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STUDIES IN THE ADSORPTION FROM SOLUTION FROM THE STANDPOINT OF CAPILLARITY[1]—I

BY W. A. PATRICK AND D. C. JONES[2]

It is the purpose of this paper to present data on the adsorption from solution involving various liquid (and a few solid) solutes and a large number of solvents differing widely in their physical and chemical properties in order to show the relation between the solubility of liquids in one another and the curvature of the surface between the two liquids at equilibrium when the solubility is measured.

That the above relation can be ascertained by a study of the adsorption from solution by silica gel, is readily understood when one remembers that silica gel is a net work of capillaries formed by the juxtaposition of very small spherical particles of more or less hydrated silica[3]. These capillaries are obviously V-shaped, and therefore the magnitude of the radius of curvature of a liquid surface formed by an adsorbed liquid in these capillaries depends upon the amount of liquid adsorbed. As the capillary forces are stronger the smaller the capillary, a very small amount of liquid adsorbed means that the liquid surfaces are very concave. As an example, let us take a capillary system as above containing, say, water, and immerse this system in kerosene. By virtue of the fact that the water presents highly concave surfaces to the kerosene, the water's solubility in the kerosene will now be less than if the water were allowed to dissolve in the kerosene from a plane surface. Now let us take the opposite case which is the basis of the experiments subsequently performed. This time an "empty" capillary system is immersed in a saturated solution of water in kerosene. Here, some water, which wets the capillary, will "condense" or separate out in the capillaries, and the same equilibrium point as in the first case will be reached. That is to say, water is *adsorbed* from the solution by virtue of the capillary forces bringing about a phase separation.

Thus, one observes the opposite state of affairs to that which has received the greater amount of attention. A study of the higher vapor pressure of small drops and the greater solubility of small particles is no more important than the opposite case we have here—that of a liquid in a small capillary presenting correspondingly a lower vapor pressure and a lower solubility.

The following experiments also show that many of the generalizations in regard to adsorption from solution—such as those stated by Freundlich[4] based on early work by van Bemmelen[5] and others—will have to be greatly

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

[2] National Research Fellow.

[3] Patrick and McGavack: J. Am. Chem. Soc. 42, 946 (1920).

[4] "Kapillarchemie," 259: Second edition.

[5] "Die Absorption."

modified. For example, the idea that adsorption is greater from solvents having the higher surface tension is not borne out in the following experiments. In fact, this erroneous idea is responsible for the little work that has been done on adsorption by silica gel from liquids other than water. For, it was assumed that since there is very little adsorption from water—a liquid having a very high surface tension—there would be still less from organic liquids, which generally have much lower surface tensions. It will be shown, on the other hand, that there is great adsorption by silica gel from organic liquids.

Experimental

Preparation of Materials

The silica gel was prepared in the usual manner from sodium silicate and hydrochloric acid.[1] After activation it contained 6.2% water. A small amount of acid is usually present in gels prepared in this manner. In this case the hydrochloric acid was estimated by passing a stream of air over the gel heated in an electric furnace, and then through tubes containing KI and KIO_3 solution. The iodine liberated was determined at various temperatures. No acid came off below 700°C, and the total acid content, released mainly at 900°—1000° was but 0.14%.

The formic acid was dehydrated by P_2O_5 followed by distillation under diminished pressure.[2]

The purified acid had a M.P. of 8.3°C. The acetic acid was purified by several distillations in an all galss apparatus through a 6-column Young evaporator still-head. This acid was further dehydrated by fractional freezing until the M.P. was 16.6°. The n-butyric acid was dehydrated and distilled through a 12-column Young still-head. The acid finally obtained had a M.P. of −5.2° and a critical solution temperature[3] with water of −3.5°. The carbon disulfide, chloroform, toluene and carbon tetrachloride were purified by distillation until the various fractions gave the same ternary critical solution temperatures[4]. (This method consists in finding the C.S.T. of three liquids, one of which is the one whose purity is desired, the other two (pure) are selected so as to give a convenient temperature. In the case of toluene, for example, the latter was added to an acetic acid water mixture of certain concentration. By observing the C.S.T. according to the method described by D. C. Jones, one can test the purity of the toluene, or, if the curves were originally determined and the impurity known, one can estimate the amount of impurity. Small amounts of substances, especially those very dissimilar in chemical nature from the liquid in which they are dissolved, cause a great alteration in the C.S.T.) Nitrobenzene was purified to constant M.P. of 5.9°. Similarly the benzene was finally obtained with a melting

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[1] Patrick and McGavack: loc. cit.

[2] D. C. Jones: J. Soc. Chem. Ind. 1919, 362T.

[3] Faucon: Ann. Chim. Phys. 19, 84 (1910).

[4] D. C. Jones: Ph.D. Dissertation, Johns Hopkins University (1921).

point of 5.45.° The petroleum products were purified by chemical treatment and then by prolonged treatment with silica gel itself. All solvents were finally shaken for long periods with silica gel before using. The gasoline used in the experiments had a boiling point of 60°–70°C and the kerosene a boiling point of 270°–290°C.

The experimental manipulations necessary to obtain the data for the adsorption isotherms were of a simple kind. In general, a series of solutions of varying concentration and of definite volume (25 or 50 cc.) were made up in bottles and a definite weight of gel was then added. The bottles were transferred to a shaker in an air thermostat maintained at 27°. It was found that 24 hours was sufficient to attain equilibrium. In certain cases the concentrations were found unchanged after six months from the values attained after 24 hours.

Methods of Analysis

In a certain number of cases it was possible to estimate the concentration by some titration process, but this method is limited in scope and other methods of analysis had to be employed. For the estimation of various acids, titration by N/20 or N/100 baryta was used. The iodine was estimated by very dilute thiosulfate solution. The Zeiss interferometer was used to determine sulfur in benzene, and nitrobenzene in petroleum, while ternary critical solution temperature methods (see above) were used to estimate sulfur in carbon disulfide, benzene in petroleum and n-butyl alcohol in benzene. Where this latter method is available and sufficiently delicate, i.e.—where sufficient difference in solubility exists, the method is convenient and necessitates only the simplest type of apparatus.[1]

Expression of Results

In the accompanying tables C_o expresses the initial concentration of the solution in mols per litre and C represents the equilibrium concentration in the same units. In all cases the ordinary formula weight is taken, i.e.—no association effects are considered. A represents the millimols solute adsorbed per gram of gel, and is in all cases found by dividing the amount of solute lost to the solution (as found by above analytical methods) by the weight of gel added. It is to be noted that the quantity A is strictly empiric; that is to say, no attempt has been made to take into account any effects produced by the possible adsorption of solvent or changes in volume brought about by the removal of the solute. However, when adsorption takes place in moderately dilute solutions, which is usually the case, the above two effects are so small that for all practical purposes the factor A can be regarded as equivalent to the *a* of the Freundlich adsorption equation

$$a = KC^{\frac{1}{n}}$$

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[1] D. C. Jones: loc. cit.

TABLE I

Adsorption of formic, acetic and n-butyric acid from various solvents by silica gel.

Formic acid from toluene

C_o	C	A
1.034	0.601	5.56
1.034	0.348	4.36
0.607	0.450	4.89
1.034	0.104	3.02
0.245	0.138	2.85
0.150	0.072	2.52
0.059	0.146	1.46

Formic acid from nitrobenzene

5.220	4.700	5.19
1.128	0.898	2.93
0.583	0.419	2.19
0.322	0.191	1.63
0.176	0.100	1.19
0.124	0.041	0.80

Acetic acid from gasoline

2.980	2.660	3.91
1.370	1.116	3.56
0.678	0.441	3.14
0.362	0.195	2.44
0.198	0.053	2.25
0.135	0.021	2.00

Acetic acid from toluene

C_o	C	A
1.913	1.780	2.28
0.640	0.498	2.18
0.266	0.138	1.75
0.116	0.028	1.40
0.043	0.010.	0.53

Acetic acid from nitrobenzene

3.550	3.171	3.47
1.483	1.316	2.06
0.713	0.585	1.64
0.241	0.140	1.43
0.068	0.038	0.63
0.055	0.028	0.55

Acetic acid from carbon disulfide

C_o	C	A
0.071	——	1.18
0.171	0.040	2.15
0.340	0.183	2.48
0.693	0.448	3.26
1.405	1.115	3.90
3.167	2.853	3.95
3.845	2.893	3.82
3.991	3.385	3.55
5.441	4.628	3.55
6.710	5.970	3.03
8.027	7.205	2.36
8.066	7.475	2.38
9.778	9.170	2.10
12.450	11.925	1.23
15.410	15.320	0.38

Acetic acid from carbon tetrachloride

3.470	3.245	3.04
1.330	1.100	2.66
0.710	0.441	2.70
0.337	0.195	2.33
0.168	0.055	2.08
0.073	0.001	1.08
0.023	——	0.35

N-butyric acid from kerosene

C_o	C	A
1.358	1.120	4.13
0.547	0.353	3.41
0.272	0.156	2.09
0.131	0.068	2.07
0.021	0.002	0.67

N-butyric acid from gasoline

2.480	2.280	1.93
1.050	0.846	2.33
0.270	0.126	2.04
0.126	0.016	1.70
0.054	0.0008	1.20
0.015	0.0001	0.34

TABLE I (continued)

Acetic acid from kerosene

2.086	1.786	4.74
1.055	0.745	4.54
0.698	0.445	3.81
0.361	0.130	3.13
0.178	0.008	2.13
0.085	0.001	1.25

N-butyric acid from toluene

1.250	1.130	1.36
0.113	0.086	1.00
0.029	0.022	0.73

TABLE II

Nitrobenzene from kerosene

C_0	C	A
1.150	0.952	2.44
0.962	0.705	2.44
0.775	0.517	2.36
0.580	0.365	2.19
0.785	0.482	2.19
0.386	0.201	1.98
0.272	0.987	1.62
0.186	0.046	1.54
0.084	— —	0.87

Benzene from kerosene

C_0	C	A
1.025	0.748	1.21
0.588	0.320	1.19
0.269	0.013	1.23
0.127	— —	0.86

TABLE III

Benzoic acid from benzene

0.688	0.660	0.74
0.674	0.628	0.70
0.311	0.266	0.72
0.156	0.114	0.63
0.078	0.052	0.45
0.036	0.019	0.30
0.012	0.009	0.12

Benzoic acid from carbon tetrachloride

0.484	0.452	1.29
0.456	0.365	1.19
0.084	0.039	0.92
0.178	0.110	1.11
0.028	0.007	0.66

Benzoic acid from chloroform

1.340	1.300	0.67
0.307	0.275	0.45
0.146	0.125	0.37
0.073	0.063	0.25

Benzoic acid from kerosene

0.058	0.008	0.93
0.024	— —	0.48

TABLE IV

Iodine from kerosene

C_0	C	A
.0128	.0122	.0059
.0043	.0039	.0024
.0017	.0016	.0016

Iodine from carbon tetrachloride

C_0	C	A
.0954	.0946	.0039
.0400	.0397	.0024
.0179	.0178	.0012

Preliminary Qualitative Experiments

Before discussing the results given in the accompanying curves, it is necessary to describe a few qualitative experiments of a very simple nature which throw light upon the solubility relationships of liquids in connection with the adsorption phenomena.

A definite weight of gel was added to a definite volume of liquid A in a graduate cylinder. A second liquid B, heavier than A, was then added until the gel was completely immersed in this liquid. In many cases it was found that liquid A was ejected from the gel to a greater or less extent and its volume could be read off above liquid B. In this way, water completely replaced kerosene. Nitrobenzene ejected 10 cc. out of 11 cc. originally present of kerosene. Water replaced 4 cc. out of 10 cc. of n-butyl alcohol. Formic acid ejected 9 cc. out of 10 cc. of kerosene.

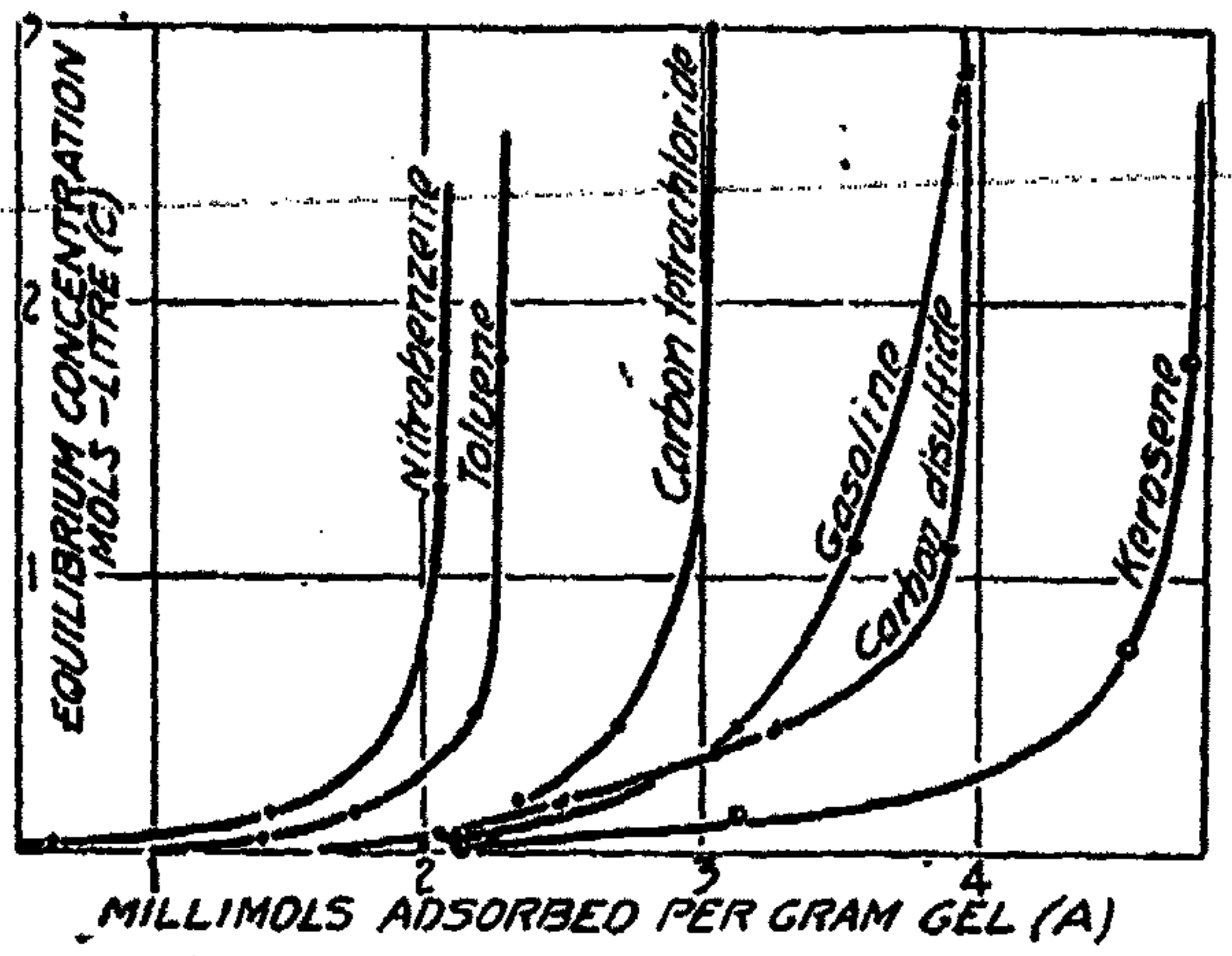

FIG. 1
Adsorption of Acetic Acid

Discussion of Results

Several outstanding facts will be immediately noticed upon an inspection of the curves:

1. Contrary to the idea that very little adsorption would take place from organic solvents which have relatively low surface tensions, it is seen that adsorption does take place to a very marked extent, and that the amount adsorbed from these solvents bears no relation to their surface tensions. From Fig. 1 in the case of acetic acid, the greatest adsorption occurs from kerosene, and becomes less and less in the order CS_2, gasoline CCl_4, $C_6H_5CH_3$, $C_6H_5NO_2$; while the surface tensions of these substances, respectively, are 26, 32, 15, 25, 29 and 43.

2. In the case of the acids, including benzoic, the solvents are arranged in the same order.

3. The petroleums, which have the lowest surface tensions, are the solvents from which the greatest adsorption occurs.

4. In general, adsorption of a solute increases as its solubility in the solvent decreases.

For example, the adsorption of benzoic acid from the four solvents is in inverse order of its solubility in these solvents. Likewise formic acid, much less soluble in toluene than butyric acid, is much more strongly adsorbed. Iodine is adsorbed, to a small extent it is true, according to the same laws. The adsorption of sulfur in benzene and CS_2 was also studied. In the first case a small negative result was found, while with the second system no effect was observed. Again, nitrobenzene is adsorbed to a very great extent from kerosene, with which it is only partially miscible, while benzene, much closer to kerosene in the solubility series, is adsorbed to a considerably less extent. The benzene-kerosene curve (Fig. 3) is peculiar in that it does not resemble the other curves,—in fact, it does not resemble an adsorption curve at all, but rather suggests a chemical reaction between benzene and the gel.

