03883	102.38	0.58481	59.87	7.19	52.68	0.5344	98.6
190	11154	0.6441	0.04751	100.70	0.56008	56.40	6.92	49.48	0.5014	98.7
200	13253	0.6210	0.05797	98.05	0.53758	52.71	6.60	46.11	0.4662	98.9
210	15639	0.5944	0.07128	93.27	0.51709	48.23	6.15	42.08	0.4262	98.7
220	18343	0.5648	0.08905	85.53	0.49841	42.63	5.52	37.11	0.3800	97.7*
230	21393	0.5281	0.1131	74.89	0.48136	36.05	4.73	31.32	0.3247	96.5*
240	24825	0.4778	0.1499	58.33	0.46577	27.17	3.62	23.55	0.2506	94.0**
245	26693	0.4401	0.1802	45.35	0.45847	20.79	2.79	18.00	0.1959	91.9**
247	27471	0.4195	0.1996	37.57	0.45565	17.12	2.30	14.82	0.1642	90.3**
249	28266	0.3893	0.2288	26.56	0.45286	12.03	1.62	10.41	0.1186	87.8**

TABLE 8

Methyl propionate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P. \Delta V. T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0° C	21.90	0.9387	$0.0_3 1131$	52.85	1.90872	100.87	6.16	94.71	0.9687	97.77
80	764.65	0.8408	0.003190	84.29	1.03594	87.32	7.60	79.72	0.7966	100.08
90	1047.4	0.8273	0.004301	87.96	0.96862	85.20	7.71	77.49	0.7762	99.83
100	1406.2	0.8137	0.005682	91.68	0.90772	83.22	7.82	75.40	0.7576	99.52
110	1853.8	0.7996	0.007407	94.94	0.85262	80.95	7.89	73.06	0.7333	99.63
120	2404.0	0.7852	0.009569	97.50	0.80273	78.27	7.90	70.37	0.7103	99.07
130	3071.2	0.7705	0.01215	100.26	0.75754	75.95	7.92	68.03	0.6869	99.04
140	3871.1	0.7553	0.01529	102.46	0.71659	73.42	7.90	65.52	0.6625	98.90
150	4819.6	0.7390	0.01905	104.27	0.67945	70.85	7.85	63.00	0.6370	98.90
160	5934.5	0.7221	0.02353	105.65	0.64576	68.22	7.77	60.45	0.6106	99.06
170	7233.7	0.7045	0.02907	105.69	0.61518	65.02	7.59	57.43	0.5823	98.63
180	8737.0	0.6856	0.03552	105.64	0.58739	62.05	7.42	54.63	0.5531	98.77
190	10465	0.6657	0.04320	104.87	0.56212	58.95	7.21	51.74	0.5223	99.06
200	12441	0.6445	0.05236	103.25	0.53914	55.67	6.95	48.72	0.4897	99.49
210	14687	0.6207	0.06390	99.60	0.51820	51.61	6.56	45.05	0.4532	99.40
220	17231	0.5938	0.07812	94.45	0.49910	47.14	6.10	41.04	0.4130	99.37
230	20101	0.5635	0.09662	86.72	0.48168	41.77	5.49	36.28	0.3671	98.83
240	23325	0.5220	0.1236	73.87	0.46576	34.41	4.58	29.83	0.3071	97.13
245	25080	0.4976	0.1418	65.47	0.45831	30.00	4.02	25.98	0.2709	95.90*
250	26937	0.4655	0.1675	53.87	0.45119	24.30	3.28	21.02	0.2238	93.92*
253	28102	0.4401	0.1890	44.61	0.44708	19.94	2.70	17.24	0.1868	92.29**
255	28900	0.4151	0.2118	35.26	0.44439	15.67	2.12	13.55	0.1499	90.39**
256	29306	0.3982	0.2294	28.67	0.44305	12.70	1.72	10.98	0.1235	88.91**

TABLE 9

Propyl acetate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P.\Delta V.T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0° C	7.38	0.9102	$0.0_4 4419$	45.59	2.10644	96.03	5.32	90.71	0.9338	97.14*
100	721.9	0.7957	0.003322	80.70	0.99040	79.92	6.89	73.03	0.7775	93.93
110	975.5	0.7830	0.004405	84.32	0.92775	78.23	7.01	71.22	0.7578	93.98
120	1294	0.7702	0.005764	87.56	0.87096	76.26	7.09	69.17	0.7373	93.82
130	1687	0.7571	0.007407	90.87	0.81951	74.47	7.17	67.30	0.7165	93.93
140	2166	0.7435	0.009434	93.59	0.77290	72.34	7.20	65.14	0.6946	93.78
150	2743	0.7297	0.01195	95.51	0.73068	69.79	7.18	62.61	0.6717	93.21
160	3432	0.7149	0.01488	97.77	0.69246	67.70	7.18	60.52	0.6482	93.35
170	4240	0.6997	0.01842	99.32	0.65786	65.34	7.14	58.20	0.6237	93.31
180	5190	0.6835	0.02262	100.47	0.62654	62.94	7.06	55.88	0.5981	93.43
190	6287	0.6667	0.02778	100.42	0.59822	60.07	6.90	53.17	0.5707	93.17
200	7556	0.6488	0.03390	99.94	0.57260	57.23	6.72	50.51	0.5421	93.17
210	9011	0.6301	0.04115	98.82	0.54945	54.29	6.51	47.78	0.5121	93.30
220	10673	0.6087	0.05025	96.08	0.52853	50.78	6.20	44.58	0.4785	93.16
230	12563	0.5855	0.06154	91.85	0.50965	46.81	5.81	41.00	0.4418	92.80
240	14704	0.5586	0.07576	86.08	0.49260	42.40	5.34	37.06	0.4005	92.53
250	17123	0.5289	0.09390	78.45	0.47724	37.44	4.77	32.67	0.3542	92.23
260	19849	0.4908	0.1205	66.25	0.46340	30.70	3.96	26.74	0.2949	90.67
266	21645	0.4611	0.1445	55.40	0.45575	25.25	3.27	21.98	0.2478	88.70*
270	22913	0.4333	0.1661	45.61	0.45092	20.57	2.67	17.90	0.2070	86.47**
273	23903	0.4063	0.1912	36.14	0.44743	16.17	2.11	14.06	0.1646	85.42**
275	24584	0.3769	0.2169	26.36	0.44517	11.73	1.53	10.20	0.1215	83.95**

TABLE 10

Ethyl propionate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P.\Delta V.T}{10^6}$	A	Latent heat	E_1	$L-E_1$	$\sqrt[3]{d}-\sqrt[3]{D}$	$\frac{L-E_1}{\sqrt[3]{d}-\sqrt[3]{D}}$
0° C	8.10	0.9142	0.0_44850	45.59	2.11346	96.35	5.32	91.03	0.9340	97.46**
100	778.4	0.7951	0.003571	80.90	0.97945	79.24	6.90	72.34	0.7736	93.50
110	1048	0.7823	0.004739	84.15	0.91690	77.16	6.99	70.17	0.7534	93.14
120	1386	0.7692	0.006192	87.25	0.86040	75.07	7.07	68.00	0.7326	92.82
130	1801	0.7548	0.008000	89.79	0.80939	72.67	7.09	65.58	0.7105	92.30
140	2305	0.7413	0.01021	91.98	0.76336	70.21	7.09	63.12	0.6880	91.74
150	2911	0.7267	0.01292	93.56	0.72182	67.53	7.04	60.49	0.6644	91.04
160	3630	0.7115	0.01615	95.09	0.68438	65.08	6.99	58.09	0.6399	90.78
170	4476	0.6958	0.02008	95.95	0.65065	62.43	6.89	55.54	0.6143	90.41
180	5465	0.6795	0.02469	96.53	0.62028	59.88	6.78	53.10	0.5879	90.32
190	6611	0.6625	0.03012	97.05	0.59295	57.55	6.67	50.88	0.5607	90.74
200	7934	0.6443	0.03676	96.25	0.56839	54.71	6.47	48.24	0.5312	90.81
210	9452	0.6243	0.04464	94.96	0.54633	51.88	6.26	45.62	0.5000	91.24
220	11186	0.6027	0.05435	92.29	0.52654	48.59	5.96	42.63	0.4659	91.50
230	13161	0.5784	0.06667	87.82	0.50882	44.68	5.56	39.12	0.4277	91.47
240	15402	0.5501	0.08230	81.62	0.49295	40.23	5.06	35.17	0.3844	91.49
250	17941	0.5181	0.1030	73.01	0.47879	34.96	4.44	30.52	0.3344	91.27
260	20811	0.4744	0.1337	59.53	0.46617	27.75	3.56	24.19	0.2685	90.10
265	22381	0.4459	0.1562	50.08	0.46038	23.06	2.96	20.10	0.2254	89.17*
268	23370	0.4227	0.1751	42.27	0.45707	19.32	2.49	16.83	0.1910	88.11**
270	24050	0.4018	0.1957	34.22	0.45493	15.57	2.01	13.56	0.1573	86.20**

TABLE II

Methyl butyrate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P.\Delta V.T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0° C	7.13	0.9200	$0.0_4 4269$	45.59	2.12503	96.87	5.32	91.55	0.9376	97.64**
110	942.6	0.7945	0.004386	81.88	0.92397	75.66	6.80	68.86	0.7625	90.31
120	1249	0.7816	0.005682	85.71	0.86790	74.39	6.94	67.45	0.7427	90.81
130	1627	0.7685	0.007299	88.94	0.81721	72.68	7.02	65.66	0.7220	90.94
140	2088	0.7551	0.009302	91.56	0.77137	70.63	7.06	63.57	0.7003	90.78
150	2643	0.7415	0.01166	94.46	0.72989	68.95	7.11	61.84	0.6783	91.17
160	3304	0.7270	0.01451	96.56	0.69236	66.85	7.10	59.75	0.6553	91.18
170	4085	0.7122	0.01799	98.08	0.65837	64.57	7.05	57.52	0.6310	91.16
180	4998	0.6964	0.02208	99.30	0.62756	62.32	6.98	55.34	0.6059	91.33
190	6061	0.6800	0.02695	100.01	0.59959	59.96	6.87	53.09	0.5796	91.60
200	7287	0.6633	0.03268	100.28	0.57428	57.59	6.74	50.85	0.5524	92.05
210	8696	0.6448	0.03968	99.35	0.55127	54.77	6.55	48.22	0.5228	92.23
220	10306	0.6251	0.04831	97.02	0.53036	51.45	6.26	45.19	0.4908	92.07
230	12137	0.6018	0.05848	94.26	0.51133	48.20	5.96	42.24	0.4561	92.61
240	14213	0.5773	0.07143	89.46	0.49400	44.19	5.55	38.64	0.4178	92.49
250	16557	0.5505	0.08696	83.84	0.47821	40.09	5.10	34.99	0.3766	92.91
260	19197	0.5166	0.1091	74.04	0.46381	34.34	4.42	29.92	0.3246	92.18
270	22161	0.4721	0.1416	59.46	0.45065	26.79	3.48	23.31	0.2575	90.52
275	23774	0.4386	0.1689	47.41	0.44449	21.07	2.75	18.32	0.2070	88.50*
278	24787	0.4100	0.1942	37.01	0.44094	16.32	2.14	14.18	0.1638	86.57**
280	25482	0.3812	0.2268	25.18	0.43861	11.04	1.45	9.59	0.1153	83.18**

TABLE 12

Methyl isobutyrate

Temperature	Pressure	Density of liquid	Density of vapor	$\frac{P.\Delta V.T}{10^6}$	A	Latent heat	E_1	$L - E_1$	$\sqrt[3]{d} - \sqrt[3]{D}$	$\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$
0° C	12.15	0.9113	$0.0_4 7275$	45.59	2.01348	91.78	5.32	86.46	0.9277	93.19**
90	701.5	0.8069	0.003367	75.32	1.00796	75.92	6.61	69.31	0.7811	88.73
100	952.8	0.7945	0.004474	78.96	0.94311	74.47	6.74	67.73	0.7614	88.95
110	1269	0.7815	0.005882	81.92	0.88450	72.46	6.81	65.65	0.7406	88.63
120	1662	0.7680	0.007634	84.65	0.83146	70.38	6.86	63.52	0.7189	88.35
130	2142	0.7539	0.009524	89.51	0.78347	70.13	7.07	63.06	0.6981	90.33*
140	2720	0.7396	0.01227	90.03	0.74003	66.62	6.93	59.69	0.6737	88.60
150	3411	0.7248	0.01536	91.96	0.70067	64.43	6.92	57.51	0.6497	88.52
160	4226	0.7095	0.01899	93.74	0.66499	62.34	6.89	55.45	0.6251	88.70
170	5180	0.6933	0.02342	94.67	0.63264	59.89	6.80	53.09	0.5990	88.63
180	6291	0.6767	0.02865	95.22	0.60329	57.44	6.69	50.75	0.5719	88.74
190	7571	0.6593	0.03490	95.09	0.57663	54.83	6.54	48.29	0.5436	88.83
200	9040	0.6411	0.04228	94.48	0.55240	52.19	6.36	45.83	0.5139	89.18
210	10715	0.6200	0.05141	92.30	0.53035	48.95	6.08	42.87	0.4809	89.14
220	12617	0.5961	0.06289	88.45	0.51029	45.13	5.71	39.42	0.4439	88.80
230	14768	0.5690	0.07722	83.14	0.49200	40.91	5.26	35.65	0.4029	88.48
240	17190	0.5386	0.09615	75.31	0.47530	35.79	4.67	31.12	0.3555	87.54
250	19910	0.5021	0.1218	64.75	0.46005	29.79	3.94	25.85	0.2991	86.42
256	21695	0.4735	0.1437	55.64	0.45154	25.12	3.34	21.78	0.2556	85.21*
260	22954	0.4495	0.1623	48.18	0.44611	21.49	2.87	18.62	0.2205	84.45*
263	23935	0.4258	0.1838	39.64	0.44216	17.53	2.35	15.18	0.1837	82.63**
265	24608	0.4036	0.2033	32.33	0.43958	14.21	1.91	12.30	0.1510	81.46**
266.5	25121	0.3790	0.2268	24.01	0.43768	10.51	1.42	9.09	0.1139	79.80**

The mean value for μ', which we have adopted for the different esters, is given at the top of Table 13. The average value of the uncrossed results is shown at the bottom of the table. In the summary shown in this table the results given by the three esters previously examined[1] are also shown in order that the behavior of the ten esters may be seen at a glance.

We have already critically discussed[2] the extent to which errors of observation occurring in the various measurements used will affect the value of the constant given by the ratio, $\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}}$. From that discussion, we concluded, that since the errors of measurement were always compounded and were often multiplied in their proportionate effect upon the constant, that a divergence from the mean values of the constant of less than 2 percent could be regarded as within the limit of error of observation, even when using measurements that had been most carefully carried out. In the tables all values that differ from these mean values by more than 2 percent are marked with an asterisk. All values that differ by more than 5 percent with a double asterisk.

Examining the results it will be noted that always there is a divergence from the mean value—the results being too low—as the critical temperature is approached. We have already recalled, in this paper, the fact previously established, that this was due largely, if not wholly, to an error introduced by using the Biot formula from which to obtain the $\frac{dP}{dT}$. There are also four substances which show a considerable divergence at 0° C. While we are quite unable to explain that divergence, yet we would call attention to the fact that the density of the vapor used at that temperature was calculated, assuming the gas laws to hold. Ordinarily we would have expected them to hold, but as Lord Rayleigh has pointed out within recent years, it is quite possible that the gas laws

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[1] Jour. Phys. Chem 10, 1 (1906).

[2] Ibid., 8, 392, etc. (1904).

TABLE 13

Temperature	Methyl formate	Ethyl formate	Methyl acetate	Propyl formate	Ethyl acetate	Methyl propionate	Propyl acetate	Ethyl propionate	Methyl butyrate	Methyl isobutyrate
Mean value....	121.5	107.2	109.0	99.0	100.2	98.20	92.52	91.90	91.55	88.0
0° C	123.9	108.8	110.7	100.8	102.2	97.8	97.1*	97.5**	97.6**	93.2**
30	125.6*	—	—	—	—	—	—	—	—	—
40	124.6*	—	—	—	—	—	—	—	—	—
50	122.5	—	—	—	—	—	—	—	—	—
60	121.2	108.8	110.8	—	—	—	—	—	—	—
70	120.5	108.3	110.8	—	—	—	—	—	—	—
80	119.1	108.4	110.5	99.1	99.2	100.1	—	—	—	—
90	119.2	108.2	110.0	99.3	99.9	99.8	—	—	—	88.7
100	119.9	107.5	109.8	99.0	99.7	99.5	93.9	93.5	—	88.9
110	120.0	107.3	109.4	99.2	100.0	99.6	94.0	93.1	90.3	88.6
120	120.2	107.2	109.1	99.1	99.6	99.1	93.8	92.8	90.8	88.3
130	119.8	107.4	109.5	98.8	99.2	99.0	93.9	92.3	90.9	90.3*
140	119.8	107.3	109.6	98.6	99.2	98.9	93.8	91.7	90.8	88.6
150	119.7	106.5	109.9	98.2	99.0	98.9	93.2	91.0	91.2	88.5
160	119.2	106.5	109.8	97.8	98.2	99.1	93.3	90.8	91.2	88.7
170	119.1	106.0	109.5	97.6	98.6	98.6	93.3	90.4	91.2	88.6
180	118.1*	106.4	108.8	97.8	98.6	98.8	93.4	90.3	91.3	88.7
190	116.4*	106.0	108.5	98.5	98.7	99.1	93.2	90.7	91.6	88.8
200	113.3**	105.1	108.2	98.5	98.9	99.5	93.2	90.8	92.0	89.2
210	106.6**	103.8*	107.0	98.4	98.7	99.4	93.3	91.2	92.2	89.1
220	—	101.3**	105.0*	99.2	97.7*	99.4	93.2	91.5	92.1	88.8
230	—	97.6**	100.4**	99.5	96.5*	98.8	92.8	91.5	92.6	88.5
240	—	—	—	99.0	94.0**	97.1	92.5	91.5	92.5	87.5
250	—	—	—	97.6	—	93.9*	92.2	91.3	92.9	86.4
260	—	—	—	95.0*	—	—	90.7	90.1	92.2	84.4*
270	—	—	—	—	—	—	86.5**	86.2**	90.5	—
280	—	—	—	—	—	—	—	—	83.2**	—
Critical temp.	214.0°	235.3°	233.7°	264.85°	250.1°	257.4°	276.2°	272.9°	281.3°	267.55°
Average value	120.29	107.23	109.52	98.74	99.31	99.03	93.16	91.45	91.55	88.51

may not hold always, even at low temperatures and pressures. We hope to make these divergences the subject of investigation in the laboratory later, and in the meanwhile, since a calculated factor does enter into the result, we would not consider the divergence of serious moment. Excepting these divergences at 0° C, therefore, because of uncertain data, and those near the critical temperature for reasons given, there are only three results throughout the entire series of measurements of esters that differ from the chosen mean value by more than 2 percent. Comment is almost unnecessary. Such a result could not possibly happen unless the equation represented the facts with the greatest accuracy, and assuming its accuracy, the fact that there are only there divergences of more than 2 percent among 163 tests, each test involving a measurement of four different quantities, speaks in the highest degree for the wonderful skill and accuracy of the experimenters, Professor Young and Mr. Thomas, for the errors introduced by the measurements are, as we have in previous papers carefully pointed out, not only compounded but in certain portions of the temperature scale greatly multiplied proportionately in their effect upon the constant by the method of calculation. The service which Professor Young and his co-workers have rendered to science by such a series of measurements, carried out for thirty-one substances, is simply incalculable, and it gives me the greatest pleasure not only to express my own indebtedness to their work, but to hope that their work will meet with that universal recognition and praise which is its due.

The substantial accuracy of the equation can be again illustrated, and its meaning emphasized, by solving the equation for L thus giving,

$$9. \qquad L = \mu' (\sqrt[3]{d} - \sqrt[3]{D}) + E_1.$$

The values of μ' used in calculating L from this equation are the "average" values given at the bottom of Table 13 above. The results of this equation are given in Tables 14 to 20 inclusive, where they are compared with the heats of vaporization calculated thermodynamically. We have marked all divergences of more than one calorie between the two sets of values with an asterisk. It is clearly apparent that the theory proposed does adequately account for the heat of vaporization.

In previous papers we have already had much to say of a theory by Mr. H. Crompton and have given a considerable amount of investigation to his equation for calculating the heat of vaporization. His equation reads:

$$10. \qquad L = 2\,R\,T \log_e \frac{d}{D} = \frac{9.154\,T}{m} \log_{10} \frac{d}{D} \text{ cals.}$$

We have extended the investigation of this equation to the seven esters examined in this paper and give the results likewise in Tables 14 to 20, under the heading "Crompton," for comparison with the heats of vaporization as calculated by equations 2 and 9. It will be seen that the conclusion previously drawn regarding the equation of Mr. Crompton is further confirmed, *viz.*, at the lowest temperatures, where the vapor pressure is small, the results obtained from his equation are uniformly too high. But at higher temperatures, with increasing pressure, the results become more nearly correct, and near the critical temperature we believe them to be practically correct.

It will be noted that usually just as the critical temperature is approached the results from Crompton's equation more nearly agree with the values from equation 9 than with the values from equation 2, a fact due to the faulty Biot formula involved in the results from equation 2, as already pointed out. We would here repeat our opinion that this theory and equation of Mr. Crompton's is important, and deserving of further recognition and study. In spite of our work upon the equation we are yet quite at a loss to account for the too high values obtained from it at low vapor pressures.

TABLE 14
Propyl formate

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C	99.63	97.75*	111.35
80	86.42	86.14	89.28
100	82.61	82.43	84.22
120	78.71	78.43	79.25
140	73.84	73.94	74.01
160	68.29	68.86	68.41
180	62.80	63.32	62.48
200	56.91	57.03	55.97
220	49.62	49.40	48.23
240	39.45	39.36	38.20
250	31.99	32.29	31.20
260	21.02	21.73	20.89
264.85	0.0	0.0	0.0

TABLE 15
Ethyl acetate

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C	100.61	97.92*	109.74
80	85.45	85.53	87.00
100	81.95	81.64	81.86
120	77.45	77.22	76.49
140	72.24	72.27	70.85
160	65.91	66.53	64.63
180	59.87	60.26	58.10
200	52.71	52.90	50.64
220	42.63	43.26	41.11
240	27.17	28.51*	26.84
245	20.79	22.24*	20.88
247	17.12	18.61*	17.44
249	12.03	13.40*	12.52
250.1	0.0	0.0	0.0

TABLE 16

Methyl propionate

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C	100.87	102.09*	111.20
80	87.32	86.49	88.83
100	83.22	82.84	83.65
120	78.27	78.24	78.19
140	73.42	73.51	72.71
160	68.22	68.24	66.92
180	62.05	62.19	60.53
200	55.67	55.44	53.60
220	47.14	47.00	45.14
240	34.41	34.99	33.36
250	24.30	25.44*	24.13
253	19.94	21.20*	20.07
255	15.67	16.96*	16.03
256	12.70	13.95*	13.18
257.4	0.0	0.0	0.0

TABLE 17

Propyl acetate

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C.	96.03	92.31*	105.59
100	79.92	79.32	79.58
120	76.26	75.78	74.92
140	72.34	71.91	70.23
160	67.70	67.57	65.30
180	62.94	62.78	60.13
200	57.23	57.22	54.36
220	50.78	50.78	47.89
240	42.40	42.65	39.91
260	30.70	31.43	29.15
270	20.57	21.95*	20.27
273	16.17	17.44*	16.04
275	11.73	12.85*	11.79
276.2	0.0	0.0	0.0

TABLE 18

Ethyl propionate

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C.	96.35	90.73*	104.66
100	79.24	77.64*	78.53
120	75.07	74.06*	73.80
140	70.21	70.01	68.91
160	65.08	65.51	63.82
180	59.88	60.54	58.48
200	54.71	55.05	52.75
220	48.59	48.57	46.20
240	40.23	40.21	37.95
260	27.75	28.11	26.29
265	23.06	23.57	21.97
268	19.32	19.96	18.56
270	15.57	16.39	15.21
272.9	0.0	0.0	0.0

TABLE 19

Methyl butyrate

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C.	96.87	91.16*	106.08
120	74.39	74.93	75.36
140	70.63	71.17	70.70
160	66.85	67.09	66.00
180	62.32	62.45	60.89
200	57.59	57.31	55.44
220	51.45	51.19	49.15
240	44.19	43.80	41.75
260	34.34	34.14	32.28
270	26.79	27.05	25.44
275	21.07	21.70	20.36
278	16.32	17.13	16.04
280	11.04	12.01	11.18
281.3	0.0	0.0	0.0

TABLE 20

Methyl isobutyrate

Temperature	Heat of vaporization		
	Ther.	Mills	Crompton
0° C.	91.78	87.43*	100.31
100	74.47	74.13	75.24
120	70.38	70.49	70.57
140	66.62	66.56	65.92
160	62.34	62.22	61.05
180	57.44	57.31	55.78
200	52.19	51.84	50.07
220	45.13	45.00	43.18
240	35.79	36.13	34.42
260	21.49	22.39	21.14
263	17.53	18.61*	17.53
265	14.21	15.27*	14.37
266.5	10.51	11.50	10.79
267.55	0.0	0.0	0.0

Some Relations at the Critical Temperature

In the third paper, p. 626, we deduced, by an extension of the principles underlying the theory of molecular attraction we have outlined the equation:

11. $$L = \mu' (\sqrt[3]{d} - \sqrt[3]{D}) + 0.0_4 31833\, P\left(\frac{1}{D} - \frac{1}{d}\right) \text{cals.},$$

where *d* is the actual and D the theoretical critical density. Also in that paper by a similar application of Crompton's theory we deduced the result:

12. $$L = \frac{9.154\, T}{m} \log \frac{d}{D} \text{ cals.}$$

The two equations should give values in agreement if both theories are correct.

We show the results obtained from equation 11 in Table 21 under the heading "Mills," and the results obtained from equation 12 under the heading "Crompton." The difference is shown. The divergence never exceeds 4, and seldom exceeds 3 percent, and the agreement is therefore very satisfactory.

TABLE 21

Relations at the critical temperature

Substance	Molecular weight	μ'	Critical			Theoretical density	E_1	$\sqrt[3]{d} - \sqrt[3]{D}$	λ
			Temp.	Pressure	Density				
Methyl formate	60.032	120.29	214.0°	45030	0.3489	0.08891	12.01	0.2577	30.99
Ethyl formate	74.05	107.23	235.3	35590	0.3232	0.08302	10.14	0.2500	26.80
Methyl acetate	74.05	109.52	233.7	35180	0.3252	0.08230	10.16	0.2527	27.66
Propyl formate	88.064	98.74	264.85	30440	0.3093	0.07980	9.01	0.2458	24.27
Ethyl acetate	88.064	99.31	250.1	28880	0.3077	0.07788	8.82	0.2480	24.63
Methyl propionate	88.064	99.03	257.4	30030	0.3124	0.07983	8.91	0.2479	24.55
Propyl acetate	102.08	93.16	276.2	25210	0.2957	0.07504	7.98	0.2444	22.77
Ethyl propionate	102.08	91.45	272.9	25210	0.2965	0.07549	7.92	0.2442	22.33
Methyl butyrate	102.08	91.55	281.25	26000	0.3002	0.07669	8.03	0.2447	22.40
Methyl isobutyrate	102.08	88.51	267.55	25750	0.3012	0.07788	7.80	0.2432	21.52

TABLE 21 (*Continued*)

Substance	Latent heat		Δ	$\frac{\mu}{c}$	$\frac{\mu}{c'}$	Ratio of $\frac{\mu}{c}$ to $\frac{\mu}{c'}$	$\frac{PVM}{T}$
	Mills	Crompton					
Methyl formate	43.00	44.08	—1.08	471.1	45.11	10.44	15910
Ethyl formate	36.94	37.09	—0.15	450.1	41.99	10.72	16040
Methyl acetate	37.82	37.38	0.44	459.8	41.78	11.00	15800
Propyl formate	33.28	32.90	0.38	439.3	40.18	10.93	16110
Ethyl acetate	33.45	32.44	1.01	441.8	39.13	11.29	15800
Methyl propionate	33.46	32.67	0.79	440.6	39.50	11.15	15960
Propyl acetate	30.75	29.33	1.42	435.4	37.75	11.53	15850
Ethyl propionate	30.25	29.08	1.17	427.4	37.49	11.40	15900
Methyl butyrate	30.43	29.46	0.97	427.9	37.89	11.30	15950
Methyl isobutyrate	29.32	28.47	0.85	413.7	36.92	11.21	16150

The critical data used is shown in the same table, as is also the similar data for the three esters previously investigated. The critical data is taken from a paper by Prof. Young.[1] λ in the table denotes the internal heat of vaporization to which E_1 must be added to give L.

We also discussed in the third paper an equation (25) holding true for all substances at the critical temperature, that takes the form:

$$13. \qquad \frac{m\mu'\sqrt[3]{d}}{T} = \text{constant}.$$

The mean value of this constant as deduced in that paper for the non-associated substances was 10.76. The values for the constant for the substances now under consideration are given in Table 21 under the heading "Ratio $\frac{\mu}{c}$ to $\frac{\mu}{c'}$." The average value of the constant for the ten esters now considered is 11.10, or about 3 percent higher than the previously obtained value. We consider this agreement satisfactory.

In the fourth paper, p. 415, we showed that it followed from the theories discussed that,

$$14. \qquad \frac{PVM}{T} = \text{constant},$$

where P, V, and T are the critical volume, pressure and temperature, and m is the molecular weight. The average value of the constant for the substances there examined was 16293. The values for the esters now considered are shown in the last column of Table 21. The average value is 15920 or less than 3 percent lower than the average value previously obtained. We regard this agreement as satisfactory.

A slight divergence in the results obtained from the three previously cited equations bearing upon the critical temperature we do not consider surprising, for we know that the molecular attraction is dependent upon the constitution of the body, and with large changes of temperature

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[1] Phil. Mag. [5], 50, 291 (1900).

there must undoubtedly be incipient changes in the constitution of the substance even before these changes commence to manifest themselves in the decomposition of the body. We think the slight changes so caused in the molecular attraction would be sufficient to account for the variations above noted, which only rarely exceed 3 percent.

Summary

(1) In this paper as in previous papers of this series, our endeavor has been to show that the attraction between the molecules of a liquid varies inversely as the square of their distance apart. For this purpose we further studied the equation previously deduced,

$$\frac{L - E_t}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant},$$

applying the equation to seven esters not previously studied. The results indicate beyond any doubt the truth of the equation, and it is therefore reasonable to suppose that the assumption upon which the above equation was founded is the true one, and that the molecular force does vary inversely as the square of the distance from the attracting particle.

(2) In this paper an equation given by Crompton, $L = 2RT \log_e \frac{d}{D}$, was further examined and the conclusion hitherto reached was confirmed, *viz.*, this relation gives results for the heat of vaporization uniformly too high at low vapor pressures, but at high vapor pressures, in the neighborhood of the critical temperature, the equation is accurate.

(3) Some relations at the critical temperature, already pointed out, are examined further for the seven esters under consideration and the relations are confirmed.

Addendum

Regarding the divergence shown by methyl isobutyrate at 130° C., see Table 12, it seemed to me after inspecting the data, that the cause of the divergence shown at this temperature lay with the value used for the volume of the vapor. On looking up the original data as published, we found the smoothed value given at the temperature, which was the value used, to be 105 and the observed value 103. Thinking it possible that a misprint had occurred, we wrote Prof. Young asking him to look up the value as given in his original note book. This Prof. Young very kindly did, and in his reply just received states: "The volume of a gram of methyl isobutyrate read from the curve at 130° should be 103, not 105; in fact it is barely 103, more like 102.8, but I have not trusted the first decimal at these comparatively low temperatures. The 105 is evidently a misprint or a mistake in the original manuscript."

Making the necessary corrections, the values in Table 12, using 103 for the volume of the vapor should be: $E_1 = 6.93$, $\frac{P.\Delta V.T}{10^6} = 87.77$; Latent heat $= 68.76$, $L—E_1 = 61.83$, $\sqrt[3]{d} — \sqrt[3]{D} = 0.6968$, $\frac{L — E_1}{\sqrt[3]{d} — \sqrt[3]{D}} = 88.76$, a value in excellent accord with the average value of the ratio which was 88.51. The fact that the misprint of 105 for 103 was discovered by means of the theory which we have advanced goes to show that we have not claimed too much for the relation we have discovered in saying that it represents the facts accurately, and is not a mere approximation.—October 5, 1907.

University of North Carolina,
August 16, 1907.

ACTION OF AMMONIUM PERSULPHATE ON METALS

BY J. W. TURRENTINE

The analogy between chemical and electrochemical reactions has been studied in considerable detail in this[1] and other laboratories, and many data have been collected. Many reactions commonly considered and spoken of as purely chemical are in reality electrochemical. Still there is no sharp line of demarcation. Frequently, reactions are induced by galvanic action, set up by bringing together in a corrosive medium and in the presence of the compound with which a certain reaction is desired, two metals of differing electro-properties so that an electric couple is formed. The zinc-copper couple of Gladstone and Tribe may be cited as an example of such a case. This is producing chemical action by a concealed, electrochemical reaction. We can go a step farther and induce an electrochemical phenomenon in a purely chemical way—we can liberate ions which generally are set free only by electrolysis.[2]

When sulphate ions, SO_4, are discharged electrolytically against a metallic anode they do one of three things—in cases where the anode is soluble they dissolve the anode quantitatively forming sulphates; if the anode is insoluble and the current density low oxygen is set free; or if the current density is high and also the concentration of sulphate the sulphate ions combine to form the divalent, persulphate ion, S_2O_8.

If we decompose the persulphate in the presence of an insoluble anode (or in the absence of any anode, which amounts to the same thing) we should expect the evolution of oxygen, and that we get. This may be shown by mixing, in a gas evolution bottle, concentrated sulphuric acid with a saturated solution of ammonium persulphate, containing an excess of persulphate crystals and a small amount of man-

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[1] Bancroft: Trans. Am. Electrochem. Soc., 8, 33 (1905).

[2] Bancroft: Ibid., 8, 43 (1905).

ganous sulphate to act as catalytic agent and accelerate the reaction. An active evolution of oxygen ensues, a fact which may be demonstrated by bringing a glowing splint to the opening of the bottle. Since the addition of the sulphuric acid to the solution causes such a rise in temperature, a thin glass bottle is the safest to use.

Again, if this liberation of sulphate ions is analogous to that produced by the electrolysis of a sulphate solution we should expect a soluble metal to be attacked, thus acting as an anode, and quantitative solution to take place.

To test this point a series of determinations were made in this laboratory of the solubility of pure, metallic copper, as the ideal anode, in a dilute, aqueous solution of ammonium persulphate, the consumption of persulphate being in each case also determined. The object of this paper is to present the results of these determinations. The method of procedure was simple and was as follows: A copper strip was bent into a spiral so that a large surface could be exposed in a small space. After having been cleaned and weighed it was placed in a beaker containing a solution of ammonium persulphate (10 cc of a standard solution containing 0.0829 gram per cubic centimeter being added to 100 cc of water). This solution was stirred vigorously for an hour by a glass stirring rod attached to the axis of a small "Ajax" motor. At the end of the hour the strip was removed, washed, dried and weighed, and the loss in weight was noted. To the solution was then added a weighed amount of ferrous ammonium sulphate, 10 cc of concentrated sulphuric acid and 100 cc of boiling water.[1] It was then titrated rapidly with standard $KMnO_4$ solution. The excess of ferrous iron was calculated. Subtracting this value from the total iron added, gave the amount employed in reducing the unused persulphate. This in its turn, subtracted from the total amount of persulphate, gave the weight of that which had reacted with the copper. From this last value was calculated the equivalent weight of

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[1] Friend: Jour. Chem. Soc., 85, 1533 (1904).

copper. A comparison was then made between the calculated and observed values. The following table gives the data on copper:

	Total persulphate	Excess persulphate	Persulphate used	Cu. equiv.	Actual loss
1	0.8293	0.0990	0.730	0.2035	0.2050
2	0.8293	0.0258	0.8035	0.2240	0.2279
3	0.8293	0.0477	0.7817	0.2179	0.2185

The amount of persulphate which was not employed in dissolving the copper is indicated in the table by "excess" persulphate. The amount reduced by the copper is recorded under the head, "Persulphate Used." This weight of copper dissolved is equivalent to the action of a current of about 0.18 ampere for the same length of time.

It is seen that a varying excess of copper over that called for by the calculation is recorded. This excess loss could not be attributed to error in the analytical work as all determinations of persulphate in the standardization of solutions were easily duplicated. The possibility of the solubility of copper in (NH$_4$)$_2$SO$_4$ in the presence of oxygen being suggested, a blank run with copper in neutral ammonium sulphate was made, with the result that it was seen that an average of 0.0025 gram was dissolved per hour in the ammonium sulfate. This would bring the results for copper easily within the limits of experimental error. The addition of ammonium hydroxide to the ammonium persulphate, it may be remarked, accelerates the rate of solution of the copper.

Sulphate ions discharged electrolytically against a nickel anode normally dissolve nickel but slightly. Instead, oxygen is evolved. The presence of chlorides in the solution, it has been shown, causes corrosion and the formation of black nickelic oxide. Nickel plates in ammonium persulphate, on the other hand, do dissolve to the sulphate. The results of two typical runs are given in the subjoined table:

	Total persulphate	Excess persulphate	Persulphate used	Ni equiv.	Actual loss
1	0.8293	0.2419	0.5874	0.1510	0.1326
2	0.8293	0.3510	0.4783	0.1230	0.1047

It will be observed that the solution of the nickel in the persulphate is not quite quantitative, there being a difference of about 13 percent between the actual loss due to the corrosion and the calculated nickel equivalent of the reduced persulphate. A slight evolution of oxygen may have occurred, but was not noticed. The nickel salt produced by the corrosion may act catalytically, as does manganese sulphate, to accelerate the decomposition of the persulphate. However, this point was not investigated, but attention was turned rather to the determination of the cause of the surprisingly large solubility of the nickel in the ammonium persulphate. Chlorides were sought for as a possible cause, but were found to be absent. As passivity of an anode is generally due to the formation on its surface of films of oxides or hydroxides, and as nickel hydroxide is known to be soluble in ammonium sulphate it was deemed possible that the activity of the nickel anode in the persulphate was due to the presence of ammonium sulphate which dissolved the film of oxide that produced the passivity. Accordingly, to eliminate the ammonium salts the solubility of nickel in sodium persulphate was determined, under conditions of temperature and concentration of solution similar to those which obtained in the like experiment with ammonium persulphate. The slight loss in weight of 0.0005 gram from a surface of about 20 sq. cm. was detected after an hour's stirring. This is in agreement with the electrolytic corrosion of nickel by sulphates, the presence of ammonium salts acting here as they do in the electrolysis to render the anode active—hence the use of the double sulphate of nickel and ammonium in the electrolytic purification and deposition of nickel.

Nickel, like copper, shows a slight solubility in neutral ammonium sulphate, 10–20 mg dissolving in an hour from an exposed surface of 20 sq cm.

Cadmium

Cadmium, it was found, dissolves readily in ammonium persulphate without apparent evolution of gas. The calculated and observed values, however, do not agree. As the error gives the excess to the calculated rather than to the observed value it cannot be explained as was that in the case of the copper, by the solubility of the metal in ammonium sulphate. The source of this discrepancy was not investigated.

Aluminum

Aluminum as anode in the electrolysis of sulphates is but slightly corroded, due to the oxide films and consequent passivity. Furthermore, it tends to intercept the electric current by preventing the discharge of the anions. This phenomenon is made use of in the aluminum current rectifiers. In ammonium persulphate solution only slight corrosion of the aluminum occurs, about 20 mg in one hour from a surface of 40 cm^2 exposed to corrosion; no oxygen is evolved. The analogy then between the corrosion of aluminum in persulphate solution and as anode in sulphate solution seems to be complete.

Iron

Iron anodes are dissolved by sulphate ions, at low current densities, quantitative solution taking place. The valence assumed by the dissolved iron is that of the ferrous condition. In a solution of ammonium sulphate it reacts with the alkaline solution from the cathode region and precipitates as the slightly oxidized, green, ferrous hydroxide. At higher current densities, the rapid corrosion of the iron being prevented, oxygen is set free.