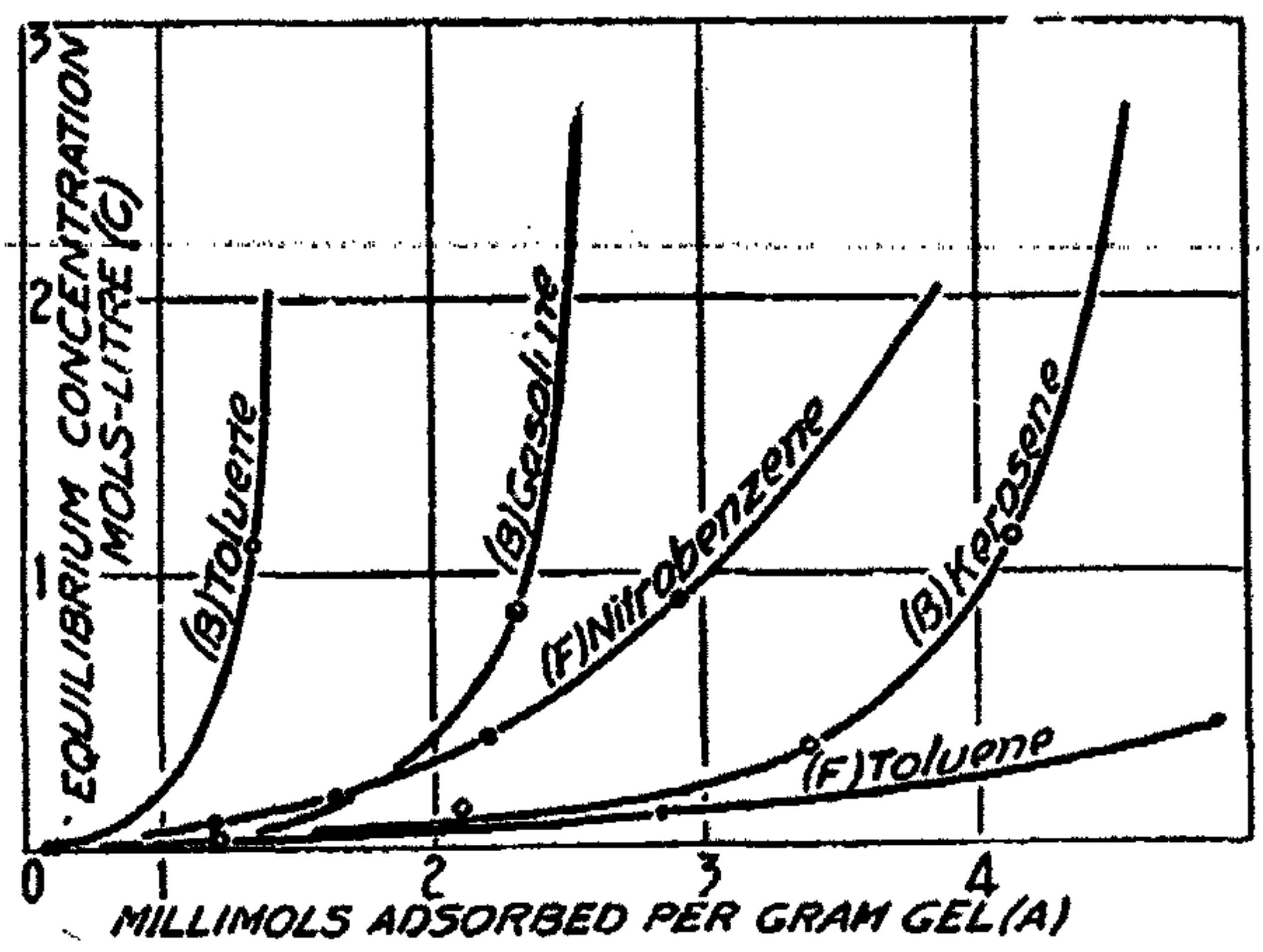

FIG. 2
Adsorption of Formic and N- Butyric Acids

It is noticed that the system acetic acid—carbon disulfide (Fig. 4) was investigated throughout the entire range of concentration. One must remember, however, that the amount adsorbed per gram gel is reckoned by a change in concentration of the solution, and therefore in a 100% acetic acid or 100% CS_2 solution, the term A is regarded as being equal to zero. By definition, therefore, a maximum of the curve must necessarily follow. But it is significant that the maximum occurs at an equilibrium concentration of about 3 mols per litre, which is equivalent to about an 8% solution of acetic acid in carbon disulfide. After changing the concentration of the solution to the extent of this maximum value, why should the gel, beginning with an equilibrium concentration of 8%, be less and less effective in changing the concentration of the solution as the percentage of acetic acid becomes greater? The cause of this lies undoubtedly in the phase compositions. Apparently there is a concentration range where the adsorbent does most work in altering the concentration of the solution. Before it reaches this point it is only the finer capillaries i.e.—those that give opportunity for very great concave curvature, that can withdraw acetic acid from solution. After the maximum is passed, less and less work is required of the adsorbent, *because the exterior phase and the interior adsorbed phase are approaching one another in composition.*

In the case of adsorption of nitrobenzene from kerosene, we have another phenomenon which is not in agreement with the ordinary accepted ideas of adsorption. For here, not only has kerosene a very low surface tension, but nitrobenzene, dissolved in kerosene, tends to raise the surface tension of the latter. Nevertheless, nitrobenzene is adsorbed very strongly from kerosene.

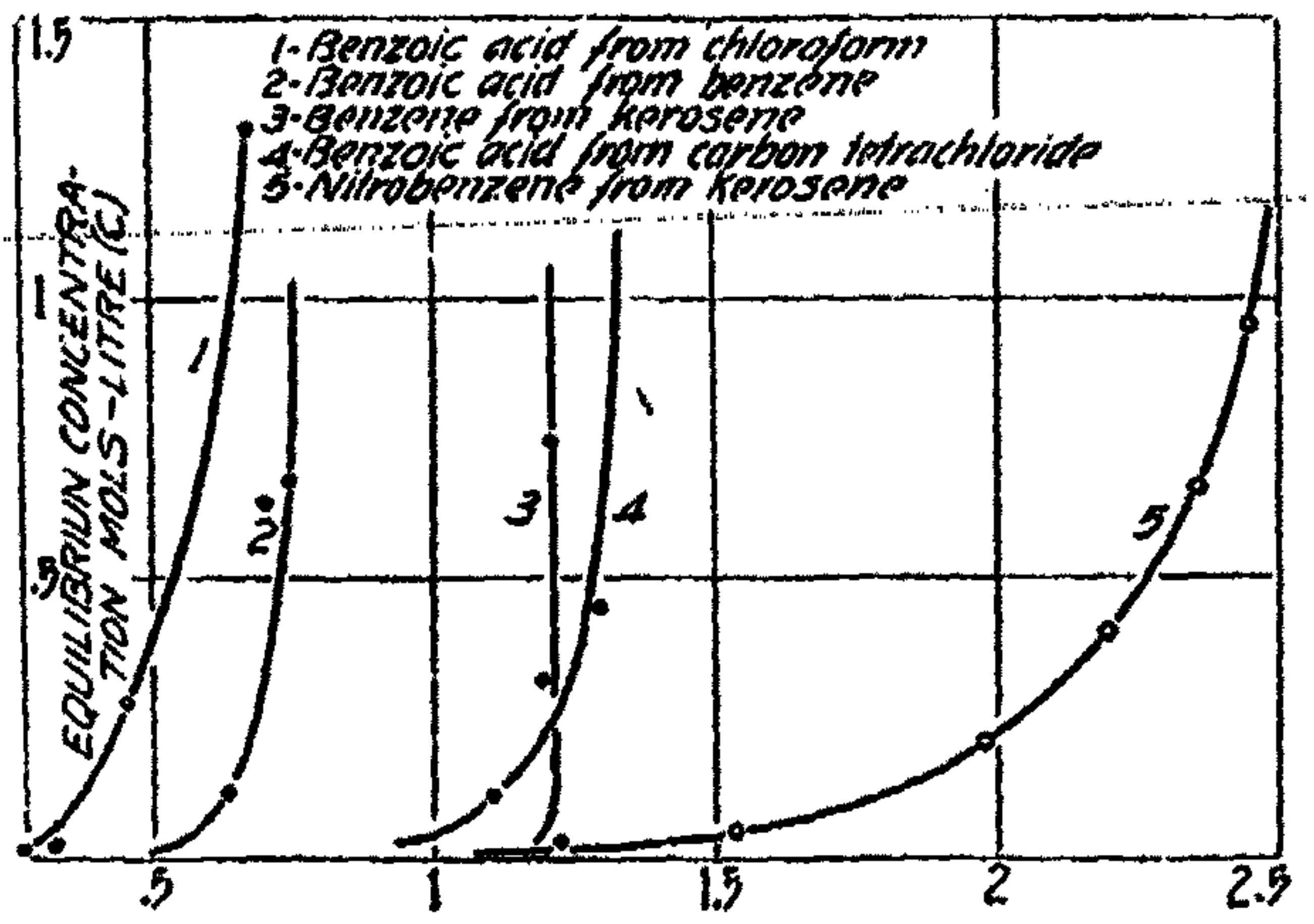

Fig. 3
Millimols adsorbed per Gram Gel. (a)

A rigid application of the Gibbs' theory to the experiments under consideration here, would have to take into account not the surface tension of the solvent against air or vapor, but the interfacial tension between the solvent and the gel. Since, however, the gel contains water, and in all probability presents a water surface to the solvent, one has to do with a water-solvent interface. But even if this were not the case, and the system was comprised of, say, a silica-solvent interface, the Gibbs' generalization would still apply relatively; for, since solids present enormous surface tensions, the interface in question—silica-solvent—would be greater than either a water-solvent or air-solvent interface.

Now, assuming a water-solvent interface (since in studies with silica gel it is apparent that a water layer surrounds the silica particles), in the case of adsorption from kerosene, a water-kerosene interface exists. This is one of the largest known liquid-liquid interfaces. Since most liquids have a larger surface tension than petroleum (about 20) and a smaller tension than water

(75), this interface is reduced in two ways when a solute concentrates (i.e. is adsorbed) in the adsorbent. This partly explains the great adsorption observed in all cases from kerosene.

However, from the facts discussed above, and from the large adsorption effects observed in some cases—35% of gel weight—it is obvious that the Gibbs' theory cannot entirely account for the adsorption in the case of silica gel,—nor do the generalizations of Freundlich largely apply. As above indicated, adsorption—at least in the case of silica gel—can best be accounted for by lowering of the solubility of a solute in its solvent due to the highly concave surfaces it (the solute) presents to the solvent when concentrated in pores of the adsorbent—which pores first of all the *solute* preferentially wets.

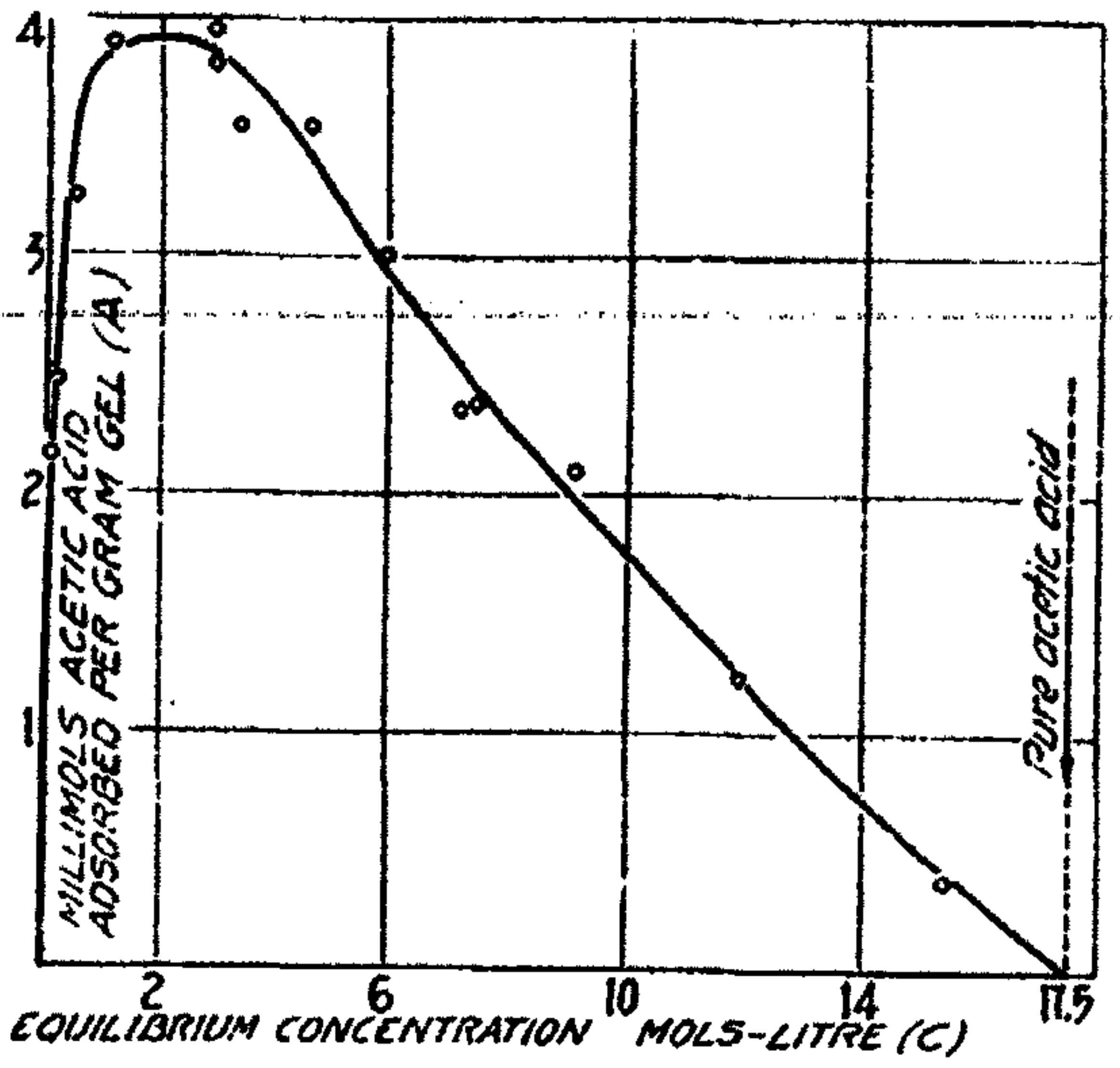

FIG. 4

Complete Adsorption Isotherm HAc-CS_2

No exception has been found to the generalization that greater adsorption always follows lower solubility of the solute adsorbed in the solvent. The complete ejection of kerosene from kerosene-saturated gel by water may be taken as an extreme case.

As an example of the application of the above mechanism, let us take the case of the adsorption of acetic acid from CS_2. On the introduction of the gel to such a system, the acid (which, in preference to the CS_2, wets the gel) is adsorbed as a Gibbs' layer owing to its lowering of the interfacial tension gel-CS_2. The gel now fills up with a phase rich in acetic acid due to the marked concave curvature that this phase presents to the body of the solution; i.e.—a phase separation is induced by the presence of the capillaries. Exactly the same equilibrium position (if the concentration were chosen correctly) would be reached by first filling the capillaries with acetic acid, and immersing in CS_2. In other words, acetic acid, although miscible in all proportions with CS_2 when the surfaces are plane, no longer is so if the curvatures of the separating surfaces are sufficiently concave. This is merely applying to adsorption from solution our ideas, largely enunciated by Patrick and McGavack.[1] as to the mechanism of adsorption from a gaseous phase. In this latter case, analogously, a gas is condensed in capillaries (i.e.—adsorbed) at pressures lower than the saturation pressure at the temperature, due to the presentation of highly concave surfaces of liquefied gas—in the pores of the gel which is wetted—to the main body of gas.

In a few words, then, the state of affairs in general is as follows: liquids presenting highly concave surfaces, can exist in contact with vapor above the critical temperature, and in contact with another liquid, well above the critical solution temperature.

The above conception leads to some interesting conclusions concerning what is ordinarily termed solubility. Since acetic acid *is* adsorbed from carbon disulfide—with which it is assumed to be completely miscible, it follows that, at least under certain circumstances, acetic acid possesses a definite solubility in carbon disulfide. In a later paper, it will be shown how "solubility," considered from this standpoint, can be calculated from adsorption formulae. Furthermore, the above experiments indicate a possible method by which adsorption from solution may be calculated from adsorption from the vapor state and vice versa. This would be important and necessary in those cases where adsorption from the vapor or the liquid would be difficult or impossible to measure. For, neglecting implications involved in the so-called van Schroeder's paradox—which has been largely disproved,[2] to calculate adsorption from solution from measurements of adsorption from vapor, all that would have to be known would be the vapor pressure-composition curves of the two liquids involved, (i.e. how nearly the liquids obey Raoult's Law) which would immediately give the equilibrium concentration (C) of the solution which is in equilibrium with the amount of solute adsorbed (A) either from the vapor or the liquid. It must be remembered, of course, that the phenomena of preferential wetting applies to the vapor state as well as to the liquid.

Summary

1. The adsorption from solution by silica gel has been investigated in the following systems: formic acid, acetic and butyric acid in a series of solvents; nitrobenzene and benzene from kerosene; benzoic acid and iodine from a series of solvents; and acetic acid from carbon disulfide throughout the entire range of concentration.

2. A discussion of the results is given, leading to the conclusion that adsorption by silica gel is due to a phase separation in the capillaries, caused by preferential wetting followed by the production of highly concave surfaces of solute which brings about a lowering of the solubility of the solute in the solvent.

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[1] J. Am. Chem. Soc. 42, 946 (1920).

[2] Freundlich: "Kapillarchemie," 925.

ON THE MECHANISM OF THE INHIBITION OF THE CATALYTIC ACTION OF PLATINUM BLACK AND PARTIALLY REDUCED NICKEL OXIDE BY CHLORINE

BY M. C. BOSWELL AND C. H. BAYLEY

Recently the senior author and R. R. McLaughlin have published[1] experimental results which seem to justify the conclusions that a normal platinum catalyst consists of particles of platinum with an interior content of oxygen, the particles being surrounded by a surface layer of dissociated water in the form of charged hydrogens and hydroxyls, and that this external layer is the seat of the catalysis of oxidation, reduction and hydrolysis, commonly observed with platinum black. Analogous results and conclusions had been reached with regard to the nature of partially reduced nickel oxide.[2] If these conclusions are accepted as a working hypothesis, it may reasonably be deduced, that the observed interference by chlorine, even in very small concentrations and very small absolute amounts, with the normal behaviour of these complexes as catalysts, is due to the disturbance or destruction of these surface films. It was also shown in these two papers the remarkable protection afforded by these surface films for the underlying interior content of oxygen, and also the necessity for the presence of this interior oxygen in order to maintain the surface films in their active condition, especially in the catalysis of hydrogenation reactions where the surface oxygen and interior oxygen are, to some extent, removed. If then the so-called poisoning action of chlorine on these catalysts is due to the destruction of the protective surface films, this should show itself by a very greatly increased accessibility of the interior oxygen, and increased ease of its removal by free hydrogen. The experiments described in this paper have given results which confirm these deductions from the theory. As a consequence not only can a fairly satisfactory picture be given of the mechanism of this poisoning action, but also confidence in the original working hypothesis of the mechanism of catalysis by these platinum and nickel complexes is considerably increased.

Experimental

Materials:—

Platinum catalyst: This was prepared by a modification of Loew's method as described in the above-mentioned platinum paper. The moist platinum black so obtained was mixed with an equal weight of fine asbestos previously purified by acid extraction and washing. The whole was dried at 110°C. for three hours and transferred to the U-tube employed

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[1] Proc. Roy. Soc. Canada, 17, 1 (1923).

[2] Proc. Roy. Soc. Canada, 16, 1 (1922).

in the experiments. Care was taken to prevent contamination of this platinum by laboratory gases.

Nickel oxide: This was prepared by igniting crystallized nickel nitrate in a porcelain casserole, dissolving the resulting oxide in nitric acid, evaporating to dryness on the water bath, dissolving 5 grams of the nitrate in distilled water, adding 5 grams purified asbestos, the whole ignited and cooled in a vacuum desiccator and one-half placed in a U-tube used in the experiments, care being taken to prevent contamination from laboratory gases.

Hydrogen: Electrolytic hydrogen was used. This was freed from traces of oxygen by passing over hot copper gauze.

Oxygen: Compressed oxygen from liquid air and containing only traces of inert gases was used.

Nitrogen: Compressed nitrogen was used containing less than ½% oxygen which was freed from oxygen by passing over hot copper gauze.

Apparatus:—

The apparatus used, except where otherwise described, was that used in the platinum and nickel experiments referred to above, and described and illustrated in the paper on nickel catalysis.[1]

Nickel Experiments

The U-tube containing nickel oxide on asbestos was made the central tube of a train of five U-tubes, the other four containing sulphuric acid (sp. gr. 1.84) on pumice. A calibrated gas burette of almost 400 cc. capacity was connected at each end of the train. The air was expelled by nitrogen while the nickel oxide was heated to 275°C. by a sodium nitrite bath. A measured volume of hydrogen was now passed between the two burettes across the heated oxide.