Ammonium persulphate acts on iron similarly and dissolves it to ferrous sulphate, thus upholding our analogy. The excess of ammonium persulphate reacts with the ferrous sulphate and oxidizes it, but only partially, to the ferric state. This is clearly shown by adding to the solution a known excess of ferrous ammonium sulphate and after following the prescribed procedure, titrating with permanganate. The presence of an amount of ferrous iron in excess of that added is indicated by the titration. The amount of the excess depends on the extent of the corrosion and on the temperature. In the case of our own experiments this condition was always shown, in one instance the ferrous iron in the solution in excess of that added to reduce the persulphate being equivalent to 0.80 gram of ferrous ammonium sulphate. The ferric sulphate formed readily hydrolyzes, precipitating ferric hydroxide. There is also a free evolution of gas which is not absorbed by alkaline pyrogallol and is also combustible in air. The origin of this gas must be either (1) from hydrogen set free by the action of acid in the solution on the iron, or (2) from hydrogen dissolved in the iron,[1] (3) from the decomposition of carbides within the iron, evolving gaseous hydrocarbons, or (4) the breaking down of ferrous sulphate to ferric sulphate with the liberation of hydrogen, in a manner analogous to the decomposition of chromous salts.

The first explanation seemed quite improbable as abundant ferric hydroxide formed in the solution, indicating a practically neutral solution in spite of a slight acid reaction to litmus. Furthermore, a piece of iron was allowed to stand without stirring in a solution of ammonium persulphate made alkaline with ammonia; the iron became covered with a deposit of ferric hydroxide. The evolution of gas was still noted. This made it seem extremely improbable that the liberation of gas was due to an acid solution.

If the gas was hydrogen dissolved in the iron then the same volume should be obtained on making the iron anode in ammonium sulphate. Accordingly, an iron anode thrust into an inverted burette with a parchment diaphragm surrounding the burette to prevent the diffusion of the cathode gases into the anode compartment, was dissolved by electrolysis in a neutral, 1 percent ammonium sulphate solution. A current density was used which would produce a slight evolution of oxygen at the anode. The cathode was of platinum.

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[1] Burgess: Trans. Am. Electrochem. Soc., 9, 197 (1906).

The gases evolved from the anode were collected in the burette and withdrawn for analysis. The results of four such runs are given in the following table:

	Total volume cc	Oxygen	Hydrogen
1	18.0	12.2	5.8
2	32.5	26.2	6.3
3	16.0	12.6	3.4
4	18.0	13.0	5.0

More iron was dissolved in these experiments than was in the corrosion with ammonium persulphate, yet a smaller volume of hydrogen was obtained, so this explanation of the source of all the hydrogen had to be abandoned. The third point, the question of the formation of hydrocarbons, was tested by making an analysis of the gas by combustion in a Winkler-Dennis combustion pipette. The total contraction in volume equaled the volume of gas taken for analysis plus one-half of its own volume—two volumes of gas combined with one of oxygen; this fact, coupled with the absence from the combustion products of carbon dioxide, showed the gas to have been only hydrogen.

If hydrogen is evolved by the transition of ferrous into ferric salts in ammonium persulphate solutions the addition of ferrous salts should accelerate the reaction. Accordingly, two parallel runs were made by placing in 1 percent ammonium persulphate solution in two beakers iron strips in inverted burettes. To one solution was added 2 grams of ferrous sulphate. From the iron in pure persulphate were obtained 14.6 cc gas in 19 hours and from the one to which had been added the ferrous salt 16.0 cc in the same time, showing a slight acceleration produced by the iron in spite of the decreased concentration of the persulphate, due to its partial reduction by the ferrous sulphate. To make the concentration more nearly comparable a third run was made using a more concentrated solution of the persulphate; the ferrous sulphate was added by squirting it, in concentrated solution, through a tube against the face of the iron strip. A still greater acceleration was recorded in this case, 16.0 cc being evolved in 6 hours, as compared with the same volume evolved in 19 hours as observed in the case of one of the others. This clearly indicated that the acceleration was due to the increase in the concentration of the iron salts and not to that of the persulphate. It is doubtful if, in the last described experiment, there was any actual increase in the concentration of persulphate in the solution immediately surrounding the iron, as the ferrous sulphate was admitted directly against the iron and tended to displace the persulphate solution. While these phenomena were in accord with our theory, when attempts were made to determine what was acting as the catalytic agent to bring about this remarkable decomposition, it was noticed that iron in pure ferric sulphate solution, unstirred, also evolved hydrogen. Litmus showed such a solution to be acid. Alkaline hydroxides precipitated ferric hydroxide, but left the solution still acid. Ferrous sulphate and iron did not react to produce hydrogen; it is clearly impossible by definition for the reduction of ferric iron to be a reaction which evolves hydrogen, and as ferric sulphate hydrolyzes to produce free sulphuric acid, this acid seemed to be the source of the hydrogen. If this were true then the action of the alkaline ammonium persulphate had to be brought into agreement with it, so reversion was made to the persulphate. It has been mentioned above that the iron in the persulphate soon became incrusted with ferric hydroxide, due to the solution of the iron in the persulphate to ferrous sulphate, the oxidation of a part of this to ferric sulphate and the precipitation of the ferric hydroxide by hydrolysis. A further solution of iron within the crust, even in the presence of free alkali in the solution, would lead to the production of ferric sulphate which, hydrolyzing, would leave an acid solution immediately surrounding the iron and would thus give rise to an evolution of hydrogen. Vigorous stirring from the beginning, on the other hand, should produce a film of hydroxide adherent and impermeable to the persulphate—should render the iron passive. This, it was found, it did. However, on standing in the solution unstirred, this film was broken through in spots, and long threads of hydroxide grew out like roots from the iron. The evidence then seems to be in favor of our first explanation, however improbable it at first appeared. We feel sure that this is the true explanation of the phenomenon.

It may be suggested that the corrosion of iron in the presence of oxygen in many so-called neutral solutions is probably due to the free acid produced by the hydrolysis of ferric salts. The free acid may serve to carry the iron into solution as ferrous salt which is then oxidized. The acid is regenerated by the hydrolysis of the resulting salt, just as in the commercial reduction of nitrobenzene to aniline by means of iron and hydrochloric acid, the acid is regenerated. While the acid is supposed to act catalytically we know that it enters into the intermediate reactions.

Summary

(1) Sulphate ions are discharged when persulphates are decomposed in aqueous solution. These ions behave analogously to sulphate ions produced electrolytically.

(2) Copper in ammonium persulphate behaves just as does copper when employed as the anode in the electrolysis of sulphates.

(3) Nickel, cadmium and aluminum bear out the analogy between the chemical corrosion in ammonium persulphate and the electrolytic corrosion in ammonium sulphate.

(4) Iron is dissolved by persulphates. A portion of the dissolved iron subsequently appears as ferric sulphate, being oxidized by the persulphates in the solution.

(5) The free acid formed by the hydrolysis of ferric sulphate acts as a catalytic agent in the reaction between iron and water.

This work was suggested by Professor Bancroft and has been carried on under his direction. The author's thanks are due him.

Cornell University.

THE ACTION OF LIME IN EXCESS ON COPPER SULPHATE SOLUTIONS[1]

J. M. BELL AND W. C. TABER

Much attention has recently been directed to the chemical means of removing metallic salts from waters which have been used in mining operations, with a view to the subsequent use of these waters for irrigation purposes. As many of the heavy metals, even in extremely dilute solution, are toxic to vegetation and especially to roots, complete removal of the metal is almost essential before the water can be safely used for agricultural purposes. Lime has been employed as a corrective to such waters and especially to copper-bearing streams, the alkaline solution of lime causing complete precipitation of the copper as hydroxide which may be removed by passing the water through sand filters, the blue copper hydroxide remaining in the filters.

Copper sulphate has recently been employed in municipal water supplies to kill certain bacteria and algae. The quantity of the copper salt is dependent partly upon the degree of alkalinity of the water, for with alkaline waters a sufficient quantity must be added to remove the free alkali from solution. Another process where copper sulphate and lime water are mixed is in the making of Bordeaux mixture for spraying purposes. In this instance it is necessary to have present a large excess of lime in order that the quantity of copper in solution may be extremely small, for even dilute solutions are harmful to leaves of trees on which the spray is customarily used.

In the present paper there are given the results of some experiments which were conducted with a view to determine the composition of the solution and of the precipitates obtained when lime and copper sulphate solutions were mixed in different proportions and concentrations. These precipi-

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tates have been analyzed by many agriculturalists, and it has been found that the composition of the solid has depended upon the ratio in which lime and copper sulphate were mixed. Consequently, Bordeaux mixture has been looked upon as of particularly complex nature. If the previous experiments had been conducted at some fixed temperature, the composition of the *solutions* would undoubtedly have been found to be constant in composition—no matter how much lime had been in excess and no matter at what concentrations the mixing had been done. This constancy in the composition of the solution is due to the presence of several chemical individuals in the solid precipitate, a change in the proportion of the original ingredients of the mixture causing only a change in the proportion of these chemical compounds in suspension, and not any change in the chemical nature of the compounds themselves.

This investigation naturally divides itself into several separate problems, the results of each of which are necessary for a complete knowledge of the four-component system, copper oxide, lime, sulphuric acid and water. In the preparation of Bordeaux mixture an excess of lime must be added and the first of the problems is the investigation of the solids and of the solutions when lime was present in the mixture in great excess. Another problem still under investigation is where lime is not present in sufficient quantity to precipitate all the copper from solution. Still another case investigated is where the sum of the bases was equivalent to the sulphuric acid present. This resolves itself into the mutual solubility of copper sulphate and calcium sulphate, and the data are given in the following paper. The final case which might be investigated is the solubility of copper and calcium sulphates in sulphuric acid solutions.

A series of solutions containing varying quantities of copper sulphate was prepared and an excess of lime (CaO) was added to each solution. The containing bottles were constantly agitated in a constant temperature bath at 25° for several weeks. The solutions were allowed to stand for some days so as to allow the subsidence of all the precipitate. The solutions were found to be alkaline and no copper could be found in the solution by the ferrocyanide test. The system, therefore, becomes in effect the mutual solubility of calcium oxide and gypsum in the presence of solid copper oxide in a more or less hydrated condition. Owing to the temperature of the laboratory rising beyond 25° before some of the solutions were drawn for analysis, the part of the curve representing solutions in contact with solid gypsum does not coincide exactly with the results obtained at 25° by Cameron and Bell,[1] but show a greater quantity of gypsum in the solutions as might be expected under these conditions. It was noticed that the color of the copper precipitate changed abruptly from blue in the case of the more alkaline solutions, to a dark olive-green in the case of the less alkaline solutions, and this abrupt change in the character of the precipitate is accompanied by a slight change in the direction of the solubility curves. This break is so slight that were it not for the obvious change in the solid phases it might be attributed to the experimental error in analysis of the solutions. The following table gives the results of the experiments:

CaO per liter Grams	SO_3 per liter Grams	Solid phases
1.206	0.0	$Ca(OH)_2$, blue copper hydroxide.
1.780	0.872	$Ca(OH)_2$, blue copper hydroxide.
1.908	1.060	$Ca(OH)_2$, $CaSO_4.2H_2O$, blue copper hydroxide.
1.888	1.052	$CaSO_4.2H_2O$, blue copper hydroxide.
1.816	1.032	$CaSO_4.2H_2O$, blue copper hydroxide.
1.420	1.084	$CaSO_4.2H_2O$, blue copper hydroxide.
1.358	1.112	$CaSO_4.2H_2O$, blue copper hydroxide.
1.120	1.144	$CaSO_4.2H_2O$, green copper hydroxide.
1.008	1.156	$CaSO_4.2H_2O$, green copper hydroxide.
0.880	1.280	$CaSO_4.2H_2O$, green copper hydroxide.

The presence of gypsum in the solid could easily be detected under the microscope and a second white solid could be seen plainly, consisting undoubtedly of calcium hydroxide.

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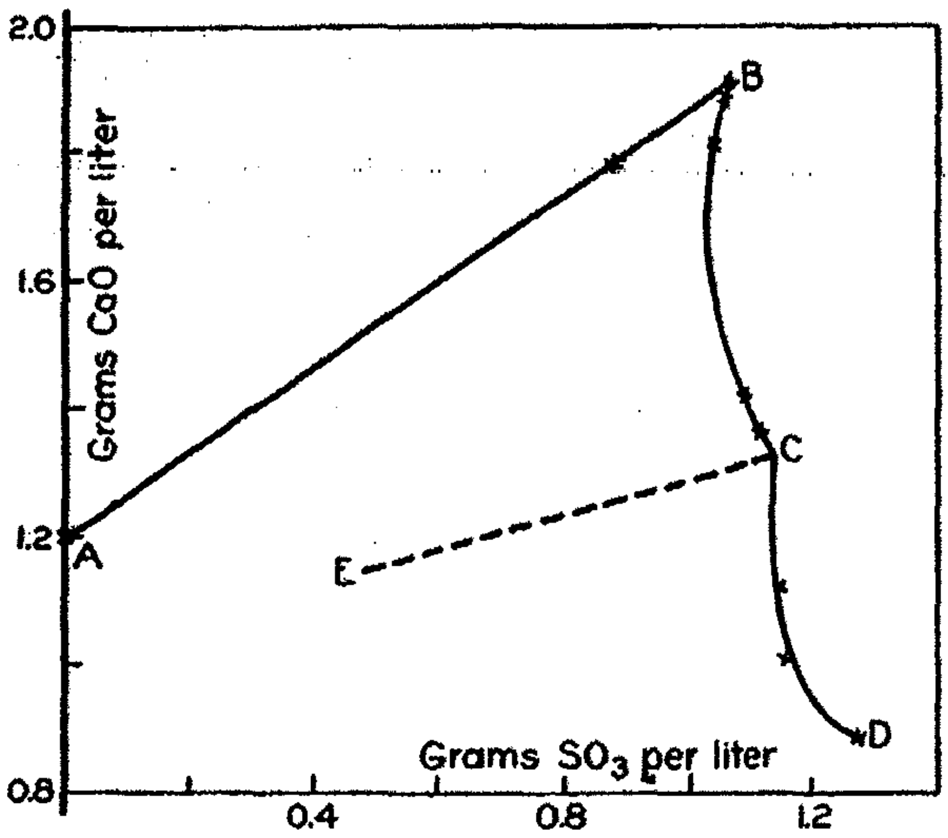
[1] Jour. Am. Chem. Soc., 28, 1220 (1906).

The copper hydroxide precipitates are no doubt copper oxide in different stages of hydration, but no method could be devised for directly determining how much water is combined with the oxide. This problem is still under investigation and by a slight modification of the conditions it is hoped that the composition of both the blue and the green modifications may be determined.

In the accompanying diagram the results given in the above table have been plotted and there are apparently three curves, A B C D, the curve A B representing solutions in contact with calcium hydroxide and the blue copper hydroxide, the curve B C representing solutions in contact with gypsum and the blue copper hydroxide, and the curve C D representing solutions in contact with gypsum and the green copper hydroxide. For a complete representation there is another curve representing solutions unsaturated with both gypsum and lime and in contact with the two modifications of copper hydroxide. This curve has not yet been determined experimentally, but is represented tentatively on the diagram by the dotted line E C. Thus, there are two fields, one representing solutions in contact with the blue copper hydroxide, and one solution in contact with the green copper hydroxide.



In the preparation of Bordeaux mixture a very great excess of lime is added, and consequently the solution will correspond to the point B on the figure, and the precipitate will consist of the three solids, lime, gypsum and the blue copper hydroxide. As the solution fails to show the presence of copper by the common tests, it would seem that the beneficial effect obtained from the use of Bordeaux mixture might be obtained by the use of a solution saturated with both lime and gypsum. This is, however, found not to be the case and this beneficial action must therefore be attributed to the blue hydroxide of copper, or to the minute quantities of copper in solution which in the presence of solid lime and gypsum must be of constant concentration. As the solution evaporates, the concentration of copper in solution remains constant. In the absence of lime dilute copper sulphate solution as a spray would after a time become more concentrated by evaporation of the water, and harmful results to foliage would ensue. The beneficial effect of the copper must therefore be attributed either to the solid copper hydroxide (and it is difficult to see how this could act unless in solution), or else to the very dilute copper solution. Such dilute solutions have been shown to be toxic to some lower organisms, such as colon bacillus and allied species, and it may be that it is also toxic to the organisms whose destruction is brought about by the Bordeaux mixture.

The compositions of the "constant" solutions and the solid phases in contact with them have been collected in the following table:

Point	Grams per liter			Solid phases
	CuO	CaO	SO_3	
A.	0	1.21	0	Lime, blue copper hydroxide.
B.	0	1.91	1.06	Lime, gypsum, blue copper hydroxide.
C.	0	1.20	1.13	Gypsum, blue copper hydroxide, green copper hydroxide.
D.	0	0.88	1.28	Gypsum, green copper hydroxide.

Bureau of Soils,
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Washington, D. C.

THE SOLUBILITY OF GYPSUM IN COPPER SULPHATE SOLUTIONS[1]

BY J. M. BELL AND W. C. TABER

In studying the mutual solubility relations of copper sulphate and calcium sulphate to which reference was made in the preceding paper, a series of solutions of copper sulphate was prepared, ranging from 0.1 percent to a saturated solution, and to each solution an excess of powdered calcium sulphate was added. After constant agitation for two weeks in a constant temperature bath at 25° the solutions were analyzed for lime and for copper.

Density of solution at $\frac{25°}{25°}$ C	Grams $CuSO_4$ per liter	Grams $CaSO_4$ per liter
1.002	1.144	2.068
1.005	3.564	1.986
1.007	6.048	1.944
1.009	7.279	1.858
1.016	14.814	1.760
1.021	19.729	1.736
1.030	29.543	1.688
1.041	39.407	1.718
1.051	49.382	1.744
1.061	58.880	1.782
1.098	97.950	1.931
1.146	146.725	2.048
1.192	196.021	2.076
1.218	224.916	2.088

These results have been plotted and show a decreasing solubility of gypsum as the concentration of copper sulphate increases, until a minimum is reached at about 30 grams of copper sulphate per liter, at which concentration there is nearly 1.7 grams of calcium sulphate in solution. From this point the curve shows a rather sharp rise to a concentration of about 150 grams copper sulphate per liter, when there are about 2.05 grams calcium sulphate per liter. From this point the curve shows a slight but gradual rise till the point of saturation with respect to copper sulphate is reached, when

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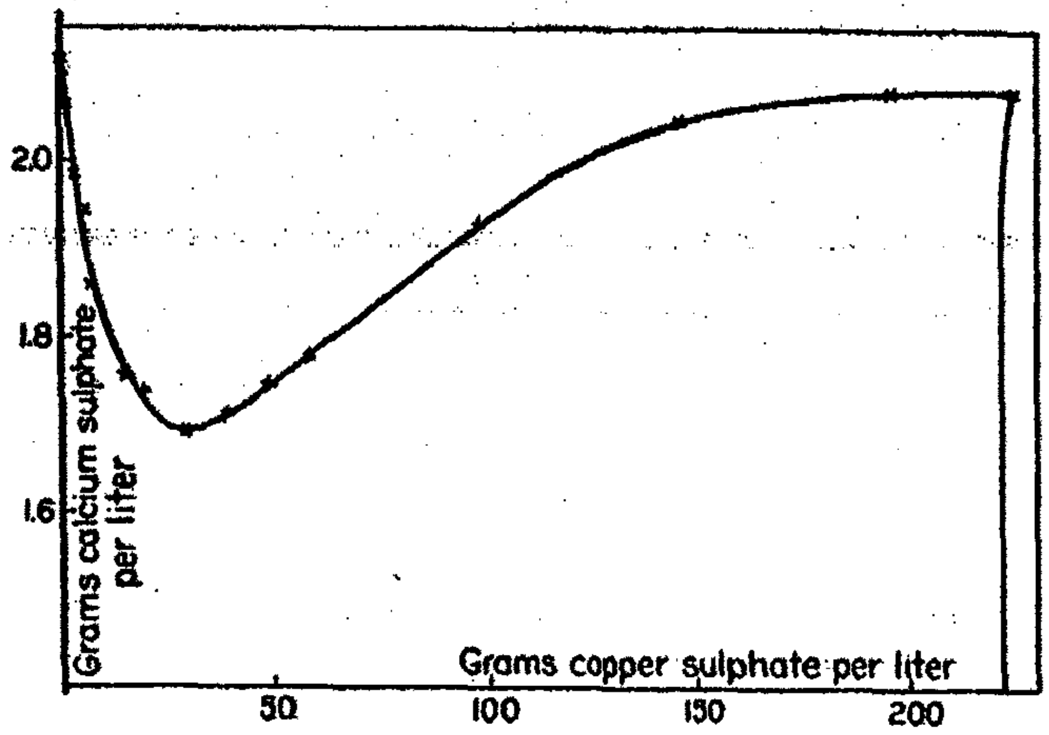
there are 2.08 grams calcium sulphate per liter in solution. At this point there are two solid phases, calcium and copper sulphates, and the solution has a "constant" composition. The remainder of the isotherm is the curve representing the solubility of copper sulphate in various solutions of gypsum. As the solubility of gypsum in water is relatively very small, its presence even in saturated solutions will probably have but little effect on the quantity of copper sulphate in solution. The correctness of this follows from the work of Trevor,[1] who found that a saturated solution of copper sulphate in water contained 22.29 grams of copper sulphate per 100 grams of water, while in the present experiments the solubility of copper sulphate in a saturated solution of gypsum was found to be 22.49 grams of copper sulphate per 100 grams of water. It will be observed that copper sulphate in common with all the sulphates, excepting sulphuric acid,[2] decreases the solubility of gypsum, as might be expected of compounds with a common ion, but at higher concentrations its solubility increases.