Volume of hydrogen at outset	762 cc.
" " " after 1st passage—	363
" " " " 2nd " —	308
" " " " 3rd " —	274
" " " " 4th " —	235
" " " " 5th " —	231
" " " " 6th " —	183
" " " " 7th " —	178
" " " " 8th " —	176
" " " " 9th " —	168
" " " " 10th " —	160

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[1] Proc. Roy. Soc. Canada, **16**, 1 (1922).

Volume of hydrogen after	11th	passage	—	158 cc.
" " " "	12th	"	—	156
" " " "	13th	"	—	154
" " " "	14th	"	—	152
" " " "	15th	"	—	150
" " " "	16th	"	—	148
" " " "	17th	"	—	146
" " " "	18th	"	—	145
" " " "	19th	"	—	145
" " " "	20th	"	—	144
" " " "	21st	"	—	144
" " " "	22nd	"	—	144
" " " "	23rd	"	—	144

The above-mentioned paper on catalysis by nickel shows that at this point a large proportion of the oxygen of the original oxide still remains. The rate of action of the hydrogen has become very slow. The surface film has formed, furnishing marked protection for the underlying interior content of oxygen.

The total water formed was .4301 g., equivalent to 534 cc. hydrogen.

Total hydrogen used up = 618 cc.

∴ Hydrogen remaining in the nickel = 84 cc.

The tube containing the partially reduced nickel oxide was allowed to cool to 23°C., the free hydrogen being completely expelled by nitrogen. (It has been shown that no hydrogen is given off in this operation at temperatures up to 300°C.). 5 cc. chlorine mixed with nitrogen was now introduced into the tube containing the catalyst and the whole allowed to stand for 3 hours at room temperature. The catalyst tube was now connected up with the original train of U-tubes and burettes, and heated to 275°C. in an atmosphere of nitrogen in order to sweep out any free chlorine as well as any water formed by the action of the chlorine on the nickel-hydrogen-oxygen complex. This passage of nitrogen was continued for 2 hours.

Water formed = .0022 g.

Hydrogen equivalent of water = 2.7 cc.

The water evolved was thus very small in comparison with the hydrogen remaining on the catalyst.

The catalyst at 275°C. was now treated with hydrogen just as at the outset, the water formed being determined after each passage.

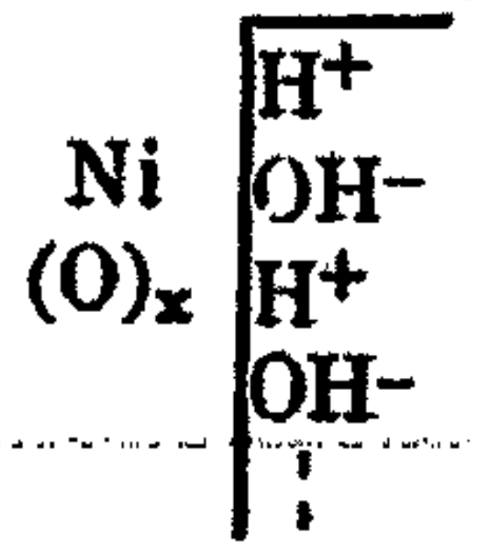
	1st passage	2nd passage	3rd passage
Hydrogen disappeared	32.0 cc.	36.0 cc.	28.0 cc.
Water formed	.0141 g.	.0080 g.	.0101 g.
Hydrogen equivalent of water	17.5 cc.	9.9 cc.	12.5 cc.
Hydrogen remaining on nickel	95.8 cc.	121.9 cc.	137.4 cc.

The apparatus was allowed to stand over night at room temperature, filled with nitrogen. The following day the catalyst was heated to 275°C. and hydrogen passed as before.

	1st passage	2nd passage	3rd passage
Hydrogen disappeared	79.0 cc.	17.0 cc.	29.0 cc.
Water formed	.0407 g.	.0001 g.	.0197 g.
Hydrogen equivalent of water	50.6 cc.	12.4 cc.	33.0 cc.
Hydrogen remaining on nickel	165.8 cc.	170.4 cc.	173.9 cc.

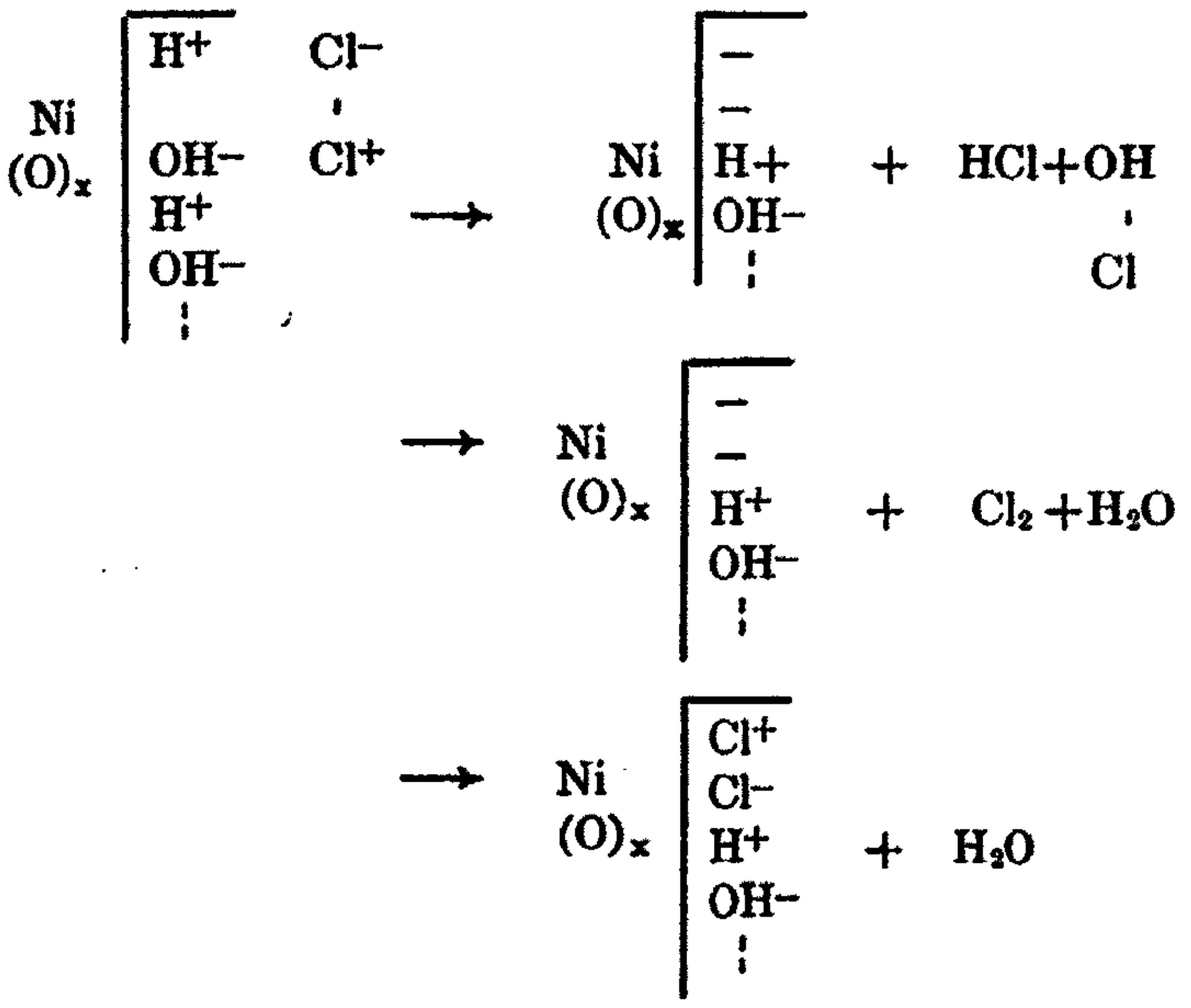
The action of chlorine did not result in the evolution of any considerable amount of water, but an amount approximately equivalent to the chlorine used (.0022 g. found, .004 g. calculated). Were all the hydrogen held on the catalyst evolved as water .0675 g. would have been obtained. That a deep-seated action occurred, however, is shown by the gradually increasing and relatively large volumes of hydrogen used upon passing this gas over the poisoned catalyst, as well as by the very large increase of hydrogen remaining on the catalyst, after each action of hydrogen. These two behaviours are characteristic of the action of hydrogen on the interior content of oxygen during the reduction of the original nickel oxide and during the process of establishing the surface film which is the seat of the normal catalytic action (see papers on the mechanism of nickel and platinum catalysis.) Thus the action of the chlorine appears to consist eventually in the destruction of the surface catalytic film, thus allowing the free hydrogen greater access to the interior content of oxygen. The presence of this oxygen being necessary for the maintenance of the surface film, the catalytic activity of the nickel complex is quickly destroyed.

Upon now passing hydrogen once more 15 cc. only disappeared. However, a relatively very large evolution of water occurred all at once (.1124 g. with a hydrogen equivalent of 139.7 cc.). Thus the amount of hydrogen held by the catalyst increased rapidly with each passage of hydrogen until the hydrogen remaining on the catalyst had increased from 84.0 cc. before the action of chlorine to 173.9 cc. after treatment with chlorine and subsequent treatments with hydrogen. Then suddenly 139.7 cc. was evolved as water and the hydrogen remaining on the catalyst fell to 49.2 cc. It seems then, that the deep-seated change brought about by only 5 cc. of chlorine gas, by which the normal catalytic properties of a normal nickel catalyst are destroyed, is due to the above mentioned changes in the surface film of the catalyst. It is a common explanation of the poisoning of a catalyst to say that the catalyst adsorbs the poison and thus prevents the adsorption of the bodies whose reaction is normally accelerated by the unpoisoned catalyst. This is very probably the whole explanation in certain cases where the poisoning material is present in so large amount as to enable the entire surface of the catalyst or a large part of it to adsorb the poisoning compound. However, in those cases usually designated as catalytic poisoning such conditions do not exist, the catalytic poison exerting its full effect even at very small concentrations and in minute absolute amounts. This latter is true in the case under consideration. It seems more reasonable to say that the poisoning is probably started by adsorption of the poisonous gas resulting in the destruction of something vital to the catalysis by the normal catalyst, and that the poisonous gas is regenerated or some active alteration product of it formed, capable of being again adsorbed by a further amount of the normal catalyst, followed by the above-mentioned destructive action and the accompanying regeneration of the poison. Thus the poison is really a catalyst for poisoning. From this point of view the poisoning of nickel catalyst by the "poison catalyst" chlorine may, in terms of our original working hypothesis of the constitution of the normal nickel catalyst, be represented as follows:—The normal nickel catalyst is represented thus



$$\begin{array}{r|l} & H^+ \\ \text{Ni} & OH^- \\ (O)_x & H^+ \\ & OH^- \\ & \vdots \end{array}$$

where Ni represents, not a nickel atom but a nickel particle made up of a number of nickel atoms, the number depending on the conditions of preparation, fineness of division, etc. This nickel particle has an interior content of oxygen $(O)_x$ and the whole is surrounded by a surface film of charged hydrogens and hydroxyls. When a large amount of this catalyst is acted on by a very small amount of chlorine, the following occurs:—

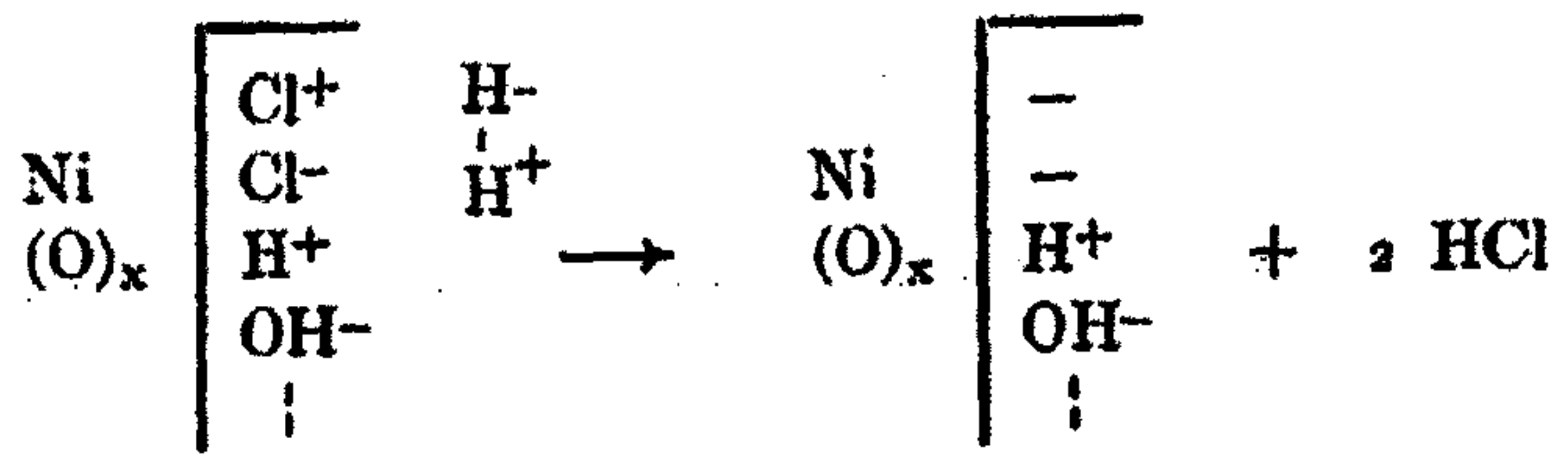


$$\begin{array}{r|ll} & H^+ & Cl^- \\ \text{Ni} & & \cdot \\ (O)_x & OH^- & Cl^+ \\ & H^+ & \\ & OH^- & \\ & \vdots & \end{array} \longrightarrow \begin{array}{r|l} & - \\ & - \\ \text{Ni} & H^+ \\ (O)_x & OH^- \\ & \vdots \end{array} + \begin{array}{l} HCl+OH \\ \qquad\quad \cdot \\ \qquad\quad Cl \end{array}$$

$$\longrightarrow \begin{array}{r|l} & - \\ \text{Ni} & - \\ (O)_x & H^+ \\ & OH^- \\ & \vdots \end{array} + Cl_2 + H_2O$$

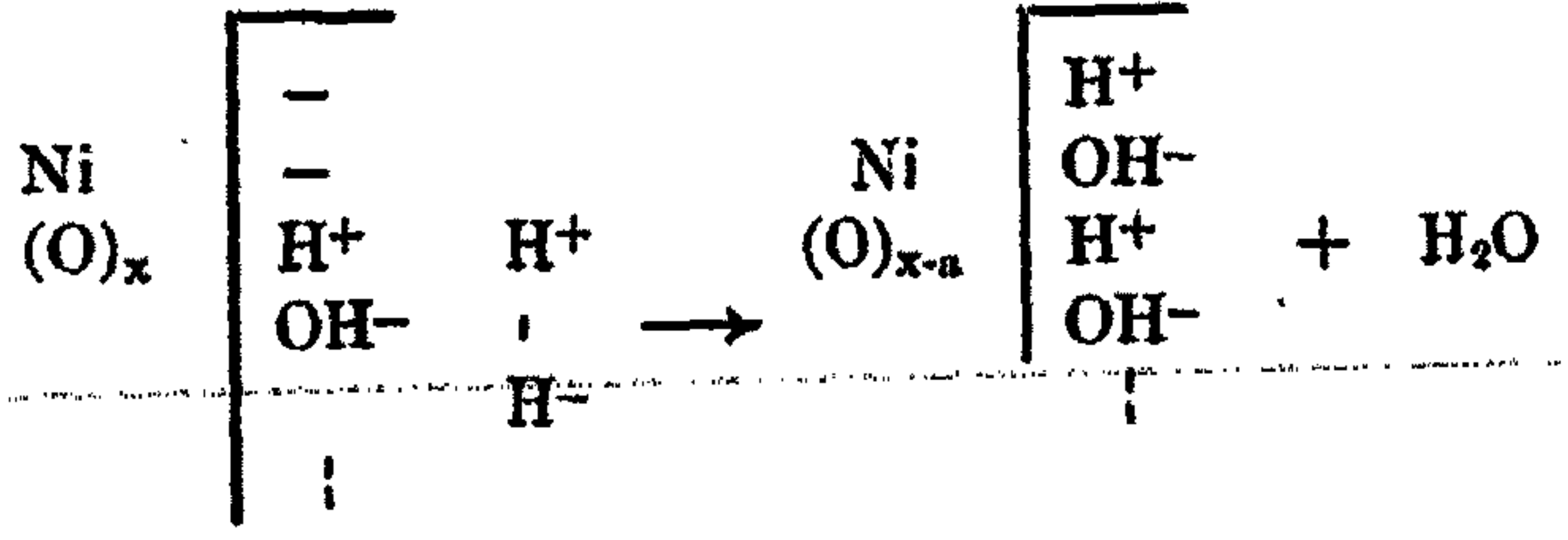
$$\longrightarrow \begin{array}{r|l} & Cl^+ \\ \text{Ni} & Cl^- \\ (O)_x & H^+ \\ & OH^- \\ & \vdots \end{array} + H_2O$$

Thus the chlorine is adsorbed and an equivalent amount of water is evolved. The water equivalent to 5 cc. chlorine is .004 g. .0022 g. were obtained. On now passing hydrogen the following occurs:



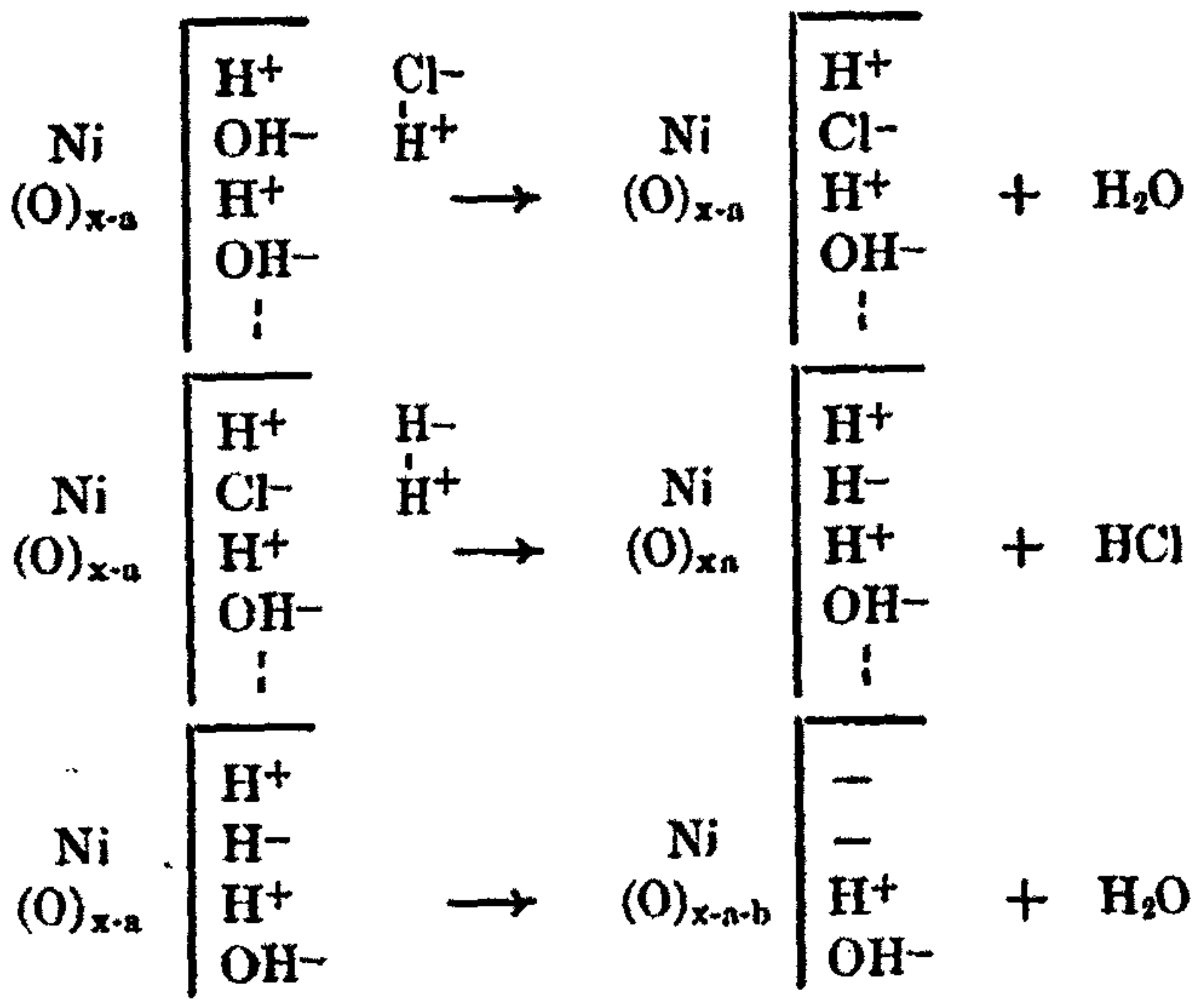
$$\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_x\end{array}\left|\begin{array}{l}\mathrm{Cl}^+\\\mathrm{Cl}^-\\\mathrm{H}^+\\\mathrm{OH}^-\\\vdots\end{array}\right.\begin{array}{l}\mathrm{H}^-\\\mathrm{H}^+\\ \\ \\ \end{array}\longrightarrow\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_x\end{array}\left|\begin{array}{l}-\\-\\\mathrm{H}^+\\\mathrm{OH}^-\\\vdots\end{array}\right.+\ 2\,\mathrm{HCl}$$

Thus the surface layer is partially removed and hydrogen being present in excess the interior content of oxygen is accessible and a considerable amount of free water is formed and at the same time an additional amount of hydrogen is fixed once more on the surface in the form of charged hydrogens and hydroxyls, in an endeavour to reestablish the original surface film of the normal catalyst.



$$\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_x\end{array}\left|\begin{array}{l}-\\-\\\mathrm{H}^+\\\mathrm{OH}^-\\ \\\vdots\end{array}\right.\begin{array}{l} \\ \\\mathrm{H}^+\\ \\\mathrm{H}^-\\ \end{array}\longrightarrow\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_{x-a}\end{array}\left|\begin{array}{l}\mathrm{H}^+\\\mathrm{OH}^-\\\mathrm{H}^+\\\mathrm{OH}^-\\\vdots\end{array}\right.+\ \mathrm{H_2O}$$

However, simultaneously the adsorption of the small amount of hydrochloric acid is constantly taking place, tending once more to remove the surface water film. As a consequence the removal of interior oxygen rapidly continues until so much oxygen has been removed that the rate of action of the hydrochloric acid in destroying the surface film predominates over the rate of the restoration of this film by the action of free hydrogen on the remaining oxygen. When this condition is reached the surface film is quickly destroyed and a relatively large amount of water is evolved.



$$\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_{x-a}\end{array}\left|\begin{array}{l}\mathrm{H}^+\\\mathrm{OH}^-\\\mathrm{H}^+\\\mathrm{OH}^-\\\vdots\end{array}\right.\begin{array}{l}\mathrm{Cl}^-\\\mathrm{H}^+\\ \\ \\ \end{array}\longrightarrow\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_{x-a}\end{array}\left|\begin{array}{l}\mathrm{H}^+\\\mathrm{Cl}^-\\\mathrm{H}^+\\\mathrm{OH}^-\\\vdots\end{array}\right.+\ \mathrm{H_2O}$$

$$\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_{x-a}\end{array}\left|\begin{array}{l}\mathrm{H}^+\\\mathrm{Cl}^-\\\mathrm{H}^+\\\mathrm{OH}^-\\\vdots\end{array}\right.\begin{array}{l}\mathrm{H}^-\\\mathrm{H}^+\\ \\ \\ \end{array}\longrightarrow\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_{xa}\end{array}\left|\begin{array}{l}\mathrm{H}^+\\\mathrm{H}^-\\\mathrm{H}^+\\\mathrm{OH}^-\\\vdots\end{array}\right.+\ \mathrm{HCl}$$

$$\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_{x-a}\end{array}\left|\begin{array}{l}\mathrm{H}^+\\\mathrm{H}^-\\\mathrm{H}^+\\\mathrm{OH}^-\end{array}\right.\longrightarrow\begin{array}{c}\mathrm{Ni}\\(\mathrm{O})_{x-a-b}\end{array}\left|\begin{array}{l}-\\-\\\mathrm{H}^+\\\mathrm{OH}^-\end{array}\right.+\ \mathrm{H_2O}$$

followed by the adsorption of the evolved hydrochloric acid, and so the cycle continues.

Platinum Experiments

In the paper on platinum catalysis already referred to, it was shown that on passing alternately hydrogen and oxygen over platinum black an equilibrium condition is reached where the hydrogen used up, the oxygen used up, and the water formed in each of these two actions, all become approximately constant. In this equilibrium condition the surface film has been fully formed and the normal platinum catalyst has been prepared. It was with this catalyst, using 2.5 g. platinum black, so prepared, that our experiments were performed. The following readings were obtained, the catalyst being at 150°C.:—

Hydrogen c.c. disappeared	Oxygen c.c. disappeared	Water formed g.	H equiv. c.c. of water	H thus added to Pt.
75		.0510	63.4	11.6
	5	.0043	5.3	6.3
37		.0225	28.0	15.3
	7	.0053	6.6	8.7
25		.0174	21.6	12.1
	8	.0054	6.7	5.4
19		.0124	15.4	9.0
	6	.0022	2.7	6.3
20		.0121	15.1	11.2
	6	.0013	1.2	10.0
20		.0140	17.3	12.7
	6	.0006	0.7	12.0
20		.0142	17.6	14.4

At this point the hydrogen used up was constant, the oxygen used up was constant and the amount of water formed approximately constant. The hydrogen in the apparatus was now displaced by nitrogen, allowed to cool to room temperature and 5 cc. chlorine introduced as in the nickel experiment just described. This was allowed to stand over night at room temperature. The following morning the apparatus was swept out by a large volume of nitrogen. Hydrogen and oxygen were now separately passed over the catalyst at 150°C., the volume of gas which disappeared and the amount of water formed by each passage of gas being measured.

Hydrogen disappeared c.c.	Oxygen disappeared c.c.	Water formed g.	H equiv. of water c.c.	H on Pt.
—	—	.0020	2.4	12.0
6	—	.0027	3.3	14.7
—	5	.0010	1.2	13.5
5	—	.0030	3.6	14.9
—	5	.0046	5.7	9.2
10	—	.0041	5.1	14.1
—	7	.0012	1.5	12.6
17	—	.0013	16.2	13.4
—	6	.0012	1.5	11.9

24	—	.0160	19.9	16.0
—	8	.0057	7.1	8.9
29	—	.0185	23.0	14.9
—	9	.0023	2.8	12.1
33	—	.0260	32.3	12.8
—	15	.0001	0.1	12.7
50	—	.0275	34.2	28.5
—	10	.0001	0.1	28.4
57	—	.0244	30.3	55.1
—	11	.0000	— —	55.1
53	—	.0293	36.4	71.7
—	11	.0001	0.1	71.6
50	—	.0494	61.4	60.2
—	25	.0117	14.5	45.7
38	—	.0282	35.1	48.6
—	12	.0018	2.2	46.4
35	—	.0213	26.5	54.9
—	2	.0000	— —	54.9
42	—	.0278	34.6	42.0
—	11	.0016	1.9	40.1
38	—	.0209	26.0	52.1
—	26	.0330	41.0	11.1
12	—	.0079	9.8	13.3
—	10	.0021	2.6	10.7
40	—	.0250	31.1	19.6
—	11	.0033	4.1	15.5
40	—	.0238	29.6	25.9
—	10	.0052	6.4	19.5
38	—	.0225	27.9	29.6
—	16	.0054	6.7	22.9
38	—	.0224	27.8	33.1
—	20	.0157	19.5	13.6
83	—	.0359	44.6	52.0
—	2	.0010	0.1	51.9
44	—	.0225	27.9	68.0
—	11	.0103	12.8	55.2
43	—	.0149	18.5	79.7
—	25	.0520	64.6	15.1
25	—	.0157	19.5	20.6

The first reading under the heading "water formed" is the water formed after treatment with chlorine. This was .0020 g. compared with .0022 g. in the case of the nickel experiment. The value calculated from the theory, as already explained, is .004 g.

From the above results it is seen that the behaviour with platinum is quite similar to that with nickel. The hydrogen which remained on the platinum after each gas treatment becomes gradually greater until it is suddenly evolved in large amount as water. The process is then repeated with again a sudden large removal of hydrogen as water. In the case of every hydrogen action there was an increase of hydrogen remaining on the catalyst. This behaviour is characteristic of the action of hydrogen on the interior content of oxygen, either when a portion of the surface film has been removed, or before the surface film has been fully formed (see paper on platinum catalysis). It seems that here, just as in the poisoning of nickel catalyst, the action of the chlorine has been to partially remove the surface film and render the interior oxygen content of the catalytic complex accessible to free hydrogen. And the same interpretation of the facts already given in the case of nickel may be used here.

It seems advisable, in connection with the general question of the mechanism of catalysis, particularly of hydrogenation by means of nickel and platinum catalysts, to point out a difficulty which has lately been stressed by several authors, and to offer a suggestion which may help to remove it. These authors question the necessity for the presence of oxygen in these catalysts. This conflict of opinion appears to be due to the failure to recognize that the catalysis, say of hydrogenation, can be accomplished chiefly in two distinct ways. One of these involves the use of finely divided metals which by their method of preparation (as for instance nickel from nickel cyanide) could not contain any oxygen, while the other by means of oxides of metals reduced by hydrogen at relatively low temperatures, when oxygen is certainly present in the catalysts. In the former case the catalysis is probably due to the adsorption of hydrogen, or of the compound hydrogenated, or of both by the catalyst, while in the latter case the catalysis has, we believe, quite a different mechanism, as outlined in the two papers referred to above. Whether all of the details of the mechanism suggested by the senior author are finally shown to be correct or not, the following statements appear to be true, and must along with other facts, receive representation in any adequate theory of catalytic action by means of partially reduced oxides. viz: (1) the catalyst contains oxygen in two distinct conditions, (2) in one of these conditions the oxygen is associated with hydrogen, and is easily reactive, (3) in the other condition the oxygen is protected in some way and is much less active, (4) this protection is removed by the action of small quantities of so-called poisons, so as to render the less active oxygen more reactive. The senior author believes that these facts receive an adequate representation by the theory advanced in the two papers above referred to, and in the present paper.

Summary

Experiments on the poisoning of nickel and platinum catalysts by chlorine seem to indicate that the poisoning is accomplished by the destruction of the surface film on the catalytic particles, which film is the seat of the normal catalytic action, thus rendering the interior oxygen content accessible to free hydrogen. This interior oxygen so vital to the maintenance of this surface film and hence of catalytic action in the normal catalyst, is thus quickly removed. The experiments appear also to lend additional support to the theory of mechanism of catalytic action already advanced by the senior author.

REMOVAL OF GAS FILMS

BY WILDER D. BANCROFT

On various occasions I have pointed out[1] that there was reason to suppose that electrification tended to displace an adsorbed gas film more or less completely. Schuster[2] studied the disruptive discharge through gases and found an apparent diminution of dielectric strength with diminution of pressure. Since no sufficient decrease in inductive capacity could be observed in the mass of the gas, he assumed that there was a condensed surface layer of gas having a large inductive capacity. Schuster pointed out that some of the most puzzling facts of the disruptive discharge admit of explanation if we assume the existence of such a contact layer, diminishing in density with decreasing gas pressure.

If we generalize from Schuster's experiments and say that an electrical stress tends to remove a film of adsorbed gas, we can account for many apparently unrelated facts. "Electrical waves will tend to remove active oxygen from an electrode and will therefore cut down the over-voltage.[3] Superposing an alternating current on a direct current also decreases the over-voltage, making other reactions possible.[4] The experiments of Margules[5] and of Ruer[6] on the dissolving of platinum find their explanation in the cutting-down of the over-voltage.[7]

"With direct current there is oxidation to a higher and insoluble stage. With alternating current the over-voltage is decreased and little or none of the insoluble compound is formed. The electrolytic detector, the crystal detector, and the coherer, as used in wireless telegraphy, seem to owe their action to the partial or complete elimination of an air film by means of electrical stress. The essential difference between the coherer and the detector is that coalescence takes place readily in the former case and not in the latter."

Campbell[8] deduced the existence of an adsorbed air film on water from his quantitative measurements on evaporation. The existence of such a film is shown directly by Rayleigh's experiments on liquid jets.[9] A vertical jet

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[1] Bancroft: J. Phys. Chem. 20, 1, 396, 402, 503 (1916); "Applied Colloid Chemistry." 22, 65 (1921).

[2] Phil. Mag. (5) 29, 197 (1880).

[3] Rothmund: Ann. Physik. (4) 15, 193 (1904); Bennewitz: Z. physik. Chem. 72, 323 (1910).

[4] Archibald and von Wartenberg: Z. Elektrochem. 17, 812 (1911); Reitlinger: 20, 261 (1914); Ghosh: J. Am. Chem. Soc. 37, 33 (1915); Stepanoff: Chem. Abs. 10, 2431 (1916).

[5] Ann. Physik. (3) 65, 629; 66, 540 (1898).

[6] Z. physik. Chem. 44, 81; Z. Elektrochem. 9, 235 (1903); 11, 10, 661 (1905); Haber: Z. anorg. Chem. 51, 365 (1906).

[7] Reitlinger: Z. Elektrochem. 20, 261 (1914).

[8] Trans. Faraday Soc. 10, 197 (1915).

[9] Rayleigh: Proc. Roy. Soc. 28, 406; 29, 71 (1879); 34, 130 (1882).

of water or any liquid slows up and breaks into drops when the head is sufficiently great relatively to the diameter of the jet. These drops scatter because they rebound when they strike one another. If a feebly electrified body is brought close to the jet, the jet becomes coherent. Under more powerful action the scattering of the drops becomes even greater than when there is no electrification. What happens is that there is formed round each drop a film of adsorbed air which prevents two drops from coalescing when they collide. When the drops are electrified, the air film is removed to such an extent that the drops come more nearly in contact and coalesce. With higher electrification, a marked charging of the drops takes place and the repulsion of the like charges causes the drops to scatter. Nipher[1] states that drops of 4 mm radius do not attract each other when charged to 0.0031 volt. That there is an air film between the drops can be shown by letting two jets impinge under such conditions that they bound apart. It was found that when the jets rebounded, the electrical insulation was practically perfect.

Since there is no direct proof as yet, that electrification tends to remove an adsorbed film or makes an adsorbed film more easily displaced by a liquid, we have to rely on cumulative, indirect evidence. It is therefore with great pleasure that I have just learned that Aitken[2] had obtained results, over thirty years ago, which confirm the explanation which I have given of Lord Rayleigh's experiments. Aitken had been studying some phenomena connected with cloudy condensation.

"When a jet of steam escapes into the air, condensation at once ensues by the expansion and the mixing of the steam with the cold air. The jet becomes distinctly visible by the light reflected by the minute drops of water carried along in the mixed gases and vapour. At first sight there is little that is interesting in the changes then taking place. The subject has, therefore, attracted little attention. On the other hand great interest has been taken in the change produced in the appearance of the jet when it is electrified; yet I hope to show that this is only one of a number of causes which alter the appearance of the condensing steam.

"R. Helmholtz was the first to show that when an ordinary jet of steam is electrified, there is a marked increase in the density of the condensation. The effect of the electricity is certainly very remarkable. The instant the jet is electrified, it at once changes and becomes much denser, and the condensed particles also become visible much closer up to the nozzle from which the steam is escaping. For the convenience of description we shall call this second form of condensation *dense condensation*, while that usually observed we shall call *ordinary condensation*. Not that there is any hard and fast line between these two forms, as the one may be made to change by imperceptible degrees into the other. All that is meant is that the one is dense compared with the other."

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[1] Science (2), 34, 442 (1911).

[2] Proc. Roy. Soc. 51, 408 (1892); "Collected Scientific Papers," 255 (1923).

"In the experiments with electricity only steam of a low pressure should be used. In these experiments slight electrification was used, as only an old-fashioned cylinder electrical machine was available for the purpose, and in the damp atmosphere produced by the steam jet the electrification was only capable of giving a spark of about 1 cm. or generally less.

"The necessary condition for the electricity producing any effect on the jet is that the particles in the jet be electrified either by direct discharge or by an induction discharge. The mere presence of an electrified body near the jet has no influence whatever. In order that it may have an effect, the electrified body must terminate in a point placed near the jet, and the potential must be great enough to cause a discharge of the electricity of the jet. When this takes place the jet at once becomes dense and remains in that condition while the discharge continues. The electrified body may, however, electrify the jet by induction. If, for instance, the electrified body be a sphere, and the nozzle from which the steam is issuing be pointed, the electricity discharged by the nozzle will electrify the particles, and the condensation becomes dense. But if the nozzle be not pointed, then the presence of the electrified body produces no change, as there is no discharge of electricity. But if now we hold a needle or other pointed conductor near the jet issuing from the rounded nozzle it at once becomes dense, by the induction discharge from the point. In place of a point in the last experiment, we may use a flame; in fact, we may use any influence which will enable the electrified bdy to electrify the particles in the jet.

"Another way of making this experiment is to insulate the boiler, and electrify it. If the nozzle be pointed, the jet becomes dense on electrification; but, if it be rounded, the electrification has no effect. If, however, we bring a needle or a flame near the rounded nozzle, the jet becomes dense. To get no effect from the electrification it is necessary that the nozzle be a ball of some size, the orifice through which the steam issues being, of course, the same diameter as that of the pointed jet.

"The effect of the electrification has been studied by R. Helmholtz and by Mr. Shelford Bidwell,[1] but neither of them seems to be satisfied with any explanation they offer. Mr. Bidwell, from a spectroscopic examination of the light transmitted through the jet under the two conditions, came to the conclusion that in the dense condition the particles were larger than in the ordinary form of condensation; and he thinks that the increase in size is due to the electricity causing the small drops of water to coalesce and form larger drops. In support of this explanation, he quotes Lord Rayleigh's experiments on the coalescence of drops in water jets while under the influence of electricity. As Mr. Bidwell does not put forth this opinion as final, there is less reason for hesitation in stating that the conclusion I have come to is diametrically opposed to Mr. Bidwell's.

"There seems to be no doubt that electricity will act on these very small drops of water in the same way as it acts on the drops in a jet of water.

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[1] Phil Mag. (4) 29, 158 (1890).

That its action is similar is easily proved by the following experiment with mist drops: Take a small open vessel full of hot water—it is better to colour the water nearly black for convenience of observation—a cup of tea without cream does very well for the purpose. Place the cup on a table between the window and the observer. On now looking at the cup from such a position that no bright light is reflected from the surface of the liquid, there will be seen what looks like scum on the surface of the tea. That scum is, however, only a multitude of small mist-drops which have condensed out of the rising steam and have fallen on the surface of the liquid, where they are seen floating. If now we take a piece of brown paper, or any convenient material, and rub it slightly and hold it over the cup, the "scum" will disappear at once, and be replaced by other drops when the electrified body is removed. As in Lord Rayleigh's experiments, a very feeble electrification is sufficient to cause the absorption of the drops into the body of the liquid. It is therefore not because there is supposed to be any difference in the action of electricity on large and on very small drops that a different conclusion from Mr. Bidwell's has been arrived at, but because all the experiments to be described point to the conclusion that the dense form of condensation is not due to an increase in the size of the drops, but to an increase in the number, accompanied of course by a diminution in the size.

"We may suppose the following to be something like the manner in which the electricity acts on the jet: In a steam jet the rapid movements of the drops give rise to frequent collisions, and these result in the coalescence of many of the drops, so that each drop in ordinary condensation is made up of a number; but, when the jet is electrified, the electrification prevents the particles coming into contact, as they repel each other, and the consequence is, we have a greater number of particles in a dense and electrified jet than in an ordinary one.

"Lord Rayleigh's experiments on the action of electricity on water jets support this view. He has shown that, in order to produce coalescence, the electrification must be very slight, and he also points out that the coalescence does not seem to be so much due to electrification as to a difference of electrification, which would appear to cause a discharge of electricity to take place between the drops, which rupture the films, so causing contact. Further, he has shown that when the electrification is strong, and the conditions are such that the drops become electrified, the effect is diametrically the opposite, and instead of coalescence, the particles now scatter far more than the unelectrified drops. Now from the conditions of the experiments with electrified steam jets it is evident that the drops are electrified, and are in the same condition as the electrified scattering water jet. We are, therefore, entitled to expect that the electricity will prevent and not aid the coalescence of the small drops in the steam jet.

"Other considerations also point to the increase in the density of the jet being due to an increase and not to a diminution in the number of drops. If we blow steam into air, we know that the fewer the dust nuclei in the air the thinner is the condensation, and that, when the dust is nearly all out of the air, only a fine rain falls which can scarcely be detected by the unaided eye. Further, the evidence from condensation produced by expanding moist air points to the same conclusion, namely, that the more dust particles there are in the air, the denser is the condensation when cooled by expansion, and the purer the air is, the thinner is the cloud.[1] These experiments all point to the conclusion that the dense form of condensation is due to a large number of water drops, and the thinner form to a smaller number, though of greater individual size. The only condition under which it seems probable that the increase in number will not give rise to increase in density is when the particles are so small that they are unable to reflect waves of any colour of light. So far as has yet been observed this never happens. However slight the amount of expansion, the greater number of particles always gives the denser form of condensation.

"The action of the electricity on the jet does not appear to be anything positive: it rather seems to prevent something which takes place under ordinary conditions. For instance, electricity has no effect in thickening the cloud of so-called steam rising from a hot and wet surface. The electrically driven current of air from a point when directed to the steaming surface has no effect whatever on the density of the condensation. Nor has electricity any effect on the steam rising from an open vessel. The small drops of water under these conditions move but slowly, and there is but little tendency for them to come into collision with each other; there are, therefore, few collisions for the electricity to prevent, and little or no thickening is produced by electrification under these conditions. Further on we shall have frequent opportunities of seeing that the dense form of condensation is the result of an increase in the number of particles, and that whatever gives rise to an increase in the number causes an increase in the density."

"We now come to the third cause of the dense form of condensation, namely, low temperature of the air. At first sight it may appear that the above statement contains an already well-known fact. But while in a certain sense this is so, yet there is one point of great importance which, so far as I am aware, has not previously been observed. If we are asked to state what is the effect of the temperature of the air on condensation of the jet, we would probably say that when the temperature of the air is high the condensation is very transparent, owing to there being less vapour condensed and to its rapid re-evaporation; and that when the temperature becomes lower and lower the jet gradually thickens as the temperature falls, owing to the greater amount of condensation caused by the colder air. Such a description is far from a full statement of the facts regarding the changes in appearance with the fall in temperature, and the explanation is correspondingly faulty. There is an influence at work in the condensing jet, which, though due to temperature, is of far more importance than the effect of the temperature on the amount of steam condensed.

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[1] Trans. Roy. Soc. Edinburgh, 30 I, 338 (1881).

"When I first encountered this new influence it greatly puzzled me. I had opened the window of the room where the experiments were being made, and when the fresh air came in, the jet began to behave itself in a most uncertain way. At one moment it was quite steady ordinary condensation, and the next it would conduct itself as if electrically excited. Even after the window was closed it continued to change from the ordinary to the dense form of condensation in a puzzling way. It was first thought that the outer air might be electrified, and tests were accordingly made to see if this were the case. These tests showed that if it were electrified it could be so but slightly, as it did not affect a gold-leaf electroscope, which it would require to have done to have produced the increased density observed in the steam jet. Electricity as the solution of the difficulty had, therefore, to be abandoned. The only other influence I could think of as likely to cause the effect was some unknown effect of cold; I, therefore, took the metal tube which had been used in a previous experiment for conveying the products of combustion from the flame to the jet and cooled it. On now presenting one end of this cold tube to the jet it at once responded, and the condensation became as dense as if a flame had been at the other end of the tube, or as if the jet had been electrified.

"This effect was all the more surprising since there was no great difference between the temperature of the air in the tube and that of the room, not more than 10° F. Some experiments were, therefore, made to find out the temperature at which this change takes place, and to see if it was as sudden as it appeared to be. The jet was supplied with air cooled in a pipe, which was surrounded with water for regulating the temperature of the air. The steam nozzle was placed just inside one end of the pipe and pointing outwards, so that the jet drew its supply of air out of the tube. No very satisfactory results were got with this apparatus. It may, however, be mentioned that when the air was cooled the jet somewhat suddenly became dense, and again became ordinary when the temperature was slightly raised; but with this apparatus it was difficult to say what the temperature of the air really was when the change took place.

"Another method of studying the effect of temperature on the density was tried with fair success; the nozzle was fitted to the end of a horizontal pipe, the nozzle also being pointed horizontally. For this experiment a morning was selected when the temperature of the room was low. When the experiments began the temperature was 40°F. At this temperature the jet was always dense, and neither electrification nor the products of combustion increased its density. The room was now slowly heated, and the jet watched while the temperature rose. Up to a temperature of 46° no change took place and the jet was not made denser by electricity or by the products of combustion. But when the temperature rose to 47° the jet began to show signs of clearing. The clearing did not, however, take place regularly; one moment the jet was dense and the next it was ordinary. These fluctuations would be due to the unequal temperature of the air coming to the jet. At one moment the air would be the air of the temperature of the room; the next it would be this air slightly heated by the metal pipe and nozzle. So that when the jet drew its supply of air horizontally its condensation was ordinary, and when the air currents in the room prevented this heated air from coming to the jet its condensation was dense.

"A slight alteration was then made in the arrangement; the jet was now directed downward at the end of the horizontal pipe. By this means the air heated in the pipe and nozzle was prevented from mixing with the jet. The jet was directed at a small angle from the vertical to prevent the hot air and vapour of the jet rising to the nozzle. With this arrangement the following was the result: up to a temperature of 46° the condensation was dense, and neither electricity nor the products of combustion had any effect on the density; but when the temperature rose to about 47° electrification began to have just a perceptible effect in increasing the density. At about 48° the electricity had an easily observed effect, and the products of combustion also had a slight effect. At a temperature of 50° the jet had become decidedly thinner, and both electricity and the products of combustion had a decided effect in increasing its density. When the temperature rose to 55° the jet lost its dense appearance and both electricity and the products of combustion had a very marked effect.

"It might be thought that by observing a steam jet in the open air we could tell if the temperature of the air was above or below a certain point. This, however, can only be done in a very rough way, as the conditions are variable and not within our knowledge. We would require to know the pressure of the steam, and the degree to which air was heated by the pipe. In a general way it may be stated that in the open air a steam jet looks dense if the temperature is below 50°, and ordinary if about 55°. But it is often difficult to say what is ordinary and what is dense condensation, even after the most careful examination as to how close to the nozzle the particles are visible. Of course if we could electrify the jet, or supply it with the products of combustion, we could tell whenever the temperature was over or under 47°.

"The sudden alteration in the appearance of the jet when supplied with air at a temperature of 46° points to some change in the influences in action in the condensing jet. The great increase in density cannot be due to an increase in the amount of vapour condensed, as the fall in the temperature is slight. Further, it will be observed that the jet had ceased to be influenced by electricity or by the products of combustion. The only explanation I could think of was that at the temperature of the mixed cold air and steam some alteration had taken place in the surface films of the water drops. The jet looked as if something came into action at that temperature which prevented the drops coalescing when they came into collision, or, what would amount to the same thing, that at high temperatures there was no tendency for the drops to recoil after impact, and that when the temperature fell this property made its appearance, and prevented contact in the same way as we have supposed the electrification to act.

"The simplest way of testing this explanation was to repeat Lord Rayleigh's experiment with water jets, but in place of cold water using hot. The result of the experiment entirely confirms this explanation. So long as the water in the jet is above a certain temperature there is no scattering whatever, but perfect coalescence of drops on contact. As a consequence the jet is not influenced in the slightest degree by the presence of an electrified body. It is only after the temperature falls below a certain point that the scattering commences, and electricity begins to have an influence.

"This experiment shows that it is only when the drops are below a certain temperature that their surface films act in the way we are accustomed to observe at ordinary temperatures, that is, repel each other; and that when the temperature is high there is an entire change, and the surface films no longer repel, but coalescence of the drops takes place at each collision. It will be noticed that the point here is, not the appearance of any new influence with the low temperature, as the films are then in the condition with which we are acquainted; it is at the high temperature that the new condition comes into action, and the films lose the resisting action with which we are acquainted.

"Now it seems extremely probable that the change in the appearance of the steam jet when the temperature of the air is lowered is due to the temperature of the jet falling to the temperature at which this repulsive action makes its appearance.

"There is, however, an experimental link wanting to bind these two phenomena together, which I have desired to complete, but unfortunately experimental difficulties stop the way. The link wanting is some experimental proof that the jet gets dense at the same temperature that the water jet begins to scatter. On attempting to take the temperature of the jet I met with considerable difficulties. If an ordinary thermometer is used, where is it to be placed? A very slight change in the position of the bulb of a thermometer placed in the jet gives an altered reading. It does not matter whether the change be made nearer or further from the centre of the jet, or nearer or further from the nozzle: in all cases a very slight change gives a considerable difference of temperature. It may, however, be stated that when the bulb was placed in the centre of the jet, and near the nozzle, it showed a temperature of about 130°, but that figure can only be looked upon as a very rough approximation to the true temperature.

"One or two attempts were, however, made to find the temperature at which water films cease to have any repulsive action. This was done by means of a small water jet; and it was found that above 155° there was no scattering. It was not till the temperature fell below that point that electrification had any effect. This was the temperature of the drops themselves, not of the supply for the jet; and it may not be quite accurate, as the drops tend to cool very quickly. Another method of finding this temperature was to observe the highest temperature at which the mist drops floated on water, in the experiment previously described. This method is not very satisfactory, on account of the difficulty of seeing the drops when the temperature is high, owing to the amount of condensed steam hanging over the water. It is also difficult to keep the surface of the water clean. The tests by this method gave a temperature considerably higher than that given by the water jet. Neither of these methods, however, promises to give satisfactory information on this point; but, if it were desired, the effect of temperature on the contact of films could be studied in a more accurate way.

"It is difficult to imagine any sudden change in the action of the films at or about the temperature indicated. There is no corresponding change, so far as I am aware, in the surface tension. We might picture to ourselves the change to be brought about by the alteration which takes place in the intervening gases. When the drops are cold, the bounding surfaces are water and air with very little vapour in it. And perhaps we may be permitted to assume that the surface film has a layer of air condensed on it, and it may be this condensed layer of air which prevents contact when the drops come into collision. But when the temperature is high, the conditions are changed. The bounding surfaces are now water and air with a large amount of vapour in it, and this vapour may play an important part in bringing about the contact, by the violent interchange of water molecules taking place at the surfaces of the films, and weakening the condensed films of air. If this explanation be correct, then there is really no sudden change in the action of the films, and the repulsion is a gradually increasing one with fall of temperature. Though the somewhat sudden change in the appearance of this jet might seem to indicate a sudden change in the action of the films, yet the change may be really a slowly increasing one, and the sudden change in the appearance of the jet may be due to the repulsion rising to such an amount that the very small particles are prevented from coalesing. If the relative temperatures given for the coalescence of water drops and mist drops be correct; then the gradual rise in the repulsion with fall in the temperature may be the explanation of why the drops in a water jet coalesce at a lower temperature than the mist drops on the surface of water. The water may require to be cooled to a lower temperature before the repulsion is sufficient to prevent the heavier drops from coalescing, while the less repulsion at the higher temperature may be sufficient to prevent the lighter drops from coming into contact. The same explanation helps to account for the increased density produced by increasing the dust particles, a less repulsion being sufficient to protect the excessively small drops.

"The explanations we have here offered of the action of electricity and low temperature are in complete agreement. In ordinary condensation when the temperature of the air is high there is no surface repulsion, owing to the high temperature in the jet, and many of the particles coalesce on collision with each other; but, when the drops are electrified, their mutual repulsions prevent contact, and the result is a large increase in the number of drops and a dense form of condensation. On the other hand, when the temperature is lowered, surface film repulsion comes into action, contact is prevented, and the drops do not coalesce on collision, and the result is exactly the same as if they were electrified."

Aitken's statement of the facts is absolutely right, that there is a surface layer of condensed air on the drops of water which prevents coalescence and that this surface layer is removed or weakened by rise of temperature. Since he did not recognize the similarity between the adsorption of gas by a liquid and the adsorption of gas by charcoal, he missed the step that the adsorption decreases with rising temperature. He failed completely to draw the general conclusion that electrification tends to remove an adsorbed gas film or, at least, tends to make the gas film more easily removable. The important thing for the moment is that he has brought out clearly that rise of temperature acts similarly to electrification under these conditions and that rise of temperature is accompanied by a decrease in the amount of adsorbed air. These experiments by Aitken are therefore a very welcome confirmation of the conclusion drawn from Schuster's work.

Zeleny[1] has convinced himself of the existence of air films at the surfaces of solids and liquids which interfere with electrical discharges. "The theory of the flow of electrical currents from pointed conductors which is generally accepted assumes that the ions which carry the discharge current are produced solely by collision with molecules of the gas of the few ions normally created in the gas by radiations from radio-active substances. Many of the general characteristics of these discharges may be explained qualitatively on this theory by the known properties of ions, without the need of assuming any action at the discharging surface such as ejection from it of ions by the impact of those colliding with it or such as would arise if the ions met with difficulty in discharging to the metal surface.

"There are some features of these discharges, however, which indicate that at least under certain circumstances a special action does take place at the discharging surface.[2] Thus for example the discharges from some metallic points begin very impulsively as the voltage applied is gradually increased, as if some resistance had been suddenly overcome; and what is even more significant, on decreasing the voltage after a discharge has started in these cases the current breaks off abruptly. An explanation of this sensitivity of some points, as such behavior is often called, must be sought in some condition at the discharging surface because points to all appearances similar differ very markedly in this property; and a point not possessing the property may be made to acquire it by treatment which does not appreciably change the form of the point."

"A possible cause of the lag phenomenon, applicable to all materials, is to be found in the condensed layer, either of water molecules or of molecules of the surrounding gas, which is believed to cover the surfaces of solid and liquid substances, for if this layer is a poor electrical conductor it is probable that under certain conditions it exerts a marked effect upon these discharges by preventing or retarding the passage of electricity from the gas to the metal point.

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[1] Phys. Rev. (2) 16, 102 (1920).

[2] See J. Zeleny: Phys. Rev. (2) 3, 69 (1914).

"That gaseous ions do not readily give up their charges to a metal surface is shown by the experiments of Gaede[1] who found that metal plates to which a discharge from a point had been allowed to flow exhibited a marked polarization when tested for the Volta effect. Gaede found that even fifteen seconds after a measured quantity of electricity was allowed to flow from a point to such a plate, on immersing the plate in an electrolyte, over half of the charge could be recovered from the plate. It is natural to assume that it is the non-conducting layer of condensed gas that keeps the ions from discharging readily to the metal.

"To account for the behavior of sensitive points of such a layer of gas or water molecules it is necessary to assume first, that this layer when solidly packed must be punctured and partially dissipated before a current of any magnitude is able to flow to the surface, and second, that the layer is able to reform and thus interrupt the discharge when the current is below a certain value."

"Some time ago the writer[2] did some work on electrical discharges from a new class of points, consisting of minute, hemispherical drops of water protruding from the ends of fine tubes. A method of measuring the electric intensity at the surface of the drops was devised and a study was made of the value of this intensity in air at atmospheric pressure, for a number of points differing in size. It was noted that the surface of the water becomes agitated when the electric current starts to flow from the point. For positive discharges this agitation is confined to small values of the current, the surface being quiescent for larger currents. A careful study was made later[3] of these initial surface disturbances and it was shown that they arise from the surface becoming unstable when the electric intensity exceeds a certain limit. Under these conditions fine threads of liquid are rapidly pulled from the surface which break up into myriads of minute drops that act as carriers of the electric charge. When water, in air at atmospheric pressure, is used, the surface instability begins at a potential which is only a little below that at which the discharge would start from an indisturbed surface. For this reason the true cause of the surface disturbance was not discovered until some work was begun on discharges in other gases than air."

"The electric intensity f at the end of the drop is obtained from the distance p, that the liquid surface in E must be lowered to maintain the drop of the same form when charged as when uncharged, by means of the relation:

$$f = \sqrt{8\pi pdg}, \qquad (I)$$

d being the density of the liquid. When the surface is not discharging a current, the electric intensity is not the same over the whole surface, being greatest at the tip end. To maintain equilibrium the shape of the drop changes slightly from the hemispherical form. This does not apply to a

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[1] Ann. Physik. (4) 14, 669 (1904).

[2] J. Zeleny: Phys. Rev. (2) 3, 69 (1914).

[3] J. Zeleny: Proc. Cambridge Phil. Soc. 18, 71 (1915); Phys. Rev. (2) 10, 1 (1917).

surface discharging a *positive* current, for the current flows from the whole hemisphere (except for very small currents) and the intensity is found to be independent of the current density.

"A noteworthy feature of the discharge from water points in air at reduced pressures is the retardation in the commencement of the current. As the voltage of the point is gradually increased the current does not begin gradually, but rises more or less suddenly to a value of the order of a microampere.