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[1] Zeit. phys. Chem., 7, 470 (1891).

[2] See Cameron and Bell: Bull. No. 33, Bureau of Soils, U. S. Dept. Agr. (1906).

NEW BOOKS

Gleichgewichte der Stereomeren. *By W. Meyerhoffer. Mit einem Begleitwort von Prof. Dr. J. H. van 't Hoff. 15 × 23 cm; pp. 71. Leipzig und Berlin: Druck und Verlag von B. G. Teubner, 1906. Price: paper, 2.40 marks.*—In the preface van 't Hoff makes the following comments on this last work of Meyerhoffer's:

"This volume illustrates one of Meyerhoffer's striking characteristics, the persistent following up of a problem once undertaken. The book on Stereochemistry which appeared simultaneously in French and German in 1892 was Meyerhoffer's first important and comprehensive work; this volume on the same theme, appearing fourteen years later, is his last. It deals with that portion of stereochemistry which appeals also to those who are not chemists, with the question whether optical activity is a vital phenomenon as Pasteur believed. A new light was thrown upon the problem by the discovery that the splitting of the optically active isomers and therefore their separation is a question of temperature and depends on an inversion phenomenon occurring at a definite temperature. This pamphlet describes the laws governing this inversion and brings the separation of optically active compounds in line with the decomposition of double salts.

"There is also evident a certain tendency to an abstract way of putting things, which was another characteristic of Meyerhoffer, and I advise the reader not to be terrified thereby, especially when this peculiarity appears in the first pages. For instance, the definition of equilibrium in the first chapter might well be left till later." *Wilder D. Bancroft*

Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen. *Ein Beitrag zur Theorie homogener Systeme. By G. Tammann. 15 × 23 cm; pp. vii + 184. Hamburg und Leipzig: Leopold Voss, 1907. Price: paper, 9 marks.*—This book is based chiefly upon the author's own work on the properties of solutions. The headings of the chapters are: thermal expansion of aqueous solutions; physical significance of the theorem that the volume of solutions varies with temperature changes as the volume of the solvent when subjected to a higher pressure; the variation of the volume of solutions with changing pressure; the pressure-temperature curves for solutions at constant volume; summary of the regularities in the change of solution volumes with varying pressure and temperature; abnormal expansion of solutions; the existing data on the thermal expansion of aqueous solutions; the thermal expansion of solutions in alcohol, ether, carbon bisulphide and acetone; volume changes during the formation, mixing and neutralization of solutions; thermal properties of solutions; effect of pressure on the properties of solutions; the change of indices of refraction caused by the dilution, formation and neutralization of solutions; surface tension in relation to internal pressure of solutions; relation of internal pressure to vapor-pressure.

The purpose of the book is set forth clearly in the introduction. "With the theory of dilute solutions began the successful study of homogeneous systems. The theory was able to accomplish what it did because it limited itself to the behavior of the solute. By means of simple assumptions it brought into relationship a series of phenomena and of properties. The solute behaves like a gas; thereby the gas laws in all their simplicity become applicable to the solute. This simple formulation, however, does not cover the whole field. The volume changes of solutions with varying temperature and pressure, the heats of dilution, the change of many properties with concentration and pressure do not come under it. We get an explanation of these phenomena only through the knowledge that the state of the solvent is also changed radically when a solution is formed. This change can be formulated quantitatively. Solutions behave in many respects like the solvent subjected to a definite, higher pressure. Through a recognition of this fact it becomes possible to understand many changes in the properties of solutions and to calculate any one quantitatively from the others. In this way one gets an insight into the internal, specific forces of affinity acting between solvent and solute. By combining the two theories it will probably be possible to extend the theory of homogeneous systems to all temperatures lying well under the critical temperatures of the components."

Wilder D. Bancroft

Flüssige Kristalle und die Theorien des Lebens. *By O. Lehmann. 14 × 21 cm; pp. 55. Leipzig: Johann Ambrosius Barth, 1906. Price: paper, 1.20 marks.*—The author points out the similarity in appearance between the forms assumed by flowing crystals and the forms of cellular tissue and of bacteria. This can be interpreted in two ways. We can say that we have at last found an intermediate step between crystals and living matter, or we can say that the appearance of life in the flowing crystals is deceptive because we can pass practically continuously from flowing crystals to the ordinary crystals. The author evidently inclines to the first view though he admits quite frankly that there is no real proof of it as yet.

Wilder D. Bancroft

Justus von Liebig und Emil Louis Ferdinand Güssefeld. Briefwechsel, 1862–1866. (*Mit Anmerkungen und erläuterungen Versehen. Herausgegeben von O. E. Güssefeld.*) *14 + 22 cm; pp. vii × 72. Leipzig: Johann Ambrosius Barth, 1907. Price: paper, 3.00 marks.*—This is a series of letters from the years 1862–1866, dealing with the introduction of guano from Baker Island in the Pacific Ocean and with the manufacture of phosphates therefrom. Liebig was tremendously interested in this development of artificial fertilizers, owing to its importance for Germany in the beet sugar and other industries. These letters are interesting as a historical document. In many cases the editor's notes consist of a re-statement of what is in the letters. From some remarks in the preface it appears that the editor believes that the letters would not otherwise be intelligible. To the reviewer this seems rather an extreme view.

Wilder D. Bancroft

FERRIC SULPHATES[1]

BY F. K. CAMERON AND W. O. ROBINSON

Introduction

The great number of basic ferric sulphates which have been recorded in the literature and the complexity of many of the formulas assigned to them make it seem probable that they are not definite compounds but solid solutions of ferric oxide, sulphuric acid and water, or mixtures of a small number of comparatively simple basic sulphates, either with one another or with the hydroxide.

The following ferric sulphates have been described:

$Fe_2O_3.4SO_3.6H_2O$, Scharizer, Zeit. Kryst. Min., **35**, 345 (1901).

$Fe_2O_3.4SO_3.8H_2O$, Recoura, Comptes rendus, **137**, 118 (1903).

$Fe_2O_3.4SO_3.9H_2O$, Komar, Chem. Zeit., **30**, 15 (1906).

$Fe_2O_3.3SO_3.10H_2O$, Oudemans, Rec. Trav. Chim. Pays-Bas, **3**, 331 (1884).

$2Fe_2O_3.5SO_3.12H_2O$, Mysite (mineral); Moissan, Traité de Chimie Minerale, IV, 375.

$2Fe_2O_3.5SO_3.18H_2O$, Copiapite (mineral); Rose, Pogg. Ann., **27**, 309, 314 (1833).

$Fe_2O_3.2SO_3.H_2O$, Maus, Pogg. Ann., **11**, 77 (1827).

$Fe_2O_3.2SO_3.7H_2O$, Frenzel, Chem. Centr., **19**, 492 (1889).

$Fe_2O_3.2SO_3.15H_2O$, Meister, Ber. chem. Ges. Berlin, **8**, 771 (1875).

$Fe_2O_3.2SO_3.10H_2O$, Field, Jour. Chem. Soc., **13**, 156 (1862).

$3Fe_2O_3.5SO_3.27H_2O$, Fibroferrite (mineral); Rose, Pogg. Ann., **27**, 315 (1883).

$3Fe_2O_3.5SO_3.2H_2O$, Apatelite (mineral); Meillet, Ann. Min., **3**, 808 (1841).

$2Fe_2O_3.3SO_3.7H_2O$, Raimondite (mineral); Breith, Berg-Hüttenm. Zeit., **25**, 149 (1866).

$2Fe_2O_3.3SO_3.15H_2O$, Illohmannite (mineral); Moissan, Traité de Chimie Minerale, IV, 375.

$2Fe_2O_3.3SO_3.8H_2O$, Wittstein, Buchner's Rep. [3], **1**, 185 (1848).

$2Fe_2O_3.3SO_3.4H_2O$, Maihle, Comptes rendus, **132**, 1560 (1901).

$4Fe_2O_3.5SO_3.13H_2O$, Carphosiderite (mineral); Breith, Schw. J., **50**, 314 (1827).

$Fe_2O_3.SO_3.3H_2O$, Souberein, Ann. Chim. Phys. (2), **44**, 329 (1830).

$3Fe_2O_3.4SO_3.9H_2O$, Athanasesco, Comptes rendus, **103**, 271 (1886).

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[1] Published by permission of the Secretary of Agriculture.

$2Fe_2O_3.SO_3.6H_2O$, Berzelius, Gilb. Ann., **40**, 293 (1812).
$2Fe_2O_3.SO_3.3H_2O$, Field, Jour. Chem. Soc., **13**, 156 (1862).
$2Fe_2O_3.SO_3.xH_2O$, Pickering, Jour. Chem. Soc., **38**, 807 (1880).
$2Fe_2SO_3.8H_2O$, Church, Zeit. Kryst. Min., **28**, 208 (1897.)
$2Fe_2O_3.2SO_3$, Scharizer, Zeit. Kryst. Min., **32**, 338 (1900.)
$3Fe_2O_3.SO_3.6H_2O$, Meister, Ber. chem. Ges. Berlin, **8**, 771 (1875).
$3Fe_2O_3.SO_3.4H_2O$, Scheerer, Pogg. Ann., **44**, 453 (1838).
$4Fe_2O_3.SO_3.11H_2O$, Anthon, Rep. Pharm., **81**, 237 (1843).
$21Fe_2O_3.3SO_3.31.5H_2O$, Moissan, Traité de Chimie Minerale, IV, 375.
14 $Fe_2O_3.2SO_3.21H_2O$, Sheerer, Pogg. Ann., **45**, 188 (1838).
$10Fe_2O_3.SO_3.H_2O$, Athanasesco, Comptes rendus, **103**, 271 (1886).

Basic Ferric Sulphates

Maus[1] found that the normal ferric sulphate in water solution has the power of dissolving considerable amounts of ferric hydroxide, forming a dark brown solution. Pickering[2] studied the precipitate obtained by diluting the normal sulphate until the resulting solution contained less than 2 percent ferric sulphate. A number of analyses of this precipitate gave results corresponding to the formula $2Fe_2O_3.SO_3.xH_2O$. Solutions containing more than 2 percent ferric sulphate gave no precipitate until the solution had been boiled, when an orange colored precipitate settled containing from 58 to 77 percent ferric oxide and varying ratios of ferric oxide to sulphuric acid. From his work the author concludes that the only definite basic sulphate has the composition $2Fe_2O_3.SO_3.xH_2O$. By washing this "compound" for 60 days the percentage of ferric oxide was increased from 80 to 83. This fact was interpreted as disproving the existence of a more basic sulphate of simple composition. In later work, Pickering[3] estimated the molecular weight of the above-described sulphate to be 1200.

Scharizer[4] studied the action of ferric sulphate solutions on freshly precipitated ferric hydroxide. From an exhaustive set of experiments the following results are quoted:

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[1] Pogg. Ann., **11**, 75 (1827).
[2] Jour. Chem. Soc., **38**, 807 (1880).
[3] Ibid., **30**, 182 (1883).
[4] Zeit. Kryst. Min., **32**, 338 (1900).

TABLE I

Solubility of ferric oxide in solutions of ferric sulphate, according to Scharizer

10 cc original solution contained		Dilution	10 cc final solution contained	
Fe_2O_3	SO_3		Fe_2O_3	SO_3
Grams	Grams		Grams	Grams
1. 0.0580	0.0879	68.5 :1	0.0572	0.0853
2. 0.2204	0.3447	17.7 :1	0.2621	0.3298
3. 0.4940	0.7870	7.8 :1	0.6690	0.7720
4. 1.258	2.0060	3.06:1	1.6930	1.9310

In these experiments enough ferric hydroxide was added to make the amount of Fe_2O_3 in the solid phase one-half the amount that was in solution. If we subtract from or add to this amount, as the case requires, the amount of ferric oxide which dissolved or precipitated and subtract from the original amount of sulphuric acid the amount found in the final solution, the ratio of the ferric oxide to sulphuric acid in the precipitate can be estimated as follows:

$$Fe_2O_3:SO_3 = 23;\ 9.2;\ 9;\ 5.2.$$

It is evident that the composition of the precipitate varies with the concentration of the solution.

In the same paper Scharizer gives a table for the solubility of basic ferric sulphate in ferric sulphate solutions, the data being recalculated and given in Table II.

TABLE II

Solubility of basic ferric sulphate in solutions of ferric sulphate, according to Scharizer

Sp. gr.	Temperature	Percent Fe_2O_3	Percent SO_3
—	—	0.346	0.519
1.0078	19° C	0.468	0.657
1.011	24.5°	0.610	0.839
1.021	18°	1.071	1.452
1.074	19°	3.716	4.355
1.169	16°	7.492	8.592

Since the curve obtained from plotting Scharizer's results is continuous and shows no break, it is evident that there can be but one solid phase in contact with the solution, and since this solid phase varies with the concentration of the solution it is a series of solid solutions of ferric oxide, sulphuric acid and probably water.

More recently Scharizer[1] prepared copiapite, $2Fe_2O_3.5SO_3.18H_2O$, by the evaporation of a solution of normal ferric sulphate and exposing the residue to dry and moist air alternately. By this procedure he obtains two forms of crystals, a yellow mass which he identifies as copiapite, and white acid ferric sulphate. These results obviously could not be obtained under conditions of stable equilibrium, and can only be accounted for by a comparatively slow rate of change of one salt to another. Theoretically, an acid and a basic salt could coexist in metastable equilibrium in contact with a solution of the composition represented by the point C, Fig. 1. From the diagram it would seem that, under the conditions of concentration described by Scharizer, the acid salt would separate first, and it is surprising that he did not realize the conditions represented by the point B, namely, the coexistence of normal and acid salt, rather than those he actually described. In one of our experiments, in which a solution of normal ferric sulphate was evaporated, the residue was at first a gummy yellow mass, in which it was difficult to identify the crystals. On standing exposed to the air for about two months the mass changed completely into the well-defined white crystals of the normal ferric sulphate. Scharizer found that the yellow residue, after washing out the white salt, gave analytical results in favor of it being the basic salt. On the other hand Recoura, as will presently be pointed out, found the yellow the more soluble portion of the mass, and at any rate the washing of the precipitate before analysis is indefensible in view of the marked and ready hydrolysis of the salt. The evidence advanced for the presence of the acid salt is equally untenable, as neither hydrolytic nor absorption

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[1] Zeit. Kryst. Min., 34, 113 (1907).

effects were considered. The procedure consisted in exposing the mixture to moist air and analyzing the first drops of the drainage, which naturally contained more acid than the formula of the normal salt requires.

In a recent paper Recoura[1] describes a basic iron sulphate to which he assigns the definite formula $7Fe_2O_3.18SO_3.39H_2O$, and states that it persists in contact with solutions over quite a wide range of concentration. Our results, however, fail to confirm the existence of this compound. Under equilibrium conditions no definite basic sulphate exists in contact with solutions of iron and sulphuric acid, but there is a series of solid solutions varying in composition from one approximating ferric hydroxide to one approximating normal ferric sulphate.

For the experimental part of this work a series of shaking bottles containing ferric sulphate solutions of varying concentrations were saturated with freshly precipitated ferric hydroxide and shaken at a constant temperature of 25° C for four months. At the end of this time the specific gravities of the solutions had become constant.

The precipitate was allowed to settle completely and the clear solution drawn out and analyzed. The ferric hydroxide was precipitated in the cold with an excess of ammonia in *dilute* solution, and after thorough washing was dissolved on the filter and reprecipitated. The sulphuric acid in the combined filtrates was estimated in the usual gravimetric manner. The accuracy of the method is shown by the results of test analyses on known solutions given in Table III.

TABLE III

Test determinations of sulphuric acid and iron.

Number	Fe_2O_3		SO_3	
	Added	Found	Added	Found
1.	0.0792	0.0792	0.2744	0.2741
2.	0.0792	0.0793	0.2744	0.2745
3.	0.1564	0.1564	0.2744	0.2742
4.	0.1564	0.1565	0.2744	0.2741

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[1] Ann. Chim. Phys., 11, 263 (1907).

The results obtained from the series of bottles are given in Table IV and plotted in Fig. 1. In this diagram the line OA represents the concentrations of solutions in equilibrium

TABLE IV

Solubility of ferric oxide in aqueous solutions of sulphuric acid

Sp. Gr. $\frac{25°}{25°}$	Percent Fe_2O_3	Percent SO_3	Solid phase
1.001	0.07	0.11	Solid solution
1.006	0.21	0.34	" "
1.011	0.62	0.94	" "
1.024	0.95	1.48	" "
1.045	2.03	2.65	" "
1.084	3.89	4.91	" "
1.131	6.18	7.40	" "
1.180	8.22	10.00	" "
1.217	10.03	11.84	" "
1.245	11.31	12.91	" "
1.300	14.05	15.98	" "
1.440	15.90	20.70	" "
—	20.48	26.18	Normal sulphate
—	19.77	28.93	" "
—	10.87	31.35	Acid sulphate
—	0.16	35.96	" "
—	0.07	41.19	" "
—	1.05	42.43	" "

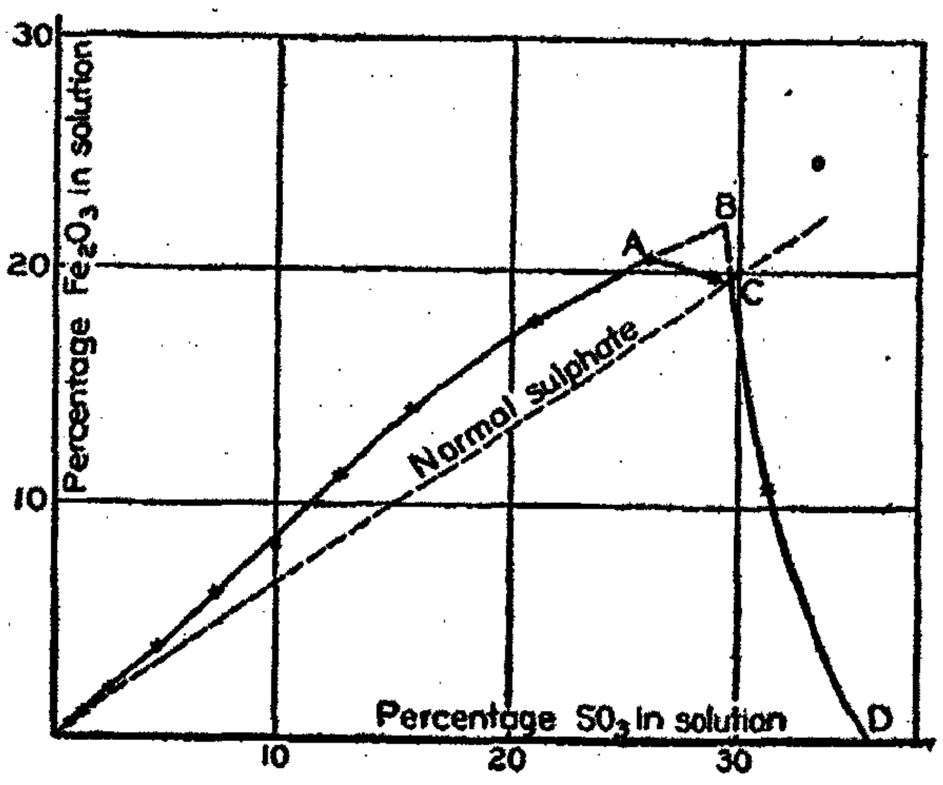

Fig. 1

with a series of solid solutions as solid phases. The line AB represents the solutions in contact with the hydrated normal sulphate, $Fe_2O_3.3SO_3.10H_2O$ as the stable solid phase, and the line BD the solutions in contact with the hydrated acid sulphate, $Fe_2O_3.4SO_3.10H_2O$ as the stable solid phase. The point C represents the composition of the solution at which the acid sulphate can coexist with a basic sulphate but in metastable equilibrium. The dotted line OB represents the solutions in which the ratio of iron to sulphuric acid corresponds to $Fe_2O_3 : SO_3$.