"The retardation for any point is not constant in amount, but depends somewhat upon the age of the liquid surface and upon the time that has elapsed since a current last flowed from the point, and upon a chance element in the formation of ions in the gas as the applied voltage is raised.

"As has been stated, a similar retardation in the current often occurs from metal points, which is larger and more frequently present with negative discharges than with positive discharges. But with many metal points the retardation is very small or not present, whereas with water points of retardation is the general rule. This retardation would in many cases be still larger than is observed were it not for the fact that a voltage is reached first at which the surface becomes unstable and the discharge starts owing to a disruption of the surface.

"When the current does start the water meniscus jerks back to a more flat position, because for the same voltage the electric pull is smaller with than without a current.

"After the current has started, the meniscus is quiescent with a positive discharge (but not with a negative discharge, and large changes in the magnitude of the current produce very little or no effect upon the electric pull upon the surface.

"As is the case with sensitive metal points in a lesser degree, the discharge current may be diminished below the value it suddenly assumed at commencement, and as the voltage is lowered to within about 50 volts of the value at which the current would disappear if it kept on diminishing at its previous rate of diminution, the meniscus as a rule suddenly elongates and the current stops. The increase in the electric pull with dimunition of voltage is so rapid during this final stage that it is extremely difficult to regulate both the voltage from the static machine and the liquid pressure necessary for maintaining the drop hemispherical, without having the water overflow to the sides of the glass tube. The most successful readings taken in this region showed that as the current fell to zero value, the total increase in the electric intensity as measured by the increase in the electric pull, may be as much as ten per cent. of the whole value.

"The retardation which has been discussed, occurs both with positive and negative discharges, and accordingly it is not possible to get any very definite voltages nor surface electric intensities for which currents begin to flow from these points.

"It is possible however to obtain definite values for the electric intensities at the surface of points from which positive currents above a certain minimum are flowing, and to obtain the voltages for which these currents stop; and this has been done. Such measurements cannot be made with negative discharges because with them the surface of the liquid is agitated, owing to an intermittent element in the current and to the fact that the negative discharge is confined to a minor portion only of the surface. Often with some of the larger negative currents, however, the surface becomes almost quiescent.

"As explained above, the electric intensity at the surface of a point changes but little with the current except just as the current is about to stop, where its value rises rather rapidly about 10 per cent. The values which will be recorded were taken in the region of small currents where the intensity begins to be constant in magnitude, but they apply equally well to larger currents."

In a second paper Zeleny[1] summarizes the results of the first paper by saying that "evidence was presented which on the whole favors the view that the lag phenomena of these points are due to the presence on their surfaces of a layer of gas molecules which, owing to the condition of the surface, is more uniformly and therefore less easily penetrable, by ions than is the case for a similar layer on the surfaces of points which do not show lag in the commencement of the discharge."

It is evident that Zeleny's results are in absolute agreement with the earlier experiments of Schuster along a somewhat different line. The only awkward thing about it all is that Zeleny was dealing with hundreds of volts and Lord Rayleigh with fractions of volts. It is not clear why an adsorbed gas film should be so sensitive to electrical stress in one case and so insensitive in another. The only thing that occurs to me at present is that in Rayleigh's experiments we have two conducting surfaces almost in contact whereas this is not the case in Zeleny's experiments.

Austin Bailey[2] has recently studied the effect of adsorbed gas on the high-frequency resistance of a loop of copper wire. This resistance is known to be higher than would be expected theoretically if the surface layers have the same resistivity as the core. The results indicated that the copper oxide film on the surface of a copper wire does adsorb gases readily at room temperature and that adsorbed gases do increase the resistance. When the copper wire was glowed, the gases were given off and the resistance dropped.

The general results of this paper may be summarized as follows:

1. Aitken has shown that Rayleigh's experiment with impinging jets fails when hot water is used because the adsorption of air is insufficient at the higher temperature.

2. Since a slight electrification at ordinary temperature has the same effect as an increase in temperature, it is probable that the electrical stress either decreases the amount of adsorbed gas or makes it easier to displace the adsorbed gas.

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[1] Phys. Rev. (2) 19, 566 (1922).

[2] Phys. Rev. (2) 20, 154 (1923).

3. Zeleny has shown that there is a film of adsorbed gas on solids and liquids which resists the passage of an electrical discharge from a point to the solid or liquid surface. This is in line with Schuster's experiment on the arc at different pressures.

4. The voltage necessary to displace the adsorbed gas film in Rayleigh's experiments is so small that one would not have expected that any effect could be detected in Zeleny's experiments. It seems probable that an adsorbed gas film becomes more sensitive to electrical stress when the arrangement is such that little or no free gas is present near the surfaces in question.

5. Bailey has shown that the copper oxide film on a copper wire adsorbs enough gas even at low pressures to increase the resistance of the wire perceptibly for high-frequency currents.

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THE SOLUBILITY OF YTTRIUM SALTS[1]

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The solubility of salts of the rare earth metals is of special importance because their separation depends so largely upon slight differences in solubility. In spite of this fact there is very little accurate information available in regard to the solubility of individual salts of this group of elements. This investigation was undertaken for the purpose of determining the solubility in water of yttrium chloride, bromide, nitrate and sulfate.

The yttrium material used was a part of that purified in the determination of the atomic weight of this element.[2] The fractions used for determining the solubility were only slightly short of atomic weight purity. They contained traces of both holmium and erbium but no other known impurity. The yttrium material was twice precipitated as the oxalate and twice as the hydroxide. The final precipitation was as the oxalate, which was dried and ignited in platinum to the oxide. This was then dissolved in either hydrochloric, nitric or sulfuric acid and the solution evaporated to crystallization. After standing the crystals were filtered off and thoroly drained from the mother liquor in a high-powered centrifuge. The crystals were washed and whirled again. In preparing the bromide it was found to be more satisfactory to dissolve yttrium hydroxide in hydrobromic acid because this acid dissolves Y_2O_3 only slowly. By keeping the $Y(OH)_3$ in excess, a salt was obtained free from occluded acid.

The reagents used were carefully purified. The water was newly distilled conductivity water which was carefully protected from the air. Nitric and hydrochloric acids were freshly redistilled from quartz apparatus; oxalic acid was recrystallized until it left no weighable residue on ignition. Hydrobromic acid was made by the hydrolysis of phosphorus tribromide. The gas was dissolved in water and this solution was distilled before using.

For the purpose of obtaining a saturated solution at a definite temperature a thermostat was used. This was equipped with a stirring device, an electric heating coil and a sensitive heat regulator. In order to obtain a saturated solution an Erlenmeyer flask containing both solute and solvent was immersed in the thermostat. On account of the small quantity of material with which it was necessary to work a stirring device within the flask was impossible. To enable the solution to reach the saturation point promptly the flask was vigorously shaken at intervals. The flask was kept at a constant temperature for at least five hours before the samples for the determination were with-

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[1] This paper is No. 17 of the series "Observations on the Rare Earths" from the laboratory of the University of Illinois.

[2] Egan and Balke: J. Am. Chem. Soc. 35, 365 (1913); Hopkins and Balke: 38, 2332 (1916); Kremers and Hopkins: 41, 718 (1919).

drawn. An occasional test was made in which a much longer period of time was allowed for the solution to reach the saturation point, but in no case was any change observed after the elapse of five hours. Since the chloride, bromide and nitrate are more soluble in hot water than in cold it was found that the point of saturation could be more quickly reached by first holding these salts for a time at a temperature somewhat above that desired for the determination, then gradually lowering to the required point. In the case of the sulfate saturation was best obtained at a lower temperature, then raising to the required point, since the solubility of $Y_2(SO_4)_3$ decreases as the temperature rises. Danger of supersaturation was avoided by vigorous shaking in the presence of an excess of the solute.

The method used in making a determination was to place a convenient quantity of the pulverized salt in the flask and add to it a quantity of water insufficient to dissolve all the salt at the temperature under consideration. After it was certain that a saturated solution had been obtained in the thermostat duplicate samples were drawn off for analysis. For this purpose a cylindrical separatory funnel was used by which the solution could be drawn up into the stem and held by turning the stop cock. To prevent drawing up fine particles of the undissolved solute, the end of the funnel was covered with a strainer consisting of a double thickness of fine mesh silk cloth, held in place by a rubber band. A new strainer was used for each determination. Before the solution was drawn into the funnel the latter was brought to a temperature as closely as possible to that of the solution in order that the solution might not be exposed to a sudden change of temperature with consequent change in its condition. After filling the stem of the funnel with the solution, the strainer was quickly removed and the solution at once poured into a tared platinum crucible. This was immediately covered and dropped into a wide weighing bottle whose tightly fitting stopper was adjusted quickly. Then the weighing bottle, crucible, cover and solution were weighed and the actual weight of the solution was determined. In the case of the nitrate and sulfate, these solutions were then evaporated to dryness and ignited directly to the oxide in the same platinum dish. The oxide was then weighed and its weight multiplied by the factor $2.43\left(\frac{2Y(NO_3)_3}{Y_2O_3}\right)$ gave the weight of the anhydrous nitrate in the solution. The factor 2.0596 was used for converting the weight of oxide to that of the sulfate. From the data so obtained, the weight of solute in solution in 100 grams of water was determined. Since the halogens are not converted to the oxide on ignition, the solutions of the chloride and of the bromide were diluted, pure oxalic acid added, the precipitate filtered, washed, dried and ignited to the oxide. The factor 1.73 was used for converting the oxide to chloride and the factor 2.9043 for converting the oxide to chloride and the factor 2.9043 for converting the oxide to bromide. Duplicates of all determinations were made and where the results failed to check closely or, where there was doubt concerning any value additional checks were made. The values obtained are shown in the tables and summarized in the accompanying curve.

TABLE I

Solubility of $Y(NO_3)_3$ in 100 grams of water

Temperature	Wt. Solution	Wt. Oxide	Wt. $Y(NO_3)_3$	Wt. H_2O	Solubility in 100 grams H_2O
0°	1.3078	.2596	.6308	.6770	93.1
22.5°	1.2234	.2888	.7050	.5184	136
	1.2721	.2988	.7240	.5481	133
35°	.7403	.1853	.4510	.2893	155
60.2°	.5738	.1561	.3804	.1934	197
	.7974	.2193	.5350	.2624	203.1
66.5°	.9248	.2585	.6280	.2968	211

TABLE II

Solubility of YCl_3 in 100 grams of water

Temperature	Wt. Solution	Wt. Oxide	Wt. Chloride	Wt. H_2O	Solubility in 100 grams H_2O
0°	.7788	.1917	.3319	.4469	74.3
	.4919	.1195	.2069	.2850	72.7
16°	2.5405	.6370	1.1010	1.4395	76.6
	2.7712	.6861	1.1880	1.5832	75.1
25.1°	1.2507	.3354	.5800	.7707	75.4
	.6352	.1552	.2694	.3658	75.3
45°	.5540	.1392	.2410	.3130	77.0
	.9599	.2405	.4164	.5435	76.3
60°	1.5632	.3924	.6800	.8832	77.
	3.0338	.7664	1.3270	1.7068	77.6
80°	.7082	.1798	.3120	.3962	78.1
	1.0225	.2593	.4499	.5756	78.1

TABLE III

Solubility of YBr_3 in 100 grams of water

Temperature	Wt. Solution	Wt. Oxide	Wt. YBr_3	Wt. H_2O	Solubility in 100 grams H_2O
0°	2.0425	.2686	.7802	1.2823	61.81
	1.7876	.2452	.7122	1.0754	66.23
30°	4.5571	.7187	2.0874	2.4697	84.52
	2.4427	.3793	1.1017	1.3410	82.15
50°	.9094	.1533	.4453	.4641	95.95
	1.2197	.2059	.5981	.6216	96.21
75°	.6816	.1236	.3591	.3225	111.32
95°	1.8688	.3611	1.0488	.8200	127.91
	2.5979	.5078	1.4749	1.1230	131.33

TABLE IV

Solubility of $Y_2(SO_4)_3$ in 100 grams of water

Temperature	Wt. Solution	Wt. Oxide	Wt. $Y_2(SO_4)_3$	Wt. H_2O	Solubility in 100 grams H_2O
3.6°	4.9015	.1766	.3637	4.5378	8.016
	4.8791	.1729	.3561	4.5230	7.873
15.8°	5.7067	.1921	.3957	5.3110	7.450
	3.7850	.1287	.2651	3.5199	7.531
25°	5.3215	.1729	.3561	4.9654	7.172
	5.1094	.1673	.3446	4.7648	7.232
50°	4.8899	.1189	.2449	4.645	5.272
	2.7950	.0704	.1450	2.650	5.472
75°	1.8939	.0289	.0595	1.8344	3.245
	5.0812	.0766	.1578	4.9234	3.2045
95°	4.484	.044	.0906	4.3934	2.063
	3.4865	.0333	.0686	3.4179	2.007

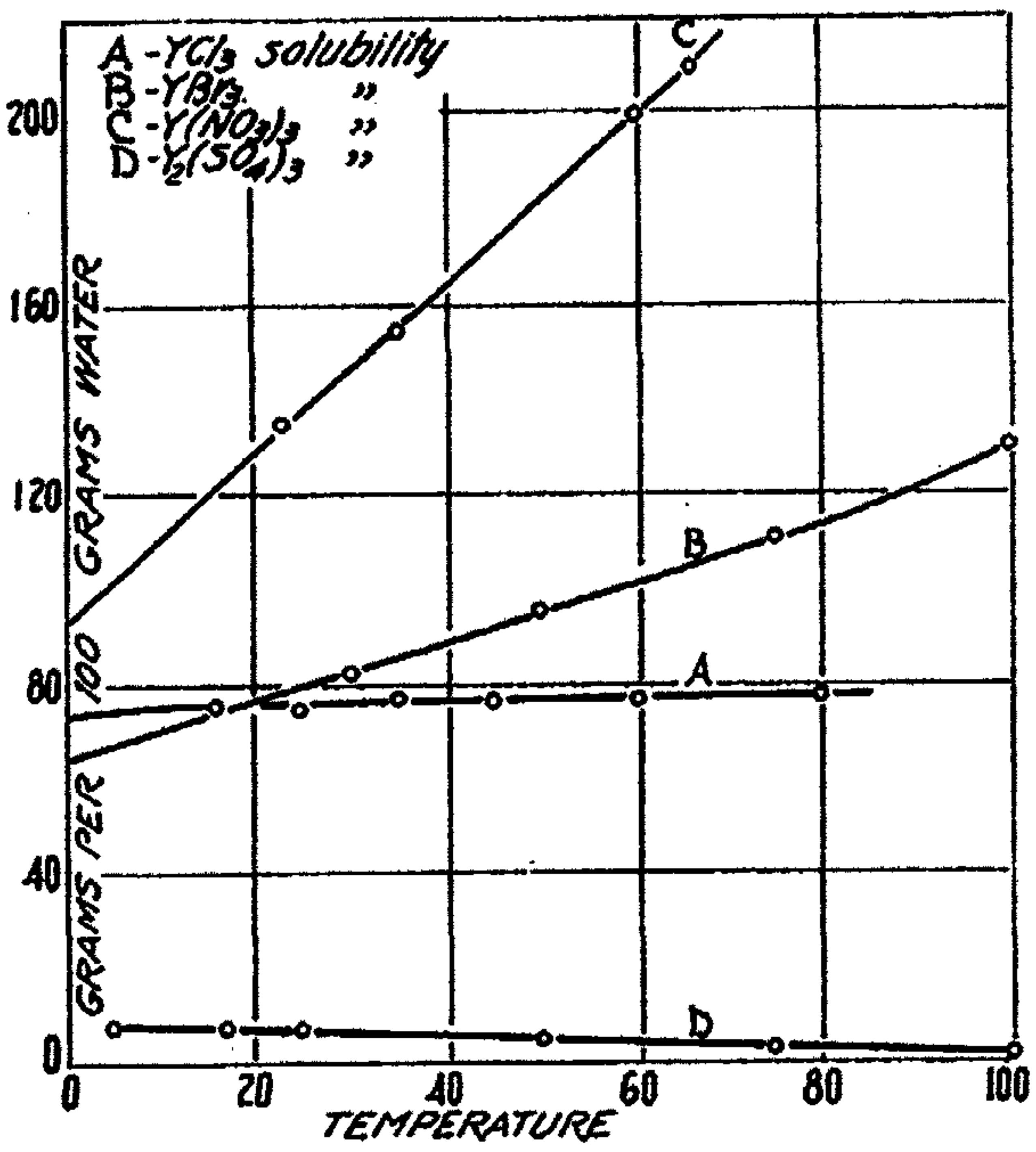

FIG. 1

This method of determining the amount of solute in solution was selected because of the difficulty in getting salts of a definite degree of hydration[1]. The accuracy of the results obtained was decreased by the fact that in the final calculations the experimental error was multiplied in some cases by 200 on account of the small quantities of material with which we were compelled

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[1] Hopkins and Balke: J. Am. Chem. Soc. 38, 2343 (1916).

to work. Duplicates which checked within 1.5% were accepted as satisfactory if the mean of these determinations gave a point within 1% of a smooth curve joining all the points obtained. In determining the value of $Y(NO_3)_3$ at 0° the duplicate determination was lost. Since the one value obtained gave a point exactly in line with the other values, it was accepted because of the difficulty of working at that temperature.

In order to test the degree of hydration of the solute about one gram of each of the hydrated salts was placed in a dilatometer and enough nujol added to fill the tube. This apparatus was mounted on a meter stick which served as a scale and was then immersed in a thermostat. The temperature was raised gradually from room temperature to 95° and at regular intervals the height of the nujol column and the temperature were recorded. When these results were plotted, in every case a smooth curve was obtained. This was interpreted as indicating that there were no changes in the hydration of these salts between 25° and 95°, since if any change took place a break in the temperature-pressure curve could be expected.

Urbana, Illinois,
June 26, 1924

STUDIES IN THE EXPERIMENTAL TECHNIQUE OF PHOTOCHEMISTRY

I. THE QUARTZ MERCURY LAMP AS A PHOTOCHEMICAL LIGHT SOURCE

BY LEWIS REEVE

INTRODUCTORY: By A. J. ALLMAND

Significant advance in photochemistry at the present time is essentially bound up with the possibility of doing accurate quantitative work under explicitly defined conditions. This, in its turn, is a matter of disposing of light sources of an adequate intensity which can be rendered sufficiently monochromatic, and of accurate measurement—comparative and absolute—of light intensity and of the light absorbed by the system undergoing photochemical change. In recent years, much has been done in the matter of the latter problem, though much still remains to do. But there is still a real dearth of constant and monochromatic light sources suitable for experimental work. A book—"Plotnikow's Photochemische Versuchstechnik"—has been written, dealing with these and with related matters. Even on its first appearance, it contained little of real value and is now, in any case, out of date. Luckiesh's "Ultra-Violet Radiation" contains much of interest. Beyond this, (Coblentz' valuable papers and Houstoun's "Studies in Light Production" may also be mentioned), practically no systemative attention has been paid to the subject. It is consequently proposed to publish from this laboratory, from time to time, together with the results of our own investigations, such information as we have collected and found useful in this connection, in the hope that the papers may prove of interest to others working in the field of photochemistry.