It is interesting to compare this curve with a line representing the composition of the normal sulphate. Up to concentrations of about 2 percent ferric sulphate the solution contains an excess of sulphuric acid; from that concentration up to about 30 percent sulphuric anhydride the solution contains an excess of ferric oxide; from this point on the solution again contains an excess of acid. This comparison shows why, on high dilution, solutions of normal ferric sulphate give a deposit, while solutions of moderately great concentration have the power of dissolving ferric oxide as Maus and later investigators have shown.

As a further proof of the conclusion drawn from Scharizer's work, the composition of some of the solutions and their respective precipitates with adhering mother-liquor have been determined and are given in Table V. The graphic

TABLE V

Showing the composition of solid phases

Solution		Solid with adhering mother-liquor	
Fe_2O_3	SO_3	Fe_2O_3	SO_3
Percent	Percent	Percent	Percent
0.07	0.11	26.40	1.95
1.66	2.18	22.70	3.17
4.03	5.22	28.10	5.45
5.69	7.40	46.40	7.58
6.87	8.99	80.20	8.20
15.24	11.09	45.51	18.48
15.90	20.70	45.46	22.34
0.16	36.00	18.60	45.30
0.08	41.20	17.60	46.10

representation of their analyses in Fig. 2 shows no common point, and in no case is it possible for the precipitate to contain more than 9 percent SO_3 for the lower concentrations. Should the precipitate correspond to the formula assigned by Pickering these lines would cross the line joining the H_2O apex and a point representing 20 percent SO_3 and 80 percent Fe_2O_3.

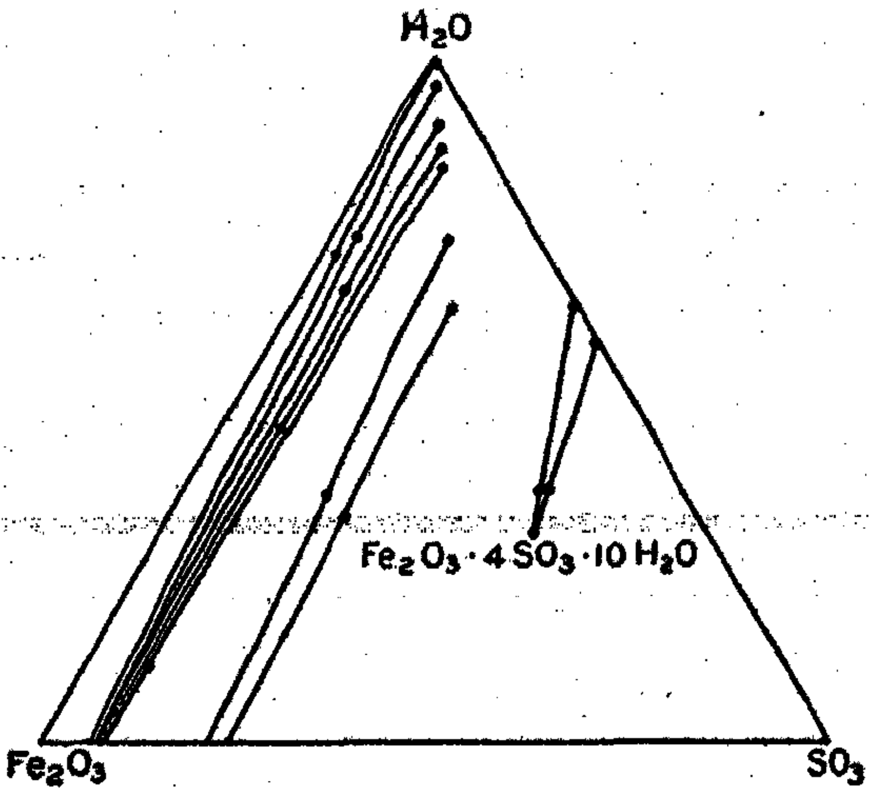

Fig. 2

Normal Ferric Sulphates

The anhydrous normal ferric sulphate is a light yellowish powder, which can be obtained readily by dissolving ferric oxide in an excess of sulphuric acid and then evaporating the excess of acid. In contact with water or moist air it is more or less slowly transformed to the hydrate, $Fe_2O_3.3SO_3.10H_2O$, as a white or pale yellow mass of very fine crystals.

Oudemans[1] found that normal ferric sulphate with ten molecules of water of crystallization was formed when a ferrous sulphate solution was oxidized with nitric acid and evaporated.

To prepare this compound, anhydrous ferric sulphate containing an excess of sulphuric acid was treated with water

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[1] Rec. Trav. Chim. Pays-Bas., 3, 331 (1884).

and shaken at 25° for two weeks. The residual solid was separated by filtering through asbestos, pressed between filter-papers and was found to contain 26.37 percent Fe_2O_3, 41.75 percent SO_3, and by difference 31.88 percent H_2O. These figures correspond to the formula $Fe_2O_3.3.16SO_3.10.7H_2O$. The high results for sulphuric acid and water are due to occluded or adsorbed mother-liquor, and this sulphate is probably identical in composition with that described by Oudemans.

Recoura ascribes 9 molecules of water to this compound and states that when ground still finer and exposed to a small amount of water or even moist air it changes to a second isomeric modification. This last hydrate, described as a white compound in contradistinction to the yellow one, shows different *rates* of solubility in water and alcohol. But both hydrates as well as the anhydrous salt yield identical aqueous solutions.

Our observations would indicate that this supposed second hydrate was identical with the yellow modification, except in being somewhat purer and more finely divided. The different rates of solution which Recoura observed were due probably to the presence of mother-liquor in or upon the yellow crystals. This view was confirmed by a microscopic examination of the supposed modifications as obtained by us.

Acid Ferric Sulphates

Scharizer[1] isolated an acid ferric sulphate to which he ascribed the formula $Fe_2O_3.4SO_3.6H_2O$. Recoura[2] and Komar[3] found an acid ferric sulphate of the composition $Fe_2O_3.4SO_3.9H_2O$. Recoura states that on heating above 80° this compound slowly loses water to form the trihydrate, which last breaks down above 135°, or in the presence of concentrated sulphuric acid at 250°, forming the anhydrous normal sulphate.

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[1] Zeit. Kryst. Min., 35, 345 (1901).

[2] Comptes rendus, 137, 118 (1903). Ann. Chim. Phys. [8], 11, 263 (1907).

[3] Chem. Zeit., 30, 15 (1906).

In Fig. 2 there is a graphical representation of the results obtained by the analysis of two mother-liquors and their corresponding precipitates. The lines intersect at a point representing a solid of the composition $Fe_2O_3.4SO_3.10H_2O$.

Conclusions

It has been shown in this paper, that at 25° C:

(1) There are no definite basic ferric sulphates formed. In contact with a solution containing less than about 25 percent sulphuric acid (SO_3), the stable solid is one of a series of solid solutions containing ferric oxide, sulphuric acid, and probably water.

(2) In contact with solutions containing from about 25 to 28 percent sulphuric acid (SO_3), the stable solid is a hydrated normal sulphate of iron of the composition $Fe_2O_3.3SO_3.10H_2O$.

(3) In contact with solutions of a concentration greater than about 28 percent sulphuric acid (SO_3), the stable solid is a hydrated acid sulphate of the composition $Fe_2O_3.4SO_3.10H_2O$.

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THE SOLUBLE BASIC SULPHATES OF BERYLLIUM

BY CHAS. L. PARSONS, W. O. ROBINSON AND C. T. FULLER

Normal salts of beryllium in aqueous solution have the property of dissolving large amounts of beryllium hydroxid or basic beryllium carbonate. This property is much more marked with this element than with the normal salts of iron, aluminum and zinc, all of which have been shown to dissolve considerable amounts of their own hydroxids. With beryllium the excess of base dissolved varies with the anion of the salt, the temperature, and the concentration. With the sulphate, in concentrated solutions, it is as great as three equivalents of beryllium oxide to one of sulphur trioxide and even greater in case of the nitrate, chloride, and acetate. When these concentrated solutions are diluted with water, precipitates of a highly basic nature are thrown out. These general reactions were pointed out by one of us,[1] and the precipitate in the case of the sulphate shown to be the hydroxid containing small variable amounts of occluded or dissolved normal salt. The same was also found to be true in the case of the oxalate.[2] The object of this research was to determine the character of the *soluble* basic beryllium sulphates.

A number of authors have shown that beryllium hydroxid dissolves readily in solutions of the hydroxids of sodium and potassium and it has been assumed that beryllonates are formed. This is confirmed by experiments to be cited later. The fact that the normal and basic sulphates are strongly acid in reaction to indicators, readily set free carbon dioxid from carbonates, and give off hydrogen when treated with zinc, probably indicate a high concentration of hydrogen ions, although Stewart[3] has proven that a very small excess of base completely destroys the power to invert cane sugar.

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[1] Parsons: Jour. Am. Chem. Soc., 26, 1347 (1904).

[2] Parsons and Robinson: Ibid., 28, 555 (1906).

[3] Jour. Am. Chem. Soc., 26, 1432 (1904).

Further, Leys[1] and Brunner,[2] have shown that the salts of beryllium are less hydrolyzed than the corresponding salts of iron and aluminum.

It was hoped that light might be thrown on the nature of solutions of basic beryllium salts by freezing-point, dialysis, transference, and conductivity experiments with the sulphate.

Preparation of Material

The normal sulphate was prepared in the usual manner[3] from a pure oxide and a very pure product obtained by several crystallizations from alcohol and finally from distilled water in platinum. A very pure beryllium hydroxid containing a slight amount of carbon dioxid was made by dissolving in ammonium carbonate and precipitating the basic carbonate with steam. After thorough washing with hot water the basic carbonate was boiled with frequently renewed water and air bubbled continuously through the mass. Another unpublished investigation has shown that the ammonia could not be nearly all removed by washing alone but by the treatment outlined above the hydroxid contained only the merest trace of ammonia and a very little carbon dioxid which was immediately given off when the hydroxid was dissolved in the hot solution of the sulphate. The hydroxid thus obtained contained 52.59 percent BeO.

Freezing-point Determinations

Cryoscopic determinations were carried out, using from 50 to 60 cc for the concentrated solutions and larger apparatus and 500 cc for the dilute solution measurements.

As the normal tetrahydrated sulphate was stable in air, small successive portions were dissolved in a weighed amount of water. The usual precautions were carried out and three determinations made for each point. The data are given in Table I and are graphically represented in Fig. 1.

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[1] Zeit. phys. Chem., 30, 11, 213 (1899).

[2] Ibid., 32, 133 (1900).

[3] Jour. Am. Chem. Soc., 26, 1434 (1904)

TABLE I

	Grams $BeSO_4.4H_2O$ per 100 grams H_2O	Grams SO_3	Lowering
1	0.0000	0.0000	0.000°
2	0.6680	0.3018	0.103
3	1.4950	0.6754	0.206
4	2.3680	1.0700	0.305
5	3.0210	1.3650	0.374
6	4.0500	1.8300	0.474
7	6.9000	3.1170	0.772
8	8.8960	4.0170	1.033
9	11.3000	5.1050	1.283
10	17.1500	7.7470	2.000
11	20.1000	9.0800	2.390
12	22.33	10.09	2.780
13	27.43	12.39	3.525
14	31.59	14.27	4.285

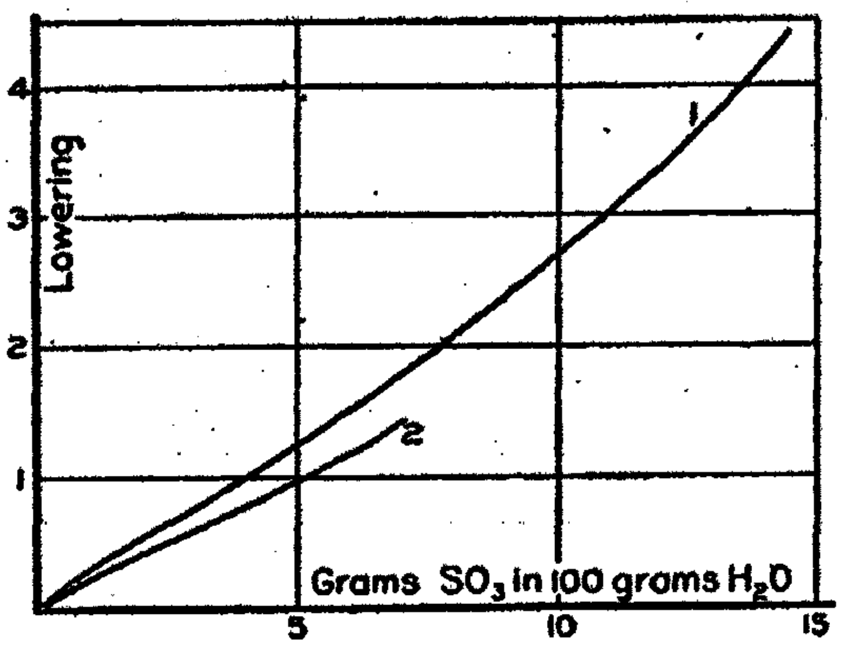

Fig. 1

To determine the effect of the dissolved hydroxid upon the freezing point, a concentrated solution was prepared by dissolving an amount of beryllium hydroxid in an analyzed solution of the normal salt so that the resulting solution contained 12.00 percent BeO, 25.51 percent SO_3 and 62.49 percent H_2O. This solution was added in small successive portions to 50 cc of water and the determinations made as with the normal sulphate. The ratio $\frac{BeO}{SO_3} = 3:2$ was chosen because it is the highest basicity that is soluble in all concentrations. The basic salt was weighed out in the form of a concentrated solution already in equilibrium with the atmosphere, because the solid residue was so hygroscopic that it could not be weighed. The results are given in Table II and plotted in Fig. 1 as curve (2).

TABLE II

Initial weight of water = 49.842 grams
Basic solution contains 25.51 percent SO_3, 12.00 percent BeO and 62.49 percent H_2O

	Wt. sol.	Wt. SO_3	Wt. H_2O	Total H_2O	Grams SO_3 per 100 g.	Lowering
1	0.8040	0.2050	0.502	50.34	0.407	0.118°
2	1.6375	0.4178	1.023	50.87	0.821	0.203
3	3.0345	0.7739	1.896	51.74	1.496	0.329
4	4.4285	1.132	2.768	52.61	2.152	0.451
5	6.2492	1.593	3.904	54.75	2.911	0.603
6	8.6690	2.212	5.544	55.39	3.992	0.787
7	11.1685	2.847	6.977	56.86	5.012	0.991
8	14.2060	3.624	8.880	58.12	6.173	1.228
9	16.5955	4.234	10.37	60.21	7.031	1.431

It is apparent that, in concentrated solutions at least, the solution of beryllium hydroxid in beryllium sulphate diminishes the osmotic effect and consequently raises the freezing-point. It is also interesting, though of doubtful application, that the curve for the normal sulphate starts out like any dissociated salt, showing a decrease in ionization with the concentration. After a certain point the curve changes its direction and becomes convex toward the axis and exactly coincides with a theoretical curve formed by the tetrahydrate withdrawing water from the solution to form a decahydrate molecule.

The freezing-point lowering in dilute solution was also measured, using 500 grams water and the same basic solution as was employed in Table II. The results obtained are given in Table III. Each determination is the mean of from three to five observations.

TABLE III

	Grams solution	SO_3 per 1000 g. H_2O	Lowering
1	0.4028	0.2056	0.0107°
2	0.8451	0.4312	0.0210
3	1.5014	0.7658	0.0313
4	2.1619	1.1028	0.0423
5	2.7852	1.4206	0.0503

The results are plotted in Fig. 2, curve (2), together with the curve for the normal salt taken under the same conditions. Here, again, it is plain that there is a distinct rise in the freezing-point due to the dissolved hydroxid.

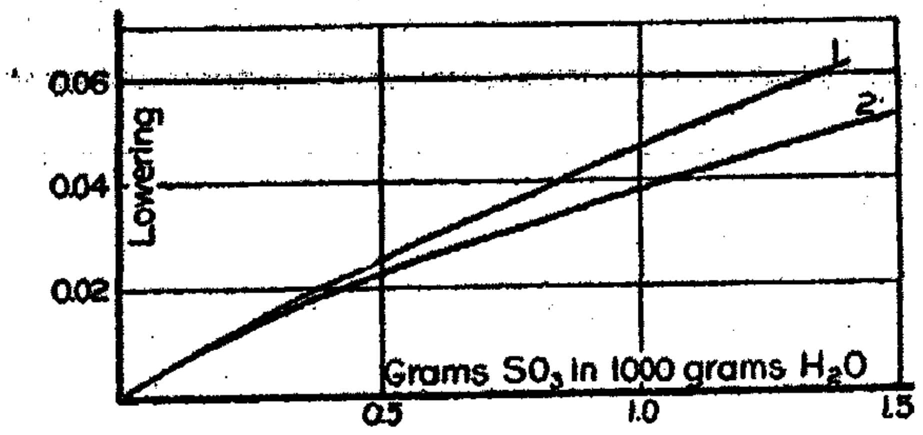

Fig. 2

The results from the freezing-point determinations alone would seem to indicate that (1) there is an actual compound formed between the normal sulphate and the hydroxid giving a less number of effective osmotic parts; or (2) there is in some way an aggregation of the dissolved molecules; or (3) that the excess of hydroxid is colloidal in its nature and interferes with the free movement of the crystalloid particles.

Dialysis

Trials to precipitate the soluble basic sulphate by electrolytes gave negative results. Dialysis through parchment tubes and gold beaters' skin, although unsatisfactory from a quantitative standpoint, showed conclusively that the membranes tended to separate the excess of base from the normal salt when the basic sulphate was dialyzed, though large amounts of the basic material came through.

The qualitative results entirely confirmed the conclusion drawn from the experiments with the electrolytes, that we were not dealing with a true colloid. Two characteristic trials may be cited to advantage. (1) A solution of basic beryllium sulphate, BeO : SO_3 = 3 : 1, was put inside a carefully tested membrane and dialyzed in a beaker of pure water. The dialyzed solution varied in composition from 1.66 BeO : 1 SO_3 to 1.81 BeO : 1 SO_3, and a considerable portion of $Be(OH)_2$ was found on the inside of the tube. (2) Another solution BeO : SO_3 = 1.5 : 1 was dialyzed through gold beaters' skin. Analyzed portions of the outside liquid after twenty-four to forty-eight hours showed ratios varying from 1.1 BeO : 1 SO_3 to 1.2 BeO : 1 SO_3 and again $Be(OH)_2$ was thrown out on the inside of the tube. When normal beryllium sulphate was dialyzed, no such separation of the hydroxid took place. These conditions are perfectly analogous to the results obtained when a solution of camphor in aqueous acetic acid is dialyzed as will be shown in the following paper.

Ion Transference

If beryllium sulphate formed a complex ion with beryllium hydroxid, it would be difficult to conceive of its existing in any other form than an anion. If the excess of beryllium over the amount present in the normal salt does not exist, it can be easily shown by qualitative transference experiments. To see whether complex ions were formed or not, the following experiments were carried out in the usual form of apparatus used for that purpose, the cut of which is shown in Fig. 3. A coil of platinum wire was used as the cathode and a piece of pure silver as the anode. The voltage between the terminals varied between sixty and seventy-five. The resistance of the solution was such that less than one-tenth ampere passed during the first stages of the electrolysis. The whole apparatus was immersed in a thermostat regulated at 25°. It was first entirely filled with half normal sulphuric acid and when the temperatures had been equalized, half normal sulphuric acid containing normal beryllium sulphate was drawn into portion B through the tube T. The current was passed for four hours. At the end of this time portions EE were carefully removed with a pipette and were found to contain no beryllium.

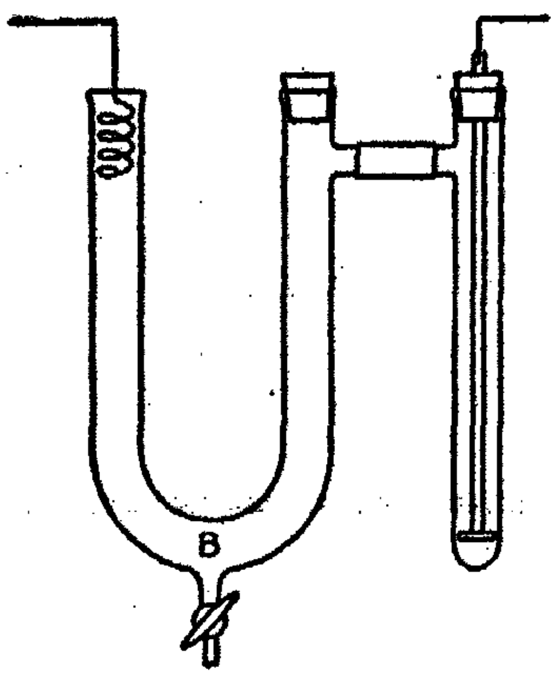

Fig. 3

The experiment was repeated, using half normal potassium nitrate. In this case as before the beryllium formed no anion.

The basic solution, $BeO:SO_3 = 3:2$, was drawn into section B and electrolyzed for four hours in a solution of half normal potassium nitrate. No anion of beryllium was formed.

Beryllium sulphate was dissolved in potassium hydroxid drawn into section B and electrolyzed in a half normal solution of potassium hydroxid as before. At the end of the experiment beryllium was found in both the anode and cathode portions.

These experiments show that the basic sulphate solutions contain no complex anion, of which beryllium is a constituent.

Conductivity

The conductivity was determined in the usual manner at 25° upon the normal sulphate and upon the basic sulphate solution of the ratio $1.5\ BeO : 1\ SO_3$, with the following results:

Normal sulphate		Basic solution
Normality	μ	μ
N/50	67.1	56.9
N/100	77.2	67.0

These figures show that beryllium hydroxid diminishes the conductivity of normal beryllium sulphate solutions.

To Summarize

We have shown that dissolving beryllium hydroxid in normal beryllium sulphate solutions raises its freezing-point and diminishes its conductivity; that the solutions so obtained are not true colloids; and that they contain no beryllium in the anion.

When this paper was presented at the Ithaca meeting of the American Chemical Society in June, 1906, it was suggested by Dr. Wilder D. Bancroft, in the discussion that followed, that the facts presented were perfectly analogous to such cases as the solution of water in mixed solvents of benzene and alcohol and that the whole phenomena might be a similar case of simple solution. This is the point of view we now hold, and our reasons are discussed by one of us under the broader questions of solutions in binary mixed solvents in the following paper.

New Hampshire College,
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SOLUTION IN A DISSOLVED SOLID

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It was shown in the preceding paper that when beryllium hydroxid dissolves in a solution of one of its normal salts no evidence of any molecular complex or colloidal condition could be obtained, and it was proposed as a solution of the problem that the dissolved beryllium salt acted as a solvent for the beryllium hydroxid in exactly the same manner that acetic acid dissolved in water will dissolve camphor which is itself insoluble in water. It was stated that the two cases were perfectly analogous in their physical chemical behavior, and since no assumption of complexes was necessary in the one case none was necessary in the other. It is the purpose of this paper to study in some detail ternary mixtures in which the solute is itself insoluble or but slightly soluble in that one of the mixed solvents which first separates as a solid phase on cooling. There can be no question that the study could well be made to include the whole field of ternary mixtures and that much light would be thrown upon some obscure questions by so doing, but it is without the province of the present paper or its author to enter into the broader subject.

Two facts should be stated: First, there has been for some time in the literature of chemistry a clearly defined principle, apparently unnoticed by most writers, which will explain many of the seeming discrepancies of the dissociation theory without the assumption of complex molecules. Second, a dissolved solid itself frequently acts as a solvent or, if one prefers so to view it, alters the nature of the liquid in which it dissolves, the resultant solution becoming a true solvent with an entirely different freezing-point which is *raised* in the particular case under consideration. It may be, however, variously affected according to the solubility relations which the three components of the ternary mixture bear to each other. Unfortunately the effect must, for the present at least, remain qualitative only.

The teacher of modern physical chemistry has many seeming discrepancies among the results of experiment to explain, or to pass over as unexplainable in the present condition of the science, and in no branch of his efforts is he more handicapped than in a critical study of the theory of electrolytic dissociation. The bright student, who is told that a molecule of an undissociated substance lowers the freezing-point of water 1.86° but that if the freezing-point actually found happens to be too high it is caused by the molecules forming a smaller number of complexes, while if it is too low, it is explained by partial or complete dissociation into ions, while if altogether too low for this to apply it is due to the molecules removing water from the solution to form hydrates and thus diminishing the mass of the solvent, finds himself in the same state of mind that the modern scientist views the ancient "quintessence," although that principle, since it conveniently explained everything, was sufficient for the philosophy of an Aristotle.

Anything, therefore, which serves to remove the necessity for such supposition is to be welcomed, and while the present writer by no means doubts the existence of complex molecules he believes they have many times been assumed to exist where the facts are quite the opposite and that a logical explanation without the necessity of the assumption will help rather than injure the theory of electrolytic dissociation.

In the literature we find many instances where the freezing-point has appeared abnormally high and where consequently complex molecules have been assumed; we also find[1] a perfectly logical and irrefutable qualitative explanation of such facts without any such assumption, although no application is pointed out.

R. Mihaly[2] finds that water exerts great influence on the freezing-point of a mixture of benzene and alcohol and that the

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[1] Miller: Jour. Phys. Chem., 1, 634 (1897).

[2] Zeit. phys. Chem., 24, 13 (1897).

addition of successive amounts of water *raises* the freezing-point continuously to the point where the whole separates as two liquid layers. The results are ascribed to the formation of the complex $9C_2H_5OH.3H_2O$ which, on dilution, breaks down conveniently into $6C_2H_5OH.2H_2O$ and $3C_2H_5OH.H_2O$ as becomes necessary to satisfy the particular freezing point obtained. Mihaly finds similar results when water is added to a mixed solution of benzene and phenol and here the complex is supposed to be $2C_6H_5OH.H_2O$ which, upon dilution, dissociates into water and phenol, but even then the supposition does not fully explain the abnormal freezing point. Quite comparable results are also obtained by the addition of water to a mixture of benzene and acetic acid and also Mihaly states that when glycerine, lactic acid or other material was used which was soluble in the dissolved liquid but insoluble in benzene, perfectly analogous results were obtained and considers the result due to complex molecules.

LeBlanc and Noyes[1] find that lead nitrate added to a solution of potassium nitrate does not lower the freezing-point so much as when added to solutions of sodium nitrate and that its solubility in water is greatly increased by the addition of potassium nitrate. It is assumed that double salts must be formed. Working with $HgCl_2$ in aqueous hydrochloric acid like results were obtained, and it was concluded that all the $HgCl_2$ and HCl is combined as the double salt, $HgCl_2.2HCl$, which breaks up on dilution. If NaCl or KCl were substituted for the HCl, like effects were noticed, and in each case the solubility of the $HgCl_2$ is notably increased over that in pure water.

LeBlanc and Noyes also made a study of the effect of iodine upon a solution of potassium iodide and of silver cyanide upon a solution of potassium cyanide and in both instances found that the freezing-point was *raised* by the addition of the solute. In the case of potassium iodide the reason assigned was the formation of KI_3 and they also con-

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[1] Zeit. phys. Chem. 6, 386 (1890).

cluded that the amount of free iodine present must be very small and no greater than its solubility in pure water. With potassium cyanide the formation of $KAgCN_2$ was not sufficient to satisfy the results and the explanation was offered that AgCN was added in stages to 3KCN, forming the complexes $K_3Ag(CN)_4$, $K_3Ag_2(CN)_5$ and $K_3Ag_3(CN)_6$. LeBlanc and Noyes also studied the conductivity of most of the mixtures and the conductivity decreased in each case, a result in accord with the assumption of a smaller number of molecules being formed.

Waddell[1] shows that salicylic acid added to a mixture of acetone and water raises the freezing-point of the solution and that the same result is obtained if phenol, paranitrophenol or hydroquinone is the solute. He makes no assumption of complexes being formed as he expected these results from a study of McIntosh's generalization[2] that the "addition of a substance to a binary solution in equilibrium with a solid phase raises the freezing-point if the substance added be non-miscible with the component appearing as solid phase." McIntosh studied the addition of water to a mixture of benzene and methyl alcohol, and to a mixture of benzene and ethyl alcohol and found that the freezing-point was raised in each case. He also found that the further addition of cupric chloride, which is insoluble in benzene, to these solutions caused a further rise in the freezing-point.

The whole matter has been beautifully cleared up mathematically by Miller,[3] who, starting with a theorem of Gibbs, shows thermodynamically that in all such solutions as those so far cited the freezing-point must rise. According to Miller this becomes apparent since Gibbs has shown the connection between the potentials of the various components of a liquid or solid phase and their vapor tension,[4] and Guldberg[5] has

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[1] Jour. Phys. Chem., 3, 160 (1899).

[2] Ibid., 1, 492 (1897).

[3] Ibid., 1, 634 (1897).

[4] Gibbs, p. 225.

[5] Comptes rendus, 70, 1349 (1870).

shown the relation between vapor tension and freezing-point, and van't Hoff[1] has shown the relation between vapor tension and osmotic pressure. Miller completes the chain by showing that the potential is a function of the solubility and that if a solution of a substance S be prepared of equal concentration in different solvents, the potential will be greatest for that solution which is nearest saturated; or the greater the solubility in any solvent the less the potential for any given concentration. Therefore, when to a solution of S in a liquid mixture of A and B there be added an additional quantity of A, the potential will be increased if less S can dissolve in the mixture after addition of A than before and *vice versa.* It follows from this that where the solubility of a substance in a mixed liquid consisting of two substances A and B is diminished by addition of the substance A, which separates as the solid phase on cooling, the addition of A will raise the potential of S and its vapor tension and the temperature at which it is in equilibrium with solid A will rise also. These are exactly the conditions in every case cited above. Miller points out further the bearing upon the freezing-point, boiling-point, etc., of ternary solutions under conditions other than the particular one above cited, but the far-reaching effect upon the question of molecular complexes, dissociation and abnormal lowering is not indicated and seems to have been lost from sight by subsequent writers. This is true in the case where a dissolved solid takes the place of a second liquid, for then the number of published investigations is greatly multiplied.

Although the resemblance of a mixture of water and alcohol (or acetic acid) to a mixture of water and potassium iodide is obvious, it is certainly true that the thought of the average writer is that iodine will dissolve in the first mixture simply because it is soluble in alcohol, but the idea that it can dissolve in the second simply because it is soluble in potassium iodide seems never to have occurred to the many investigators of this interesting phenomena. It is certainly

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[1] K. Svenska Vet. Akad. Handl. 21, 21 (1884).

true that there are striking analogies in the two instances and the solubility of the iodine increases respectively with the concentration of the alcohol or the potassium iodide. It will be held by some, and perhaps correctly, that the iodine is not soluble in one component of the binary mixture but in the liquid phase considered as a single liquid. Since the difference is simply one of the melting-point of one of the components, there is no difference whatever between a dissolved solid and a dissolved liquid and we have just as good a right to consider the iodine as soluble in the potassium iodide, itself rendered liquid by its solution in water, as we have to consider it soluble in aqueous alcohol, and *per se*, there is no more necessity to assume the formation of complex molecules in the first case than in the second to explain a rise in the freezing-point. In both cases the results follow from Miller's[1] deduction, since the saturated solutions if diluted with water precipitate iodine. The value of this point of view becomes more apparent if we consider the solubility of iodine in aqueous acetic acid. Ordinarily this is considered a case of mixed liquids, but if we happen to be working at a temperature below 16.6° we are in reality dealing with a dissolved solid. Iodine raises the freezing-point of such a liquid as does camphor or any other solid which is soluble in acetic acid and insoluble or but slightly soluble in water, always providing of course we are working with such concentrations of acetic acid that it is water which first crystallizes on cooling.

The idea that there is probably little difference, if any, between a binary liquid mixture in which one component is a solid and where both components are liquid is by no means new and is discussed by Bancroft in his paper on ternary mixtures,[2] and indeed this author appears to have held clearly the idea that a solid in solution might act as a solvent.

Lumsden,[3] has recently given additional evidence as to

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[1] Loc. cit.

[2] Proc. Am. Acad., 30, 324, 365 (1894).

[3] Proc. Chem. Soc., 22, 307.

the status of a dissolved solid by showing from values deduced from atomic volumes and atomic refractions "that a solid assumes in solution the volume which the same weight of it would have if it existed as a liquid at the same temperature."

In order to study further the matter under discussion and if possible to bring additional evidence to bear on its solution, it was decided to make a study of the freezing-point, conductivity, and dialysis of some typical ternary mixtures. In a few instances only had the conductivity of such mixtures been studied and in those cases reported the conductivity had diminished where the freezing-point had risen, bearing out the assumption of the formation of complexes. It will be seen in the following pages that this is not always true but that quite to the contrary the conductivity may be notably increased while the assumed osmotic effect diminishes. It was thought, too, that dialysis might throw considerable light on the question, for where all three components of the ternary mixtures passed freely through parchment there would be a separation of that portion which diffused more readily, presumably the molecule of least molecular weight. On the other hand, if the solution contained complex molecules, these should pass through the parchment as such.

I desire to express my appreciation of the assistance of Messrs. J. C. Clark, C. A. Dodge and H. F. French in carrying out the main details of the experiments here described.

Camphor, Acetic Acid and Water

It is a well-known fact that camphor is fairly soluble in strong acetic acid, almost insoluble in water and that in a mixture of the two its solubility increases with the concentration of acetic acid. As it is difficult to imagine this substance forming a complex with the acetic acid and as it is a non-electrolyte, the case seemed worthy of study.

When camphor was added to aqueous acetic acid containing 33.1 percent CH_3COOH the following results were obtained. The exact mode of procedure was naturally to prepare the stronger solution first and dilute this with the pure solvent. The conductivities are expressed in reciprocal ohms.

Solvent, 33.1 grams acetic acid in 100 cc. solution
Solute, camphor

Grams camphor in 100 cc. solvent	Freezing-point
0.1098	+0.04
0.2606	+0.09

Specific conductivity 25°

33 percent acetic acid (1 cc. contained 0.3736 g. CH_3COOH) = 0.001521
1.5847 g. camphor in 1000 cc 33 percent acid (n/96) = 0.001505
3.1694 " " " " " " (n/48) = 0.001494
6.3388 " " " " " " (n/24) = 0.001479
12.6776 " " " " " " (n/12) = 0.001448
19.016 " " " " " " (n/8) = 0.001438

Solvent, 49.21 grams acetic acid in 100 cc
Solute, camphor

Grams camphor in 100 cc solvent	Freezing-point
0.1585	+0.125
0.4489	+0.205
0.6689	+0.475

Specific conductivity 25°

50 percent acetic acid (1 cc contained 0.5355 g. CH_3COOH) = 0.000942
1.5847 g. camphor in 1000 cc 50 percent acetic acid (n/96) = 0.0009298
3.1694 " " " " " " " (n/48) = 0.0009258
6.3387 " " " " " " " (n/24) = 0.0009118
12.6775 " " " " " " " (n/12) = 0.0008928
19.0162 " " " " " " " (n/8) = 0.0008690
38.0325 " " " " " " " (n/4) = 0.0008158
76.065 " " " " " " " (n/2) = 0.0007098

In studying the dialysis of these solutions of camphor only qualitative experiments were made but they are in perfect accord with the dialysis of beryllium hydroxid in beryllium sulphate solution mentioned in the preceding paper. The camphor passed readily through the membrane if the outer liquid was acetic acid. It was precipitated within the membrane and very little passed through if pure water was the outer liquid, while the acetic acid passed readily. If the acetic acid was allowed to concentrate in the outer liquid, more camphor passed and would probably have continued to the saturation point of this dilute acid.

Iodine, Acetic Acid, Water

The ternary mixture was prepared in the cold as it was found that the iodine attacked either the acetic acid or the water if the solution was heated in a pressure bottle to aid solution, as had been done with the camphor. The results on the freezing-point are quite similar to those with camphor, but the specific conductivity *increases* instead of diminishes.

Solvent, 49.21 grams acetic acid in 100 cc
Solute, iodine

Grams iodine in 100 cc solvents	Freezing-point
0.2180	+0.055
0.5782	+0.535

Specific conductivity 25°

50 percent acetic acid (1 cc contained 0.5355 g. CH_3COOH) = 0.0009381
1.3213 g. I in 1000 cc 50 percent CH_3COOH ($n/96$) = 0.001161
2.6427 " " " " " ($n/48$) = 0.001413
5.2854 " " " " " ($n/24$) = 0.001956
10.5708 " " " " " ($n/12$) = 0.003222

Lead Oxide, Lead Acetate, Water

The solubility of lead oxide (PbO) in lead acetate has long been known, and the resultant solution under the name of basic acetate has long been of importance for clarifying sugar solutions. The freezing-point is here again raised by the addition of the solute and we have a second instance where the conductivity increases, although not to so marked an extent. The lead oxide was made by igniting the nitrate.

Solvent, 16.248 grams lead acetate in 100 cc solution
Solute, PbO

Grams PbO in 100 cc solvent	Freezing-point
1.3316	0.09
1.8996	0.11
2.2160	0.12
2.6632	0.139
3.324	0.168

Specific conductivity 25°

3 percent lead acetate solution =0.004048
1.1600 g. PbO in 1000 cc 3 percent $Pb(C_2H_3O_2)_2$ (*n*/96)=0.004048
2.3220 " " " " " " (*n*/48)=0.004071
4.6441 " " " " " " (*n*/24)=0.004226
9.2883 " " " " " " (*n*/12)=0.004481

Iodine, Potassium Iodide, Water

The solution of iodine in aqueous potassium iodide presents striking analogies to many well-known facts connected with the solution of a solid in a binary liquid mixture. The solubility of the iodine increases with the concentration of the potassium iodide component, and it is precipitated in quantity from a saturated solution by addition of water. The freezing-point of a solution of potassium iodide is raised by the addition of iodine and its conductivity is diminished as has been shown by LeBlanc and Noyes.[1] Measurements made in this laboratory are entirely confirmatory of their experiments as the following tables will show.

Solvent, 10 grams KI in 100 cc. solution
Solute, iodine

Grams iodine to 100 cc KI solvent	Freezing-point
3.7155	+0.017
4.3348	+0.022
5.2016	+0.040
6.5022	+0.070

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[1] Zeit. phys. Chem., 6, 398 (1890)

Specific conductivity 25°

3 percent potassium iodine solution		=0.02271
1.3213 g. iodine in 1000 cc 3 percent KI	($n/96$)	=0.02248
2.6827 " " " " " "	($n/48$)	=0.02220
5.2854 " " " " " "	($n/24$)	=0.02193
10.5708 " " " " " "	($n/12$)	=0.02140
15.8562 " " " " " "	($n/8$)	=0.02080

The solubility of iodine in potassium iodide solutions has been extensively investigated with widely varying conclusions. It is not within the province of this paper to go at length into the literature or the results attained, as the subject is being studied in this laboratory and will be presented later in a special communication. It may be noted, however, that the comprehensive work of Jakowkin[1] is based wholly upon the distribution coefficient between iodine and water and if the iodine is also soluble in the potassium iodide, as it would be in a liquid like aqueous alcohol, his conclusions have nothing whatever to rest upon. The results of Noyes and Seidensticker[2] should be expected if iodine were largely soluble in potassium iodide and slightly soluble in water and the examination was made of solutions of high dilution but still strong enough to have the solvent action of the potassium iodide of account while weak enough to have the mass of the iodine dissolved in the water effective in the equation. It should also be remembered that while the mass law equation $KI_3 = KI \times I_2$ apparently holds for these dilute solutions it certainly does not hold in the strong solutions for where saturated with iodine, the equation becomes $KI_3 = KI \times$ *constant*, or the concentration of the KI_3 is directly proportional to the KI and dilution should bring about no precipitation of iodine which really occurs in large quantity.

The fact that other investigators have obtained solid residues which analyze in the ratio KI_3 is no proof whatever that this substance exists in solution; nor for that matter

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[1] Zeit. phys. Chem., 13, 539 (1894); 20, 19 (1896).

[2] Jour. Am. Chem. Soc., 21, 219 (1899).

is the solid itself necessarily more than a solid solution or perhaps even a mixture.

The last and best word upon the subject is from Abegg and Hamburger,[1] who have conclusively shown by equilibrium experiments that no polyiodide of lithium or sodium exists at 25° and that if there is a polyiodide of potassium it has a complexity of at least KI_7. Their melting-point data on mixtures of potassium iodide and iodine show that iodine is certainly soluble in large amounts in potassium iodide to form a solution which is liquid as low as 82°. It is certainly open to question whether they obtained a maximum in their curve near this temperature indicating the presence of KI_7 and the data would serve almost as well to show a flat in the curve and the probable separation into two liquid layers. Preliminary experiments made in this laboratory with mixtures of potassium iodide and iodine in the ratio $KI:3I_2$ melted easily at about 82°. The melt was sealed off in a closed tube and thoroughly mixed by shaking while melted. It was then kept for twenty-two hours in a thermostat at 85° and quickly cooled in cold water. On analysis the top portion showed a ratio as low as $1.5\ KI:I_2$ while the bottom of the mass gave $1KI:5.8\ I_2$ but both looked alike. While the mass was shown by analysis to be not homogeneous and was decidedly stronger in iodine in lower portions no evidence of two distinct liquid layers of definite concentration was obtained.