University of London,
King's College
May, 1924

The following paper is an account of some of the problems which enter into the use of the quartz mercury lamp as a quantitative light source for photochemical investigations. It is based, partly, upon an extensive survey of the literature on the subject and, partly, upon some three years of experience in the use of these lamps.

The Energy Characteristic of a Lamp

The light source used in a photochemical investigation emits certain radiations of definite wave length and intensity, some of which are absorbed by the substance under examination to give rise to chemical changes. It is necessary, therefore, in any quantitative photochemical investigation, to determine the energy characteristics of the lamp—the intensity and wave length of the radiations which it emits. This involves the measurement of:

(a) The total energy in the beam of light from the lamp (usually limited to the radiations which will pass a 1cm. quartz watercell: i.e. all the ultraviolet and visible and the very early infra-red portions of the spectrum).

(b) The relative spectral distribution of this energy.

The determination of (a) is carried out by means of a surface thermopile connected to a galvanometer of moderate sensitivity and is made absolute by comparison with a Hefner lamp. The determination of (b) involves, usually, the use of a spectro-thermopile of the highest sensitivity connected to a shielded moving-magnet galvanometer, again of the highest sensitivity; e.g. one of the Paschen or Coblentz type.

A typical energy distribution curve for a Cooper Hewitt 110 volt lamp, type Y1, age about 100 hours, burning at 62 volts 4.2 amps., determined by the writer, is shown in Fig. 1. A full description of the method employed for its determination will be given elsewhere. Meanwhile the following brief account may not be out of place.

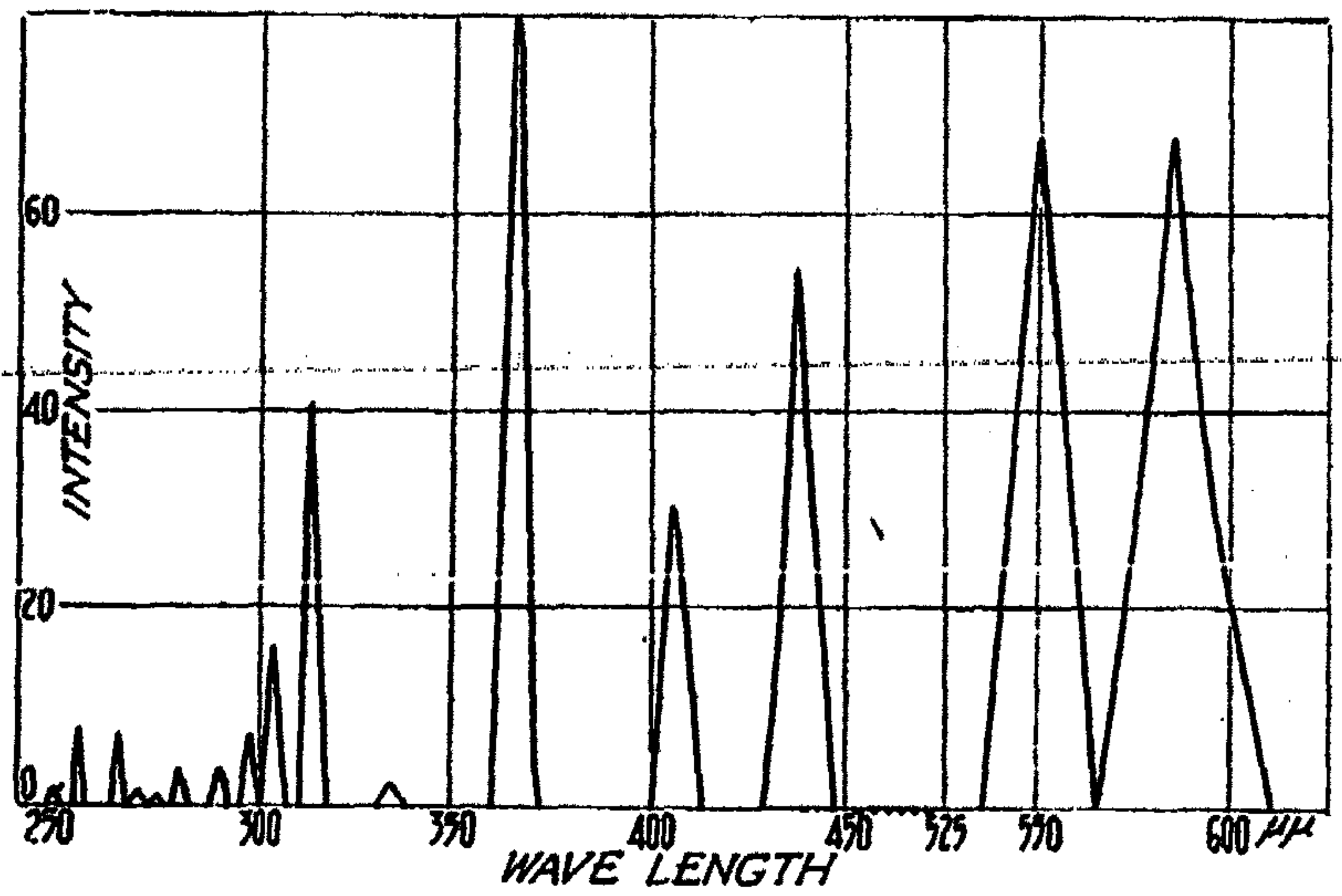

FIG. 1

The spectrometer employed was a Hilger monochromator for the ultra-violet, provided with quartz lenses and a quartz prism, and with adjustable slits for both collimator and telescope. The slit widths used were as follows: collimator 0.25 mms., telescope 0.30 mms. A Hilger spectro-thermopile of about 10 ohms internal resistance was mounted just behind the telescope slit, its terminals being connected directly to a Paschen type double-shielded galvanometer of internal resistance 11.77 ohms and a working sensitivity of about 300 mms. per microvolt at 1 metre.

The spectrum of the mercury lamp radiation was made to pass across the telescope of the spectrometer by rotating the wave-length drum fixed to the instrument, and as each spectral line passed through onto the thermopile receiver behind the slit, the galvanometer deflected. In the graphical representation of the results shown in Fig. 1, these deflections, reduced to a uniform galvanometer sensitivity, have been plotted against the corresponding wave-length readings on the drum. In this way, each line, or group of lines, has been responsible for the production on the curve of a triangular diagram. It will be observed that the bases of these diagrams cover a marked wave-range, despite the fact that most of the spectral lines corresponding to them are practically monochromatic; further this range increases with wave-length. The reason for this behaviour is to be found in the finite width of the collimator and telescope slits used. Owing to the finite width of the former the spectral lines too have a finite width, which, in the case of pure monochromatic lines is equal to the width of the collimator slit. In fact, a pure spectral line is nothing but an image, in monochromatic light of the collimator slit: and, owing to the symmetrical arrangement of collimator, prism and telescope, of exactly the same dimensions. In the case of compound lines, a number of components, each the width of the collimator slit, become superimposed and overlap to an extent depending upon the wave-length difference between them. Now, since the thermopile will register if even only a portion of a spectral line is falling upon its receiver, it is obvious that deflections will be obtained over a wave length range corresponding to the width of a spectral line plus the width of the telescope slit. The wave-length range dλ embraced by a given telescope slit varies with wave-length, increasing with the decrease in resolving power in the longer end of the spectrum. The actual values are given by the makers of the instrument. Hence the bases of our triangular diagrams, expressed as wave length ranges, will increase with wave-length (see Fig. 1): in the case of pure spectral lines in a manner exactly parallel to the increase of dλ.

It has already been mentioned that the width of a pure spectral line is equal to the width of the collimator slit. It follows that the base of its triangular diagram will be equal to the wave length range included by the total width of telescope and collimator slits. In the case of a compound line the width of the base, expressed as a wave length range, will exceed the above value by an amount equal to the overlap of the components; i.e. by $\partial\lambda$, where $\partial\lambda$ is the wave length difference between the extreme components.

The general triangular shape of the diagrams is due, of course, to the fact that as the spectral line, simple or compound, passes across the telescope slit the galvanometer deflection rises from zero to a maximum and then falls to zero again. It can be shown, however, that true triangles are given only by pure monochromatic lines and when telescope and collimator slits are of the same width. When the slits differ, and in the case of all compound lines, the diagrams are more complicated. It is hoped to discuss this matter more fully in a future paper.

It is now necessary to consider how the actual energy distribution between the various lines is to be determined from the diagrams they have given. In the case of pure spectral lines their relative energy can be obtained by comparing the heights of their triangles. For, since they are each of uniform intensity, and of the same absolute width, the maximum galvanometer deflections to which they give rise are true measurements of their energy content. We are assuming, of course, that the slit widths are kept constant throughout the determination. Mathematically, we have:

$$E_\lambda = k\,x \qquad (1)$$

where E_λ = energy content of the line λ,

x = the maximum deflection to which it gives rise,

k = a constant.

Since, however, the bases of the triangles given by pure lines are directly proportional to $d\lambda$ (defined above), equation (1) can be put in the form

$$E_\lambda = \frac{2k.\ \text{Area of triangle}}{d\lambda} \qquad (2)$$

Turning now to compound lines: since the diagrams they give are due to the superimposition of the separate triangles due to their monochromatic components, the same method of determining their relative energy content applies, viz.:

$$\text{Relative energy content} = \frac{\text{Area of diagram.}}{\text{Mean } d\lambda} \qquad (3)$$

This expression is a general one, determining the relative energy of all lines, simple or compound.

Not only, therefore, must we determine the maximum galvanometer deflection given by a line; in general we must also determine equally carefully the true base of its triangular diagram. This can be done fairly easily with the more intense lines; but in the case of weak ones, e.g. those given by our lamp below 300 $\mu\mu$, it is much more difficult, since the deflections round about the wave lengths limiting the base are necessarily extremely small. Since however most of these weak lines are pure, or at least, made up of one intense component, their relative energy can be obtained quite accurately from their maximum deflections. This, as we have pointed out, is true for all monochromatic lines, whatever their intensity.

The actual figures for the relative energy distribution of the lamp under consideration, calculated from Fig 1 in the manner described, are shown in Table I. They have been corrected for the selective reflection of the metallic mirror which forms part of the optical system of the Hilger monochromator, making use of values for this effect determined by the writer.

The figures for the relative energy distribution could be made absolute from the results of determination (a), i.e. the total energy in the beam of light from the lamp expressed as ergs per sq. cm per second. This was not determined for the lamp under consideration. In order, however, to give an idea of the magnitude of the absolute energy of lines the following figures for $\lambda 366.5\ \mu\mu$ of another, similar lamp may be given. Using a diaphragm over the centre of the lamp burner, containing an aperture 1cm in diameter, and placing this diaphragm at the focus of a quartz condenser lens 7.5 cms in diameter the energy of wave-length $\lambda 366.5\ \mu\mu$ in the resultant parallel beam was:—3.75×10^3 ergs per sq. cm per second.

Work of Other Investigators

Energy distribution determinations carried out on the above lines have been made by a number of investigators including Pflüger[1], Ladenburg[2], Hallwachs[3], Fabry and Buisson[4], Coblentz[5] and Souder[6]. None of these determinations are absolutely complete; that is, none of them could be used for calculating the absolute amount of radiant energy of a given frequency emitted by the lamps. For usually nothing but the deflections at the maxima were measured, whilst in no case are the values of dλ given. Without the latter, as we have seen, it is impossible to calculate the energy of compound lines.

TABLE I

Relative Energy of Lines in Quartz Mercury Lamp 1

Wave length.	Energy (in arbitrary units).
248.5 μμ	7.1 energy units
254 "	39.5 "
265.5 "	35.1 "
270 "	6.6 "
275 "	2.3 "
280.5 "	20.3 "
290 "	17.9 "
297 "	32.7 "
303 "	82.5 "
313.5 "	213.0 "
334 "	9.4 "
366.5 "	326.0 "
406.5 "	111.4 "
*437.5 "	166.6 "
*550 "	189 "
*585 "	207 "

*These figures are not quite correct; they should read 436, 546 and 579 μμ respectively. The differences are due to a slight misadjustment of the spectrometer, which, however, does not affect, in any way, the actual results.

Hallwachs' and Souder's results, which are given in the form of galvanometer deflections at the maxima of the lines, were used for absolute photoelectric determinations. These must, therefore, be incorrect to an extent depending upon the difference between the true energy distributions of the lamps used (calculated graphically as described above) and the energy dis-

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[1] Pflüger: Physik Z. 5, 414 (1904).

[2] Ladenburg: Physik Z. 5, 525 (1904).

[3] Hallwachs: Ann. Physik, 30, 593 (1909).

[4] Fabry and Buisson: Compt. rend. 153, 93 (1911); these investigators used an indirect method making use of a series of light filters instead of a spectrometer.

[5] Coblentz: Bureau of Standards, Bull. 9, 96.

[6] Souder: Phys. Rev. 8, 316 (1916).

tributions as calculated by them from the deflections at the maxima. The latter would have been equally correct had all the lines been pure, which however is not the case.

The most striking point however about all these energy distribution determinations, is that no two investigators obtain results even approximately identical. It will be seen below that, for various reasons, no such agreement could be expected and that there is no absolute value for the energy distribution. Ladenburg and Pflüger, at the time they carried out their determinations, apparently thought that there was. But, their results, though obtained using quartz lamps of the same type (Heraeus), were entirely different. All their figures need not be reproduced here; it will be sufficient to point out what is, perhaps, the most striking of their differences. Pflüger found the maximum deflection for the yellow line λ579 μμ to be far greater than that of the green line 546 μμ the actual figures being:

$$\frac{\lambda 579}{\lambda 546} = \frac{140}{90}$$

Whereas Ladenburg found the very reverse to be true: the green line from his lamp was more intense than the yellow. Thus:

$$\frac{\lambda 579}{\lambda 546} = \frac{27.4}{42.9}$$

(Ladenburg gives λ570 and λ540 as the maxima for these lines; his spectrometer was evidently out of adjustment).

It is evident from a further paper of Ladenburg's[1] in which he notes these differences and mentions that he has confirmed his results, that he thinks the energy distribution an absolute property of the lamp, the observed divergencies from Pflüger's results being due to other factors external to the lamp; e.g. differences between the optical systems of the spectrometers. There is little doubt, however, as to what is the main explanation for the observed divergencies. This is a difference in the electrical conditions (voltage and amperage) under which the two lamps were burning. These must have been entirely different in the two cases. Ladenburg gives the values for his lamp—2 amps. 85 volts; Pflüger does not, but, as will be seen later, his wattage must have been much higher.

This whole question of the influence of electrical conditions, together with the equally important factors of the age of the lamp and its dimensions, upon its energy distribution is fully discussed below. It will be found that these factors are of the greatest importance. Bearing this in mind it is surprising to find Ladenburg's results for the energy distribution reproduced in Plotnikow's well known "Photochemische Versuchstechnik" (Leipzig 1912) as absolute figures for use in photochemical investigations in which the mercury lamp is the light source employed. Plotnikow indeed commits the further error of calculating this energy distribution from the areas of the various triangles alone, without dividing them by the corresponding "dλ"s. As

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[1] Ladenburg: Physik. Z. 5, 556 (1904).

a result he makes the energy value for, say, the green line λ546 as compared with, say, the violet line λ403, about three times too great. Plotnikow's calculations in this matter are indeed valueless, whilst Ladenburg's figures, apart from not being absolute in any sense, cannot be used for this calculation at all since the values of dλ are not given.

Factors controlling Energy Distribution in the Quartz Mercury Lamp

Most of the later investigators (including Pflüger himself) realized the importance of the above-mentioned factors in determining the observed energy distribution and the differences between their results are undoubtedly due to differences in these factors. A full analysis of their effects has never been given, though there are sufficient data in existence to do so. Since the matter is one of the greatest importance to practical photochemists, such an analysis will here be attempted.

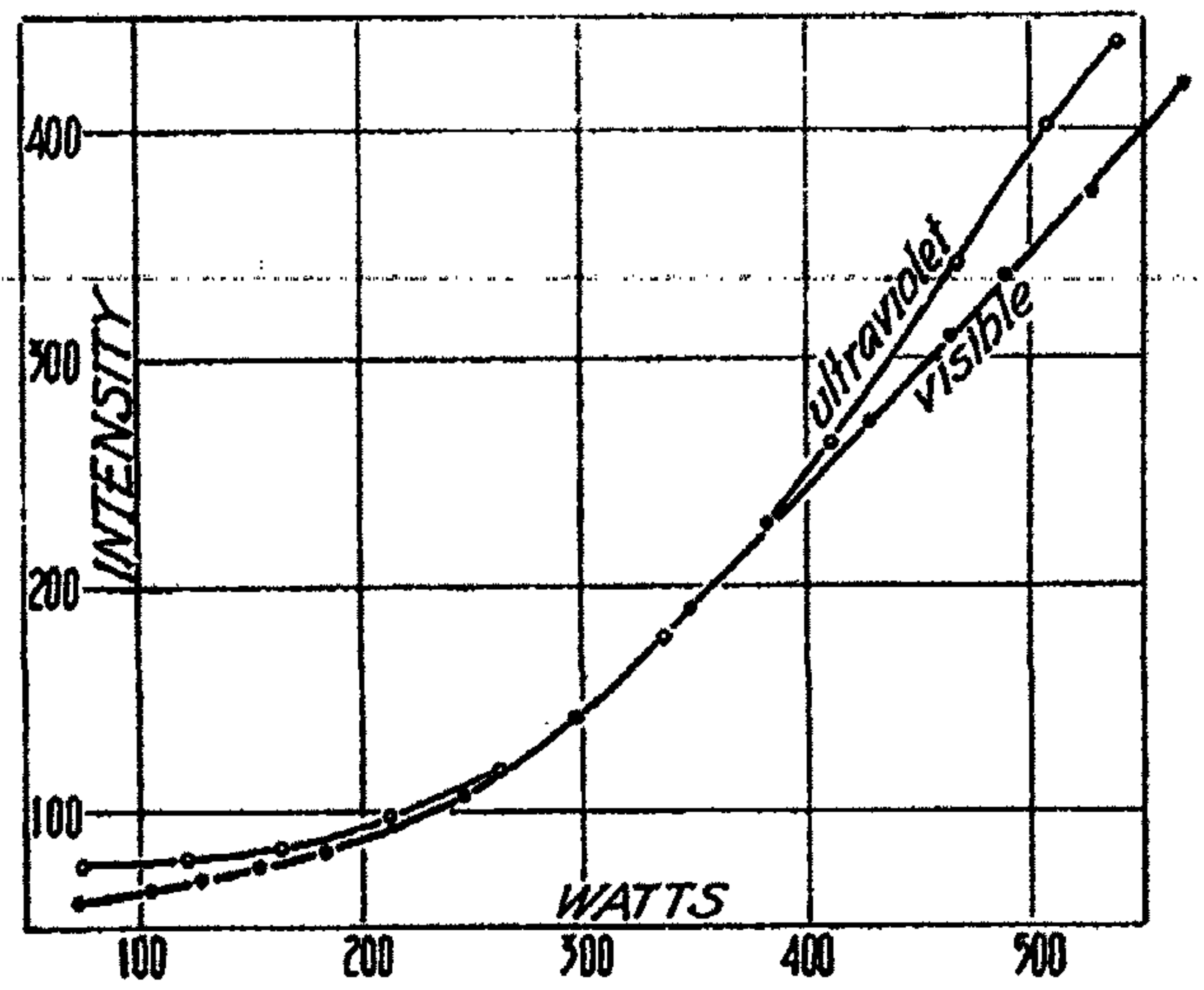

FIG. 2

As already mentioned, the factors which control this energy distribution are:

(1) the electrical conditions of the lamp

(2) the dimensions of the lamp

(3) the age of the lamp.