It is also interesting to watch the diffusion of iodine throughout a crystal of potassium iodide when the two are brought in contact although the cause therefor may be open to discussion.

Iodine and potassium iodide both pass freely through parchment when placed in contact with a liquid in which they are soluble. It was therefore reasoned that if a mixture of potassium iodide and iodine were subjected to dialysis the potassium iodide would pass much more rapidly through the membrane than the iodine if the liquid contained mixed

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[1] Zeit. anorg. Chem., 50, 403 (1906).

molecules of these two substances while if the molecule was present as KI_3 there was nothing in the nature of the membrane to cause it to separate into parts and the outer liquid should show the same $KI:I_2$ ratio on analysis. Numerous dialyses were tried and in every instance the potassium iodide passed through much more rapidly than the iodine as predicted. With a fairly strong solution solid iodine separated out in the inner compartment and this was the fact even in those cases where the inner solution was so dilute that iodine would not separate out on the addition of water. Unfortunately it is impossible, except with rather high concentration of potassium iodide, to reach a concentration of iodine so that the ratio $KI:I_2$ holds and in any less ratio than this the argument would at once be put forward that there were present molecules of KI_3 and KI and that in this mixture we should expect, even more, that the KI would diffuse the more rapidly. In order to overcome this difficulty a solution was chosen of such a strength that it contained in 100 cc 2.5 grams of KI in excess of that required for the ratio $KI:I_2$ or KI_3. From this solution no iodine was precipitated by dilution with 2.5 percent KI solution although it was precipitated by water. It was reasoned that if this solution was dialyzed into 2.5 percent KI as an outer solution the molecule KI_3 should pass as such if present, since the excess of KI, being of the same unit concentration in both inner and outer liquids, would pass equally in either direction and would in no wise influence the results. It will be at once apparent from the following data that even with this source of error removed the KI passes much more rapidly through the membrane; solid iodine separates in quantity within, owing to the lessened concentration of the dissolving KI, and there is no evidence whatever of any complex molecule passing the membrane as such. The dialysis was carried out in a parchment tube which was placed in 200 cc of the 2.5 percent potassium iodide solution so that the level of the two liquids was approximately the same, being a little higher, if anything, in the outer liquid and the two solutions were stirred throughout the experiment. At stated intervals the outer liquid was removed and replaced by a fresh portion.

Outside solution contained 5 grams KI in 200 cc of water = 30.135 m.mols.

Inside solution contained in 25 cc.

10.977 gms. KI = 66.126 m.mols.

16.163 gms. I = 63.68 m.mols.

$\frac{KI}{I_2} = 1.04.$

Analyses of outer solution after dialysis

No. of dialysis	Time in minutes	m.mols I_2	m.mols KI	$\frac{KI}{I_2}$
1	15	5.67	12.14	2.14
2	15	5.37	10.31	1.92
3	30	8.37	15.69	1.87
4	30	5.72	9.95	1.74
5	30	3.47	5.23	1.51

Inside solution after dialysis

m.mols I_2	m.mols KI	$\frac{KI}{I_2}$
6.7	13.6	2.009

besides which more than 7 grams of iodine had separated out in the crystalline condition within the tube. Of this amount 6.94 grams were collected and weighed, but a small portion could not be removed from the tube.

The total ratio of $\frac{KI}{I_2}$ was therefore less than 0.4 for the inside tube after the dialysis.

There can be no question that there was a decided separation of potassium iodide from iodine by means of the parchment, and it would scarcely seem probable that a membrane could decompose complex molecules if present while it should be remembered that an outer liquid was used which would not by itself precipitate the iodine if used as a diluent.

The free iodine was titrated with thiosulphate. The total iodine was determined in a separate aliquot part by distilling after addition of ferric chloride and sulphuric acid, in an apparatus with all joints of ground glass. The distillate which was received in potassium iodide solution was titrated with thiosulphate.

In order to run a check analysis on a compound where there could be no doubt as to the complexity of the molecule and to test the soundness of the reasoning in regard to the use of an outside solution of the same concentration as the excess of one of the components of the possible complex a solution of 2.5 grams potassium ferrocyanide in 25 cc of 1 percent KCN was dialyzed into successive portions of 200 cc each of 1 percent KCN in exactly the same manner as described in the foregoing experiments. The results are entirely in accord with the supposition made, the potassium ferrocyanide passing readily through the membrane as $K_4Fe(CN)_6$ while the concentration of the KCN in both inner and outer solution remained unchanged.

Number of dialysis	N/10 I solution taken for 25 cc	$KMnO_4$ solution taken for 50 cc	Total millimols KCN in the surrounding liquid	Total millimols $K_4Fe(CN)_6$ in the surrounding liquid
1	76 0	10.0	76 0	4.005
2	75.0	9.1	75.0	3.647
3	74.5	7.7	74.5	3.086
4	74.5	7.1	74.5	2.845
5	74.5	7.0	74.5	2.805

74.5 cc *n*/10 iodine = 25 cc 1 percent KCN

0.07382 gm. $K_4Fe(CN)_6$ = 1 cc $KMnO_4$

As shown in the table the KCN was titrated with iodine and the $K_4Fe(CN)_6$ with $KMnO_4$ solution. The number of millimols of KCN runs slightly high in the first two dialyses owing to the effect which a large excess of $K_4Fe(CN)_6$ has on the titration as pointed out by Clennell.[1]

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[1] Chem. News, 72, 227 (1895).

Silver Cyanide, Potassium Cyanide and Water

This system offers a peculiarly interesting field for the application of the method of reasoning already proposed because there can be no doubt of the existence of the complex molecule $KAg(CN)_2$. The complexes $K_3Ag(CN)_4$, $K_3Ag_2(CN)_5$ and $K_3Ag_3(CN)_6$ have also been proposed as probable by LeBlanc and Noyes[1] to explain the extent to which the solution of AgCN in KCN raises the freezing-point and decreases the conductivity.

To investigate the point at issue three experiments were carried out. First a solution of the ratio $KAg(CN)_2$ was dialyzed and, as the data below will show, there was no separation of KCN from AgCN by the membrane but the molecule $KAg(CN)_2$ passed readily as such although no attempt was made to show the exact amount. Secondly, a solution of AgCN in KCN in the proportion to form the complex $K_3Ag_2(CN)_5$ was made up and dialyzed into pure water and the amount of KCN and AgCN that passed was determined. Finally, the same solution as used in the second experiment was dialyzed into KCN solution of such concentration that it was just equal to the concentration of the excess of KCN, over the complex molecule $KAg(CN)_2$, in the inside solution. The results are entirely confirmatory. In the second experiment the KCN molecules passed through more rapidly than the $KAg(CN)_2$ which is especially apparent when we remember that there were only half so many present and in the third experiment apparently only $KAg(CN)_2$ passed at all since the passage of the KCN was equally rapid in both directions, while the $KAg(CN)_2$ in both the second and third experiment passed in amounts which agree very closely when we consider that they were carried out at room temperature on different days. It would certainly seem that the existence of any complex other than $KAg(CN)_2$ was highly improbable.

Details of the three experiments mentioned follow:

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[1] Zeit. phys. Chem., 6, 397 (1890).

Experiment No. 1

50 cc of *n*/2 $KAg(CN)_2$ (*i. e.*, 25 cc *N* KCN solution saturated with AgCN and diluted to 50 cc with H_2O) were put in a parchment tube, and dialyzed for ninety minutes into 3, 200 cc portions of H_2O, each 200 cc being used thirty minutes.

Results

Number of dialysis	N/10 $AgNO_3$ taken to produce cloudiness in outer or inner solution
1	1 drop
2	1 drop
3	1 drop

Experiment No. 2

50 cc of a solution (50 cc *N* KCN saturated with AgCN, 25 cc *N* KCN added and the whole made up to 100 cc) were placed in a dialyzing membrane and dialyzed for ninety minutes into 3, 200 cc portions of H_2O, each 200 cc being used thirty minutes. Each 200 cc portion then made up to 250 cc with H_2O and 50 cc taken from each 250 cc and analyzed.

Results

Number of dialysis	N/10 $AgNO_3$ taken to produce cloudiness in 50 cc	Wt. of AgCN present in 50 cc	Total millimols KCN which passed through the membrane	Total millimols $KAg(CN)_2$ which passed through the membrane
1	2.4	0.0928	2.4	2.27
2	1.8	0.0772	1.8	1.98
3	1.5	0.0618	1.5	1.56

Experiment No. 3

50 cc of a solution (50 cc *N* KCN saturated with AgCN, 25 cc *N* KCN added, and the whole made up to 100 cc with H_2O) were placed in a dialyzing membrane and dialyzed for ninety minutes into 3, 200 cc portions of N/4 KCN, each 200 cc being run thirty minutes. 50 cc of each 200 were then

taken and analyzed. 50 cc *n*/4 KCN required 61.5 cc *n*/10 $AgNO_3$.

Results

Number of dialysis	N/10 $AgNO_3$ taken to produce cloudiness in 50 cc	Wt. of AgCN present in 50 cc	Total millimols KCN which passed through the membrane	Total millimols $KAg(CN)_2$ which passed through the membrane
1	61.0	0.8924	none	2.39
2	61.1	0.8843	none	1.96
3	61.2	0.8811	none	1.82

Borax, Boric Acid, Water

Boric acid has long been known to be more soluble in a solution of borax than in pure water, and polyborates have been assumed as necessary to explain the abnormal conductivity and freezing point lowering.

Kahlenberg and Schreiner[1] determined the freezing point lowering and the conductivity of boric acid and various mixtures of boric acid and sodium hydroxide. They showed that when boric acid was alone present in water the freezing point was in close theoretical agreement for the slightly dissociated acid. On the other hand, when the various sodium borates were experimented with, the results had to be explained by various assumptions depending upon the ratio between the constituents and their concentration. The most striking points brought out were that when sodium hydroxide and boric acid were mixed in the proportions $2NaOH + 4H_3BO_3$ the solution was identical with one obtained by dissolving an equivalent amount of borax; that if boric acid was added to either solution a relatively high freezing point was obtained which could be explained only by the assumption of polyborates, and that no single polyborate would explain the results. The rise in the conductivity was also shown to accord with this hypothesis.

The question of the presence of polyborates was also studied by Auerbach,[2] and later in a very exhaustive manner by Mueller

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[1] Zeit. phys. Chem., 20, 547 (1896).

[2] Zeit. anorg. Chem., 37, 353 (1903).

and Abegg.[1] Their conclusions were much the same and were to the effect that polyborates did exist in solution but that the conditions pointed to several complexes present at the same time. Mueller and Abegg studied especially the distribution coefficient of boric acid between amyl alcohol and water, and between amyl alcohol and water containing borax in solution, and they found from the free boric acid present no constant which would hold for either a di- tri-, tetra-, or pentaborate and concluded that several complexes must be present in equilibrium. For the purpose of the argument put forth in this paper, however, it should be remembered that their distribution coefficient depended upon the solubility of boric acid in water. If it is soluble in dissolved borate the same as if another liquid solvent were present, it of course leads to false conclusions as to the relative distribution of the boric acid.

The question seemed one particularly susceptible to the method of treatment already put forth, as all of the constituents pass readily through a membrane and the well-known methods of titration with the addition of glycerine made the details of analysis comparatively easy. If complex borates were formed they would either fail to pass through the membrane or would diffuse more slowly than the lighter and more rapid moving molecules. In either case the outer solution would become relatively poor in the boric acid content obtained by titration. On the other hand, if complexes were not formed the boric acid would naturally diffuse more rapidly than the borax, and the amount of that component in the outer solution would increase. It will be perfectly apparent from the experiments that the last supposition is what really takes place.

Solutions representing the following ratios were made up by dissolving boric acid in sodium hydroxide solution free from carbonate and were shown to be correctly prepared by titrating each solution.

$2NaOH + 4H_3BO_3$ (or $Na_2B_4O_7$).
$2NaOH + 6H_3BO_3$ (or $Na_2B_4O_7 + 2H_3BO_3$).
$2NaOH + 8H_3BO_3$ (or $Na_2B_4O_7 + 4H_3BO_3$).
$2NaOH + 10H_3BO_3$ (or $Na_2B_4O_7 + 6H_3BO_3$).

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[1] Zeit. phys. Chem., 57, 513 (1906).

Each solution contained the equivalents of 1 mol of sodium hydroxide in 5 liters.

Fifty cc of each solution was placed in a parchment tube and dialyzed for four successive periods of thirty minutes each into 200 cc of pure water at room temperature, both inner and outer solutions being stirred and the outer solution being replaced by pure water at the end of each period. The following results were obtained:

TABLE I

Inner solution, 1 mol NaOH and 2 mols H_3BO_3 in 5 liters

$NaOH : H_3BO_3 : : 1 : 2$

Outer solutions after dialysis

Time, minutes	cc N/5 HCl	cc N/5 NaOH	$\frac{\text{mols } H_3BO_3}{\text{mols NaOH}}$
30	8.0	16.5	2.06
30	7.2	15.2	2.11
30	5.8	12.5	2.13
30	4.9	11.2	2.27

The solute dialyzed apparently as borax, although there may be a slight tendency for the boric acid to go through the more rapidly. The difference of one-tenth in the ratio is, however, of light significance as the error is well within the limits of probability, considering the small amount of reagents used in titrating.

TABLE II

Inner solution, 1 mol NaOH and 3 mols H_3BO_3 in 5 liters

$NaOH : H_3BO_3 : : 1 : 3$

Outside solutions after dialysis

Time, minutes	cc N/5 HCl	cc N/5 NaOH	$\frac{\text{mols } H_3BO_3}{\text{mols NaOH}}$
30	6.6	27.4	4.12
30	6.9	24.0	3.46
30	5.8	20.0	3.40
30	5.2	17.0	3.28

It is evident that the boric acid separates by diffusion which would not be expected if it were part of a complex molecule.

TABLE III

Inner solution, 1 mol NaOH and 4 mols H_3BO_3 in 5 liters

NaOH : H_3BO_3 : : 1 : 4

Outside solution after dialysis

Time, minutes	cc N/5 HCl	cc N/5 NaOH	$\frac{\text{mols } H_3BO_3}{\text{mols NaOH}}$
30	8.5	42.1	4.93
30	5.8	28.5	4.86
30	5.3	25.0	4.70
30	4.9	22.4	4.54

The ratio of boric acid is again increased by diffusion.

TABLE IV

Inside solution, 1 mol NaOH and 5 mols H_3BO_3 in 5 liters

NaOH : H_3BO_3 : : 1 : 5

Outside solution after dialysis

Time, minutes	cc N/5 HCl	cc N/5 NaOH	$\frac{\text{mols } H_3BO_3}{\text{mols NaOH}}$
30	5.6	37.6	6.71
30	5.2	32.8	6.30
30	5.0	31.4	6.21
30	4.2	24.0	5.62

Again the boric acid ratio notably increased.

The results of these four sets of experiments are perfectly in accord with the supposition that the boric acid is simply more soluble in borax solution than in water and that it is mixed with borax rather than combined with it as a polyborate. It is not claimed that polyborates may not exist as solids but simply that when in solution they are not present as complex molecules nor is there any more need to assume them to be so than in the case of the alums where the freezing point is known to be in accord with simple rather than double molecules.

Summary

It is argued in this paper that a solid in solution may, and frequently does, act toward other solutes exactly as if it was a liquid miscible in the solvent in which the second solute was itself soluble.

It is shown that if this is the case many so-called abnormal osmotic effects are readily explained qualitatively without any other assumption than that of simple solution.

It is experimentally shown in many such instances, where complex molecules have been assumed, that the two solutes tend to separate from each other by diffusion through a membrane, permeable to either, while in other cases of undoubtedly complex molecules no such tendency exists and that the freezing-point and conductivity do sometimes, in the first instance, lead to opposite conclusions.

New Hampshire College,
June, 1907.

IMPROVED APPARATUS FOR THE DETERMINATION OF MOLECULAR WEIGHTS

(Taken as read before a meeting of the London Chemical Society, June 21, 1906. Compare Jour. Chem. Soc., 1906, Proc., pp. 175-177.)

BY PHILIP BLACKMAN

Isotonic solutions of two substances in the same solvent have equal vapour pressures, at the same temperature. The state of equilibrium is represented by the equation

$$\frac{m_1}{m_2} = \frac{w_1}{w_2} \cdot \frac{v_2}{v_1}$$

(w_1,w_2, are the respective weights of the substances of molecular weights m_1,m_2, dissolved in the solvent of volumes v_1,v_2). If two such solutions, maintained at the same temperature, have their vapours in communication by means of a suitable gauge, the indicator will remain stationary.

Unlike the previous methods described by the author, the success of which depends entirely on the regularity with which the solutions can be made to boil, this method is entirely free from this difficulty.

Apparatus

Two graduated boiling tubes and another similar ungraduated tube are each fitted with a three-holed rubber stopper; through each stopper of the graduated tubes passes a dropping funnel with a glass tap, the lower end of the funnel being drawn out to a point and reaching the bottom of the tube (or else, a piece of glass tubing, drawn out to a point, may be fitted by means of a piece of rubber tubing to the end of the funnel just below the cork). The two boiling tubes are connected by a gauge, fitted with a tap; a suitable liquid, one that is not affected by the vapour of the solvent, is used as index. The graduated tubes are both connected with the third tube by means of inverted U-pieces, also fitted with

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[1] Jour. Chem. Soc., 87, 1474 (1905). Proc. Chem. Soc., 21, 304 (1905). Chem. News, 93, 96 (1906).

taps. The third tube is furnished with a tube with tap. The three tubes should be arranged in the form of a triangle, so that the apparatus is self-supporting.

Method

(By using equal weights of the substances whose molecular weights are to be compared, the working and calculations are considerably simplified; the above equation, by putting $w_1 = w_2$, becomes $m_1/m_2 = v_2/v_1$). The weighed quantities of the two substances (about 0.1–0.5 gram) are introduced into the graduated boiling tubes, the stoppers fixed in position, and the necessary connections with the third tube made. The taps in the funnels and gauge are kept closed; a little of the solvent is added to the funnels to ensure that no air may find its way into the apparatus. The third tube is then connected, by means of the glass tap, with an exhaust pump, and as high a vacuum as possible is obtained. The taps in the ∩-tubes are then closed. The solvent is now added from the funnels, care being taken that

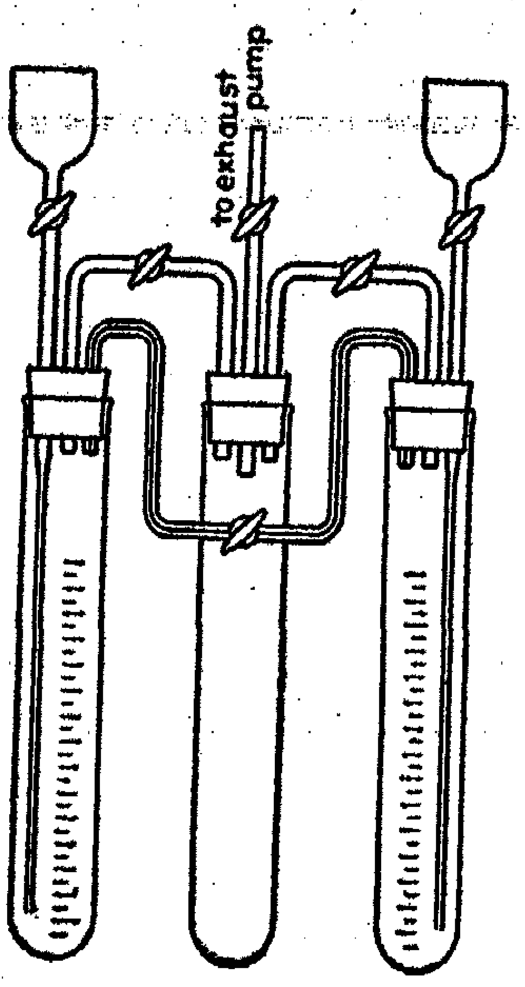

Fig. 1

it is not all drawn in, as risk of introducing air must be avoided; sufficient solvent must be introduced to cover the lower ends of the funnels. The substances must be left to dissolve, the process being quickened by slightly agitating the apparatus (which will also assist in producing uniformity of concentration). The tap in the gauge is cautiously opened (if care be not taken, the liquid serving as index may be forced into one of the solutions), and the movement of the indicator observed. This moves toward the tube in which the vapour pressure is smaller; consequently, if the solvent is added drop by drop into that tube, a stage—the equilibrium stage—is reached when the index is stationary, and the volumes of the solutions are read off. More liquid is next added to one of the solutions, and equilibrium again re-established by careful addition of solvent to the other, when another reading of the volumes is taken. This process is repeated as often as is desirable. Whenever liquid is added to the solutions, the apparatus should be agitated or left to itself for some time in order to insure uniformity of concentrations.

Precautions

The ends of the funnels should be drawn out to fine stems, otherwise thick-walled tubing will introduce error in the reading of the volumes, corrections in such cases being rather laborious to apply. It is extremely difficult to ensure that the taps are perfectly air-tight, and that no air finds its way into the tubes.

Advantages

(1) The apparatus is of fairly simple construction, and is not difficult to manipulate. (2) Good quantitative results could be obtained were it possible to completely overcome the mechanical difficulty of rendering the taps perfectly air-tight. (3) There is a wide choice of solvents (the more volatile the solvent, the better the results). (4) The method may be found useful in the study of the phenomena of "dissociation" and "association."

Suggestions

It is possible that, instead of using glass taps which are very difficult to render quite air-tight, it would be advantageous to employ pressure tubing with clips.

It may be found necessary to maintain the solutions at a uniform temperature by placing the apparatus in a trough of water or in some suitable thermostat.

The following is a simplified form of the apparatus. Each graduated tube is fitted with a two-bored rubber stopper through which pass the funnel and gauge; the funnels are fitted with one-bored rubber stoppers, connected by a T-piece in communication with an exhaust pump. The weighed quantities of the substances are introduced, the necessary connections made, the apparatus exhausted, the taps in the funnels closed, the T-piece with the stoppers removed, the solvent added, and the estimations made (see figure).

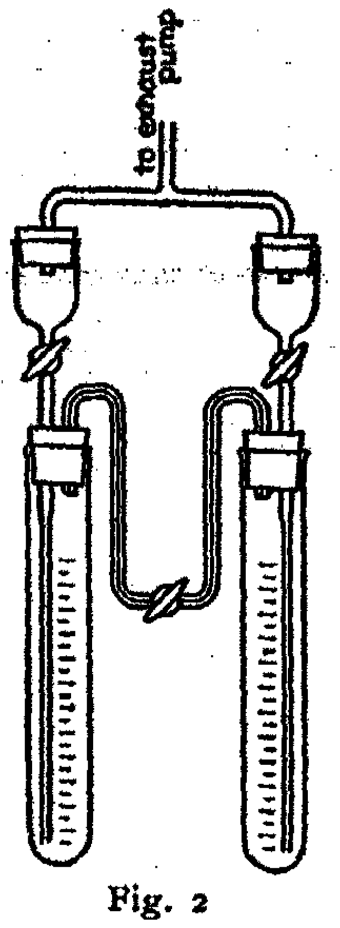

Fig. 2

Results

In all cases, ether was used as solvent, and concentrated sulphuric acid as index. The volumes (v_1v_2) were measured in cubic centimeters.

I. Compared *p*-dibrombenzene (m_1, v_1) with *p*-chlor-nitrobenzene (m_2, v_2). Equal weights of each (0.3 gram)

$m_1/m_2 = 236/157 = 1.5$

	v_1	v_2	v_2/v_1
(1)	5.0	7.5	1.50
(2)	8.0	11.75	1.47
(3)	10.0	14.75	1.48
(4)	11.0	16.25	1.48
		Mean	1.48

II (Test.) Determination of M. W. of unknown substance (m_1, v_1) by comparison with *p*-chlor-nitro-benzene (m_2, v_2). Equal weights (0.4 gram each)

	v_1	v_2	v_2/v_1
(1)	5.0	7.5	1.50
(2)	7.5	11.0	1.33
(3)	8.0	11.5	1.44
(4)	10.25	14.0	1.36
		Mean	1.41

$\therefore m_1 = m_2.v_2/v_1 = 157 \times 1.41 = 221.$

M. W. of α-brom-β-naphthol = 223.

Same compared with 1-chlor-2-4-dinitro-benzene (m_2, v_2)

	v_1	v_2	v_2/v_1
(1)	5.0	5.5	1.10
(2)	7.0	8.4	1.20
(3)	9.0	10.1	1.12
(4)	10.0	11.1	1.11
(5)	12.0	13.3	1.11
		Mean	1.13

$\therefore m_1 = 202 \times 1.13 = 228.$

III Compared picric acid (m_1, v_1) with 1-chlor-2-4-dinitro-benzene (m_2, v_2). Equal weights (each 0.35 gram)

$m_1/m_2 = 229/202 = 1.13$.

	v_1	v_2	v_2/v_1
(1)	5.0	5.5	1.10
(2)	10.0	11.5	1.15
(3)	15.0	16.5	1.10
		Mean	1.12

IV (Test.) Determination of M. W. of unknown substance (m_1, v_1) by comparison with *p*-dibrom-benzene (m_2, v_2). Equal weights (0.4 gram)

	v_1	v_2	v_1/v_2
(1)	6.5	5.0	1.30
(2)	13.2	10.0	1.32
(3)	14.5	11.0	1.32
		Mean	1.31

$\therefore m_1 = m_2 \div (v_1/v_2) = 236 \div 1.31 = 180.$

M. W. of 2-4-dinitro-toluene = 183.

Same by comparison with α-naphthylamine (m_2, v_2)

	v_1	v_2	v_2/v_1
(1)	5.0	6.3	1.26
(2)	7.0	8.9	1.27
(3)	9.0	11.1	1.23
(4)	12.0	14.9	1.24
		Mean	1.25

$\therefore m_1 = 143 \times 1.25 = 179.$

V (Test.) Determination M. W. of unknown substance (m_1, v_1) by comparison with 1-chlor-2-4-dinitro-benzene (m_2, v_2).
Equal weights (0.3 gram)

	v_1	v_2	v_1/v_2
(1)	6.5	4.0	1.62
(2)	7.25	4.5	1.61
(3)	8.25	5.5	1.50
(4)	9.0	6.0	1.50
(5)	10.75	7.0	1.55
(6)	12.25	8.0	1.53
		Mean	1.55

$\therefore m_1 = m_2 \div (v_1/v_2 = 202 \div 1.55 = 130.$

M. W. of *p*-chlor-aniline = 127.

Same by comparison with *p*-nitraniline (m_2, v_2)

	v_1	v_2	v_1/v_2
(1)	5.5	5.0	1.10
(2)	7.6	7.0	1.08
(3)	9.8	9.0	1.09
(4)	11.0	10.0	1.10
(5)	13.2	12.0	1.10
		Mean	1.07

$\therefore m_1 = m_2 \div (v_1/v_2) = 138 \div 1.09 = 127.$

VI Comparison of iodoform (m_1, v_1) with hydrazobenzene (m_2, v_2).
Equal weights of each (0.4 gram)
$m_1/m_2 = 394/184 = 2.14$

	v_1	v_2	v_2/v_1
(1)	8.0	17.5	2.19
(2)	9.75	20.0	2.05
(3)	11.5	23.75	2.07
(4)	12.0	24.75	2.06
		Mean	2.09

VII Compared hydrazobenzene (m_1, v_1) with 1-brom-2-4-dinitrobenzene (m_2, v_2). Equal weights (each 0.4 gram)
$m_2/m_1 = 247/184 = 1.34$

	v_1	v_2	v_1/v_2
(1)	6.75	5.0	1.35
(2)	8.25	6.0	1.37
(3)	12.25	9.0	1.36
(4)	13.25	10.0	1.32
(5)	16.25	12.0	1.35
(6)	17.50	13.0	1.35
(7)	20.00	15.0	1.33
		Mean	1.35

VIII Compared 1-brom-2-4-dinitro-benzene (m_1, v_1) with diphenylamine (m_2, v_2). Equal weights (0.35 gram each)
$m_1/m_2 = 247/169 = 1.46$

	v_1	v_2	v_2/v_1
(1)	5.0	7.5	1.50
(2)	8.0	12.25	1.53
(3)	10.0	15.0	1.50
(4)	12.0	17.75	1.48
		Mean	1.50

IX Compared β-naphthylamine (m_1, v_1) with picric acid (m_2, v_2). Equal weights (each 0.4 gram).
$m_2/m_1 = 229/143 = 1.60$

	v_1	v_2	v_1/v_2
(1)	8.0	5.0	1.60
(2)	10.0	6.25	1.60
(3)	12.0	7.5	1.60
(4)	12.25	7.75	1.61
(5)	16.0	10.0	1.60
(6)	18.75	12.0	1.56
		Mean	1.59

X (Test.) Determination of M. W. of unknown substance (m_1, v_1) by comparison with β-naphthylamine (m_2, v_2). 0.4 gram of each

	v_1	v_2	v_1/v_2
(1)	6.0	5.0	1.21
(2)	7.25	6.0	1.21
(3)	8.5	7.0	1.21
(4)	10.75	9.0	1.19
(5)	11.75	10.0	1.17
(6)	14.5	12.0	1.21
		Mean	1.19

$m_1 = m_2.v_2/v_1 = 143/1.19 = 120.$

M. W. of *p*-chlor-aniline = 127.

XI Compared *p*-toluidine (m_1, v_1) with α-naphthylamine (m_2, v_2). Equal weights of each (0.4 gram)

$m_2/m_1 = 143/107 = 1.33$

	v_1	v_2	v_1/v_2
(1)	7.7	5.0	1.34
(2)	10.7	8.0	1.33
(3)	13.5	10.0	1.35
(4)	17.4	13.0	1.34
		Mean	1.34

XII Comparison of *m*-dinitro-benzene (m_1, v_1) with *p*-nitro-toluene (m_2, v_2). Equal weights (each 0.4 gram)

$m_1/m_2 = 168/137 = 1.22$

	v_1	v_2	v_2/v_1
(1)	6.1	5.0	1.22
(2)	9.7	8.0	1.21
(3)	12.1	10.0	1.21
(4)	14.6	12.0	1.21
(5)	17.1	14.0	1.22
(6)	18.2	15.0	1.21
		Mean	1.21

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FERRIC CHLORIDES

BY F. K. CAMERON AND W. O. ROBINSON[1]

The classical investigation of Roozeboom and Schreinemakers[2] contains data for the solubility of ferric oxide in aqueous solutions of hydrochloric acid when the solution contains more than an equivalent amount of hydrochloric acid. The present investigation is an extension of this work at 25° C to cover the cases where there is present relatively more ferric oxide than acid. Roozeboom and Schreinemakers' results have been recalculated and included in Table I with the results obtained in the present investigation.

The hydrolysis of ferric chloride on the addition of water was noticed early by reason of the accompanying change in color and the subsequent precipitation of a dark brown body commonly identified as ferric hydroxide. It has been studied by a number of investigators, including Debray,[3] Krecke,[4] Fossereau,[5] Goodwin[6] and Spring.[7] Krecke found that the precipitated body contained no chlorine when left long in contact with solutions of ferric chloride, but gradually changed into the insoluble modification of ferric hydroxide first described by Pean de Saint Gilles.[8] He also found that the hydrolyzed iron was in the form of Graham's colloidal ferric hydroxide and measured the amount of the hydrolysis by precipitating the colloid with an electrolyte. The precipitated bodies were not oxychlorides, but ferric hydroxide.

Fossereau and Goodwin found that the hydrolysis took place slowly, as indicated by color change, and that the conductivity increased with the age of the solution.

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[1] Published by permission of the Secretary of Agriculture.

[2] Zeit. Phys. Chem., 15, 588 (1894).

[3] Bull. Soc. Chim., Paris [2], 12, 346 (1869).

[4] Jour. prakt. Chem. [2] 3, 286 (1871).

[5] Comptes rendus, 103, 42 (1886).

[6] Zeit. phys. Chem., 21, 1 (1896).

[7] Rec. Trav. Pays-Bas., 16, 237 (1897).

[8] Jahresb., 1855, 401.

Spring suggested that ferric chloride was dissociated into ferrous chloride and chlorine, supporting his views by the fact that potassium ferricyanide gives a precipitate with certain concentrations of ferric chloride and that chlorine is observed to escape from concentrated solutions of ferric chloride.

Rousseau[1] found that by heating a concentrated solution of ferric chloride in sealed tubes, crystalline precipitates even obtained, containing different ratios of Fe_2O_3 to $FeCl_3$, depending upon the temperature. The higher the temperature the less was the chloride present in the solid. By continued boiling in water, the chloride was gradually but completely removed, yielding crystalline ferric hydrates. The evidence recorded indicates the formation at higher temperatures of definite hydrated and anhydrous oxychlorides, but is not sufficient to negative the possibility that these supposed compounds actually belong to a series of solid solutions.

For the present work, aqueous solutions of varying concentrations of ferric chloride were treated with an excess of freshly precipitated ferric hydroxide and shaken at a constant temperature of 25° C for three months, when the specific

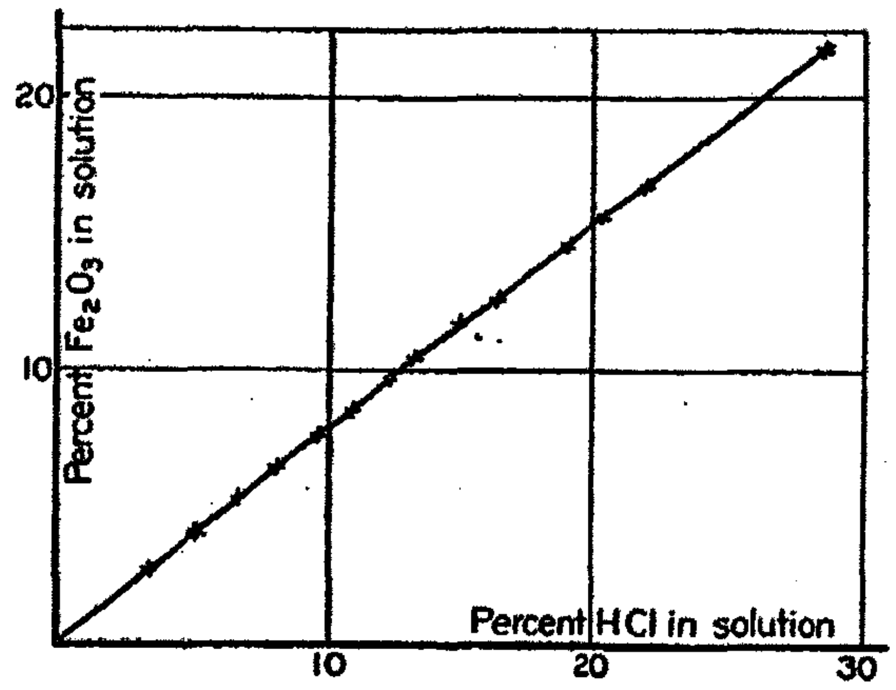

Fig. 1

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[1] Comptes rendus, 110, 1032 (1890); 111, 542 (1891).

gravities of the solutions had become constant. The concentrations of the solutions were then determined, the data obtained being given in Table I, and charted in Fig. 1. It will be seen that the curve approximates a straight line, the deviation being slight, but real. It further appears that at 25° C solutions of ferric chloride have a less solvent effect on ferric hydroxide than has ferric sulphate.[1]

TABLE I

Complete isotherm for the system, ferric oxide, hydrochloric acid and water at 25° C.

Sp. gr. $\frac{25°}{25°}$	Percent Fe_2O_3	Percent HCl	Solid phase
—	34.61	59.88	$FeCl_3.HCl.2H_2O$
—	33.27	60.23	$FeCl_3.HCl.2H_2O$
—	32.78	54.71	$FeCl_3.HCl.2H_2O + FeCl_3$
—	31.95	58.20	$FeCl_3 + FeCl_3.2H_2O$
—	34.42	59.12	$FeCl_3.2H_2O$
—	35.22	59.28	$FeCl_3.2H_2O$
—	34.07	55.71	$FeCl_3.2H_2O$
—	34.21	55.47	$FeCl_3.2H_2O + FeCl_3.2.5H_2O$
—	34.44	51.11	$FeCl_3.2.5H_2O + FeCl_3.3.5H_2O$
—	33.04	46.72	$FeCl_3.3.5H_2O + FeCl_3.6H_2O$
—	24.42	33.40	$FeCl_3.6H_2O$
1.485	21.84	29.33	$FeCl_3.6H_2O + Fe_2O_3.xHClH_2O$
1.349	16.82	22.55	$Fe_2O_3.xHClH_2O$
1.321	15.83	21.10	"
1.284	14.62	19.53	"
1.242	12.59	16.61	"
1.220	11.76	15.28	"
1.195	10.56	13.76	"
1.192	9.84	12.67	"
1.158	8.60	11.24	"
1.137	7.64	9.91	"
1.115	6.47	8.39	"
1.093	5.25	6.80	"
1.070	4.04	5.36	"
1.047	2.85	3.66	"

The compositions of some of the ferric chloride solutions with the compositions of their residues with adhering mother-

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[1] Jour. Phys. Chem., 11, 641 (1907).

liquor are given in Table II and plotted on the triangular diagram of Fig. 2.

TABLE II

Composition of ferric chloride solutions with the corresponding solid residues and adhering mother liquor

Solutions		Residues	
Percent Fe_2O_3	Percent HCl	Percent Fe_2O_3	Percent HCl
2.85	3.66	14.67	3.69
5.25	6.80	28.31	5.97
7.64	9.91	31.62	8.33
9.84	12.67	26.41	11.01
10.56	13.76	21.13	12.31
12.59	16.61	24.51	14.52
14.62	19.53	30.28	15.61
16.82	23.22	29.02	18.20
21.84	30.20	30.40	22.45

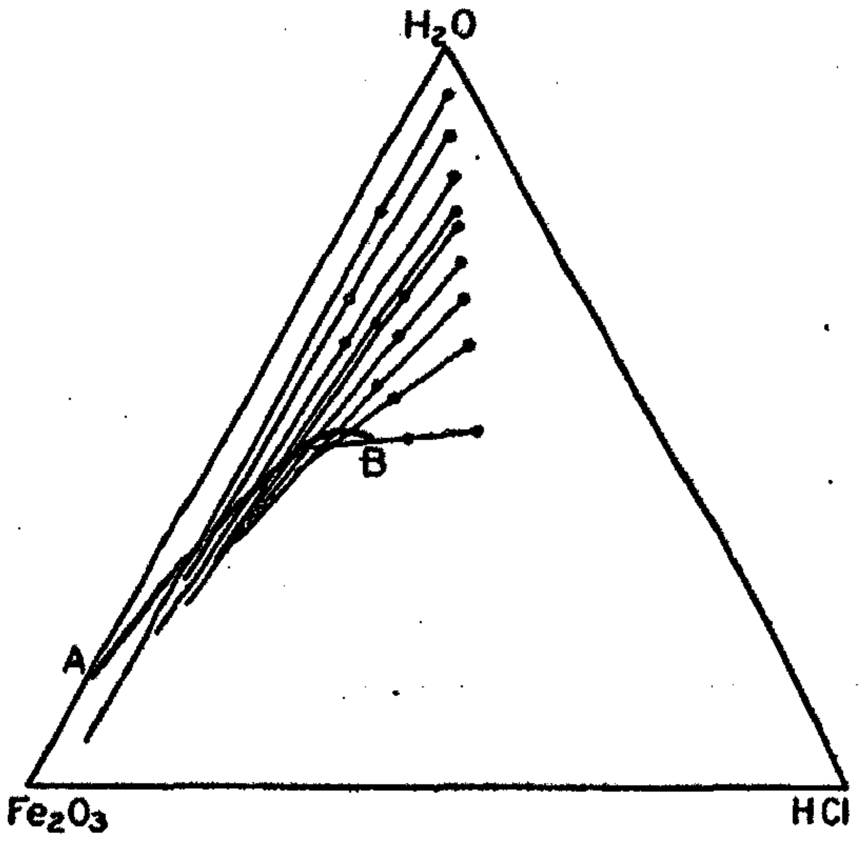

Fig. 2

By inspection of Fig. 2 it is apparent that the solid phase is of varying composition. If the lines were taken sufficiently near to each other the composition of the solid phases would be shown by the envelope of their intersections, as indicated by the line AB.

From the data which has been obtained in this investigation of the system, ferric oxide, hydrochloric acid and water, it follows that at 25° C no definite basic chloride is formed, but that the stable solid phase is one of a series of solid solutions containing ferric oxide, hydrochloric acid and water.

Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.

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