Factor (1) includes the temperature and vapour pressure inside the lamp, and will therefore depend upon the degree of cooling.

Each of these factors will now be considered in turn.

The Effect of Electrical Conditions

The effect of electrical conditions (wattage) upon the radiation emitted from the mercury lamp has been measured by a number of investigators including Pflüger[1], Kuch and Retchinsky[2], Vaillant[3], Fabry and Buisson[4], Henri[5], Boll[6], Tian[7], Souder[8], Coblentz[9], Coblentz, Long and Kahler[10], and Coblentz and Kahler[11]. Most of these investigators examined the effect of wattage upon the total radiant energy, or upon big spectral divisions of this energy; e.g. the whole of the visible or ultraviolet. These results will be considered first, after which the more complex reaction of wattage upon the distribution of energy amongst the separate spectral lines will be discussed.

The very thorough investigations of Kuch and Retchinsky[2] in the laboratories of the Heraeus Company at Hanau were the first in which the effect of wattage upon big spectral regions of radiation was considered. It was shown that both the visible and ultraviolet radiation increased with load, first slowly and then very rapidly, as shown by the curves in Fig. 2. Arbitrary units of intensity have been used in drawing these up, so chosen that for both spectral regions the intensities at 350 watts are identical.

Coblentz and Kahler[12] also have pointed out this rapid increase of total radiation with load and have given their results a more quantitative form by showing that an empirical expression of the type:

$$E = a.W^b$$

fitted the observed data. (E = the total radiant energy from the lamp, excluding radiations longer than 1.4 μ; W = wattage; a and b = constants.)

Thus, the expression:

$$E = 0.00457\ W^{2.314}$$

was found to fit observations for a Cooper Hewitt lamp between 150 and 400 watts to within 1%.

Such empirical equations must not be taken as being applicable to every lamp of the same type. The constants will undoubtedly vary from lamp to lamp; even for the same lamp they will alter if the conditions of cooling are not kept constant. For it has been shown by Kuch and Retchinsky[13], by Pflüger[14] and by Henri[15] that mercury lamps can be made to burn in a number of different ways. Most of them are designed to work off either 110 or 220 volt mains and are fitted with series resistances to cut down their electrode P.D.'s

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[1] Pflüger: Ann. Physik, 26, 789 (1908).
[2] Kuch and Retchinsky: Ann. Physik 20, 563 (1906).
[3] Vaillant: Compt. rend. 142, 81 (1906).
[4] Fabry and Buisson: Compt. rend. 153, 93 (1911).
[5] Henri: Compt. rend. 153, 265, 426 (1911).
[6] Boll: Compt. rend. 156, 313 (1913).
[7] Tian: Compt. rend. 155, 141 (1912).
[8] Souder: Phys. Rev. 8, 316 (1916).
[9] Coblentz: Bureau of Standards Bull. 9, 96.
[10] Coblentz, Long and Kahler: Bureau of Standards, Scientific Papers, No. 330.
[11] Coblentz and Kahler: ibid. No. 378.
[12] Coblentz and Kahler: loc. cit.
[13] Kuch and Retchinsky: loc. cit.
[14] Pflüger: Ann. Physik 26, 789 (1908).
[15] Henri: Compt. rend. 153, 426 (1911).

to about 70 and 140 volts respectively. If a lamp is burnt with this resistance first increased to well above its normal value and then steadily lowered the effect upon the electrode P.D. and lamp current, i.e., the form of the so-called "lamp characteristic," will depend upon what degree of cooling is applied to the lamp. If this is normal, i.e. no cooling is applied apart from that due to the cooling vanes and hot quartz surfaces, both voltage and amperage will rise steadily in a manner fixed by the designers of the lamp[1]. Thus Henri[2]

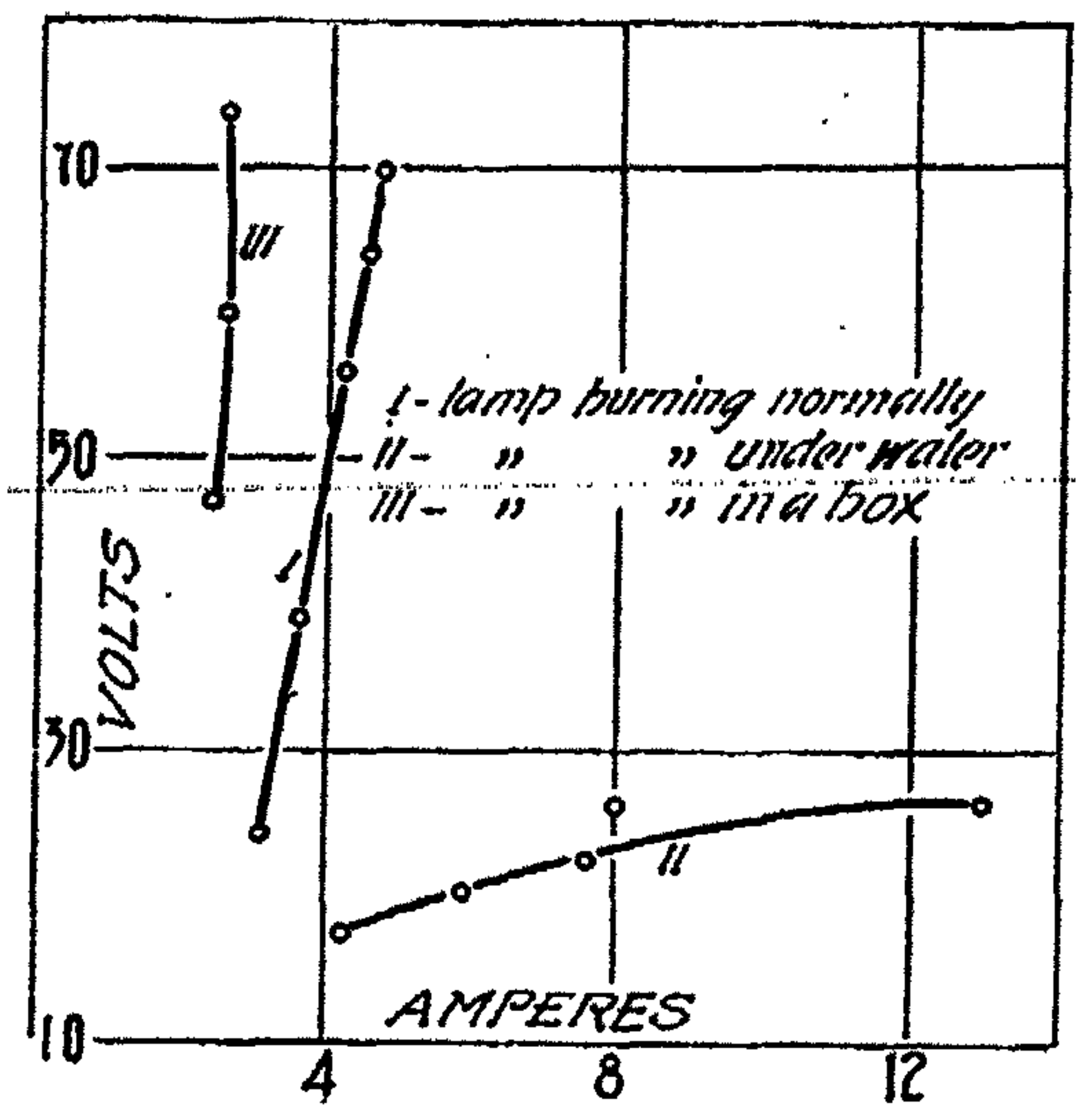

FIG. 3

gives figures for a 110 volt Westinghouse lamp (old type with bulb cooling) which are illustrated in curve I of Fig. 3. If however, very strong artificial cooling is applied the electrode P.D. tends to remain constant whilst the amperage steadily rises. This is shown in curve II of Fig. 3 which is drawn up from Henri's figures for the above lamp burning under water. Finally, if the cooling is below normal, e.g. if the lamp is burning in a box, the electrode P.D. rapidly rises whilst the amperage tends to remain constant. (See curve III Fig. 3 which is for the above lamp enclosed in a box.)

Both the total energy and the energy distribution of a given lamp burning under these different conditions must, undoubtedly, vary greatly. Thus, Henri measured the activity of his lamp in the three states of cooling, with the aid of a chemical actinometer consisting of silver citrate paper. This was allowed to darken to a standard tint and the inverse of the time required gave a measure of the lamp's activity; really, of ultraviolet activity. He obtained the results shown in curves I, II and III, Fig. 4, which correspond to the similarly marked curves of Fig. 3. It will be seen that in all cases the

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[1] See in this connection, Buttolph: Gen. Elec. Rev. 23, 741 (1920).

[2] Henri: loc. cit.

activity increases with the wattage but the rate of increase is greatest with the hottest lamp (curve III). The strikingly low activity of a lamp burning in water should be noted; it is of some practical importance since mercury lamps are often used in this way, e.g. for water sterilisation. Lamps burning directly in water are apparently very inefficient.

However, it is obvious that empirical equations connecting wattage and radiation, such as given by Coblentz and Kahler, are not absolute. They must be redetermined for each separate lamp, even if of the same type, since it is unlikely that the cooling, apart from other factors, will always be the same.

It should be noted that Henri did not determine the simultaneous change of the visible radiation with wattage and temperature, so that no conclusions as to changes in energy distribution can be drawn from his figures. As far as this question is concerned, Kuch and Retchinsky[1] have shown that at higher loads (above 370 watts) the ultraviolet tends to grow somewhat more quickly with wattage than the visible; (see Fig. 2). This has been confirmed for the extreme ultraviolet by Coblentz and Kahler[2] who, using a spectropyroheliometer of new design, examined the growth of various spectral regions of radiation from a quartz mercury lamp for wattages varying between 250 and 400. Their results for these two limiting wattages are shown in the following table:

TABLE II

Energy Input.	250 watts.	400 watts.
Deflection of galvo. for $\lambda 0.75-4.0\mu$. (infra red)	2.1 cms	9.6 6cms
Percentage of Total	15.4%	19.4%
Deflection of galvo. for $\lambda 0.39-0.75\mu$. (visible)	7.4 cms	25.2cms
Percentage of Total	54.5%	50.8%
Deflection of galvo. for $\lambda 0.30-0.39\mu$. (early U. V.)	3.3 cms	11.6 cms
Percentage of Total	24.3%	23.4%
Deflection of galvo for $\lambda 0.30\mu$. and less (extreme U. V.)	0.8 cms	3.2 cms
Percentage of Total	5.9%	6.4%

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[1] Kuch and Retchinsky: loc. cit.

[2] Coblentz and Kahler: loc. cit.

It will be seen that with increase of wattage there is a big increase in the intensity of all regions. The growth, however, is most rapid in the extreme ultraviolet and in the infra-red: the distribution of energy shifting outwards from the visible and early U. V. into those two regions.

The above conclusions as to the growth of various spectral regions, whilst of some value as indicating the general trend of the energy distribution changes, are not sufficient to give the complete energy distribution of a lamp at any given wattage. For this a detailed examination of the growth of each line with wattage is necessary. Such a complete determination, ranging throughout the infra-red, visible and ultra-violet, has not yet been carried out by a single investigator. But a number of separate investigations have been made which have led to some interesting conclusions. Thus, Kuch and Retchinsky[1] made a thorough examination of the visible lines of the mercury lamp spectrum and showed that their intensity changed in various ways, some lines being affected more than others in what is, at first sight, a very haphazard manner. On closer examination, however, a certain amount of regularity can be discerned, for it was possible to divide the curves, showing growth in intensity of lines with wattage, into three groups. This is shown in Fig. 5, curves I, II and III (reproduced from Kuch and Retchinsky's paper), in which the intensity I has been plotted against the wattage W. This intensity, at the arbitrary wattage of 75, has been given the value 20

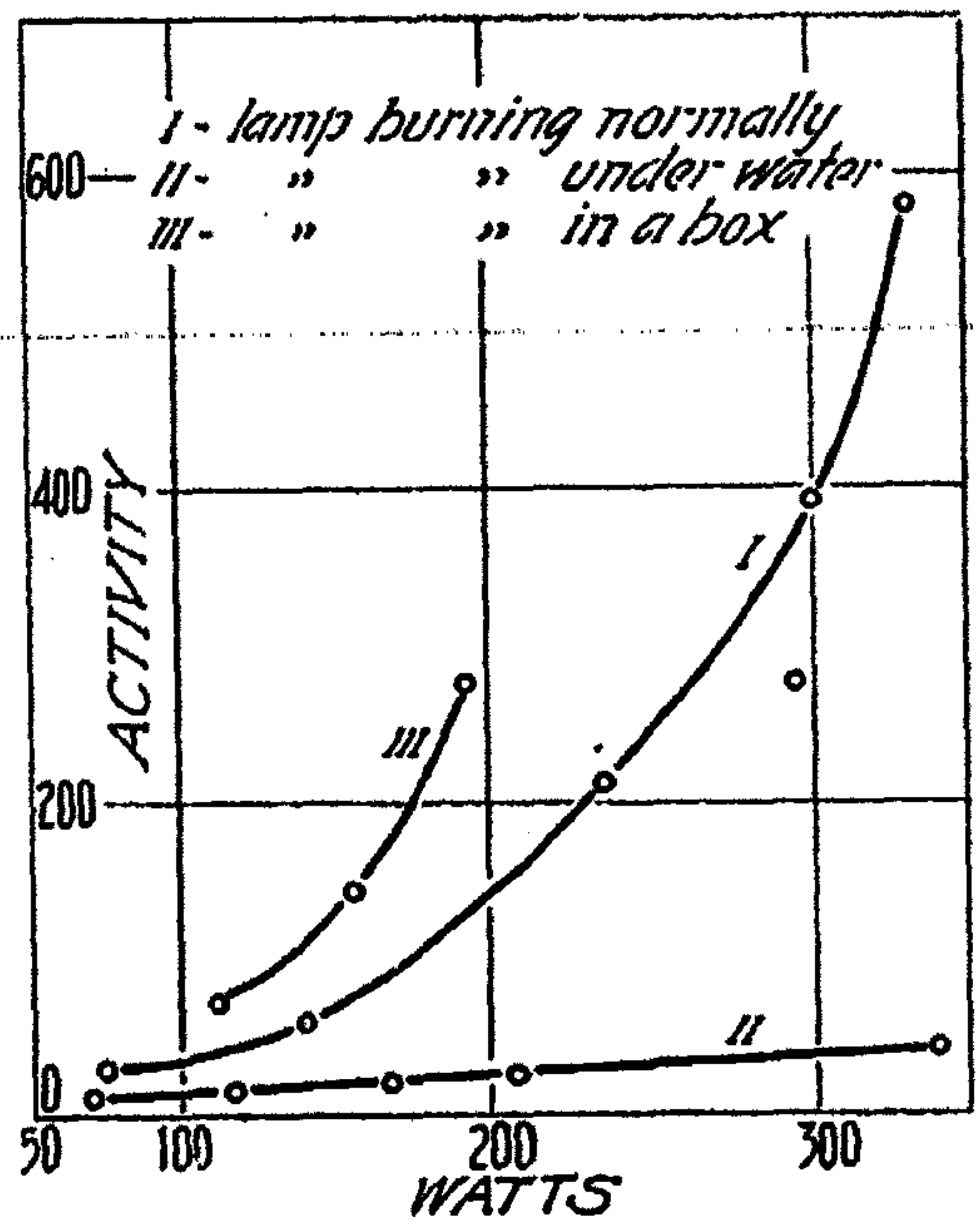

Fig. 4

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[1] Kuch and Retchinsky: loc. cit.

for all lines and the curves have been drawn up on this basis, from results determined photometrically, using a second mercury lamp, burning under constant load, as a standard.

Lines λ5461 (the green line), 4359 and 4047 μμ (curve III) which grow at the same rate are series lines building the first triplet of the second subordinate series. Note that from 100 to 400 watts the intensity of these lines grows about sevenfold. Lines λ6908, 6234, 5790 (the yellow line), 4960, 4348 and 4078 are again approximately on the same curve (I), allowing for the fact that they become somewhat indistinct on big loads. Note that from 100 to 400 watts the intensity of these lines increase about 23 times. Finally, lines λ5679, and 4916 also grow together (curve II).

The group of lines making up curve I includes the yellow line λ5790. The green line λ5461 grows at a much slower rate. It is possible, therefore, to understand the reason for the discrepancy between Ladenburg's and Pflüger's figures for the relative intensity of these two lines. At a low wattage the green line may be more intense than the yellow line (Ladenburg); but as the wattage is increased the yellow line grows much more rapidly until the relative intensities are reversed and the yellow line is stronger than the green (Pflüger). That this is actually the case has been confirmed by the writer for the Cooper Hewitt 110 volt lamp whose energy distribution is given in Fig. 1. When this burnt at 62 volts the intensities of the yellow and green lines were the same (68.2). If, however, owing to a rise in voltage at the mains, the burner voltage rose to 65, the yellow line immediately became more intense than the green (76.6 and 73.6 respectively). This rapid growth of the yellow line has been noted by other investigators; e.g. Vaillant[1], Fabry and Buisson[2], Coblentz[3], Souder[4]. Coblentz showed, further, that the infra red lines at 1.014 and 1.128 μ grew at about the same rate as the yellow line; this agrees with the shift of energy distribution into the infra-red already mentioned (Coblentz and Kahler). This work of Coblentz supplies the only data in existence as to the growth of the infra-red lines.

As far as the growth of the ultraviolet is concerned the only detailed work is that of Pflüger[5] who repeated some of Kuch and Retchinsky's work on the visible and extended it into the ultraviolet with the aid of a spectro-thermopile and galvanometer. Although he agrees with Kuch and Retchinsky that regularities of growth can only be observed on comparing series lines, he does not agree with them as to the nature of this regularity. Kuch and Retchinsky, it will be remembered, came to the conclusion as a result of a large number of measurements that, within a series, lines grew at exactly the same rate. According to Pflüger, however, the lines of shorter wave-length in a series grow faster than the longer (cf. of laws of temperature radiation);

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[1] Vaillant: loc. cit.

[2] Fabry and Buisson: loc. cit.

[3] Coblentz: loc. cit.

[4] Souder: loc. cit.

[5] Pflüger: Ann. Physik 26, 789 (1908).

though sometimes, as in the case of the triplet λ546, 436 and 406 μμ, the very reverse is the case and the line of longest wave-length grows fastest. It It should be pointed out that Pflüger's conclusions are based upon a much smaller number of observations than were carried out by Kuch and Retchinsky; further, that they apply to wattages above 400 whilst Kuch and Retchinsky's results are for wattage up to 400. Hence the latter still hold good.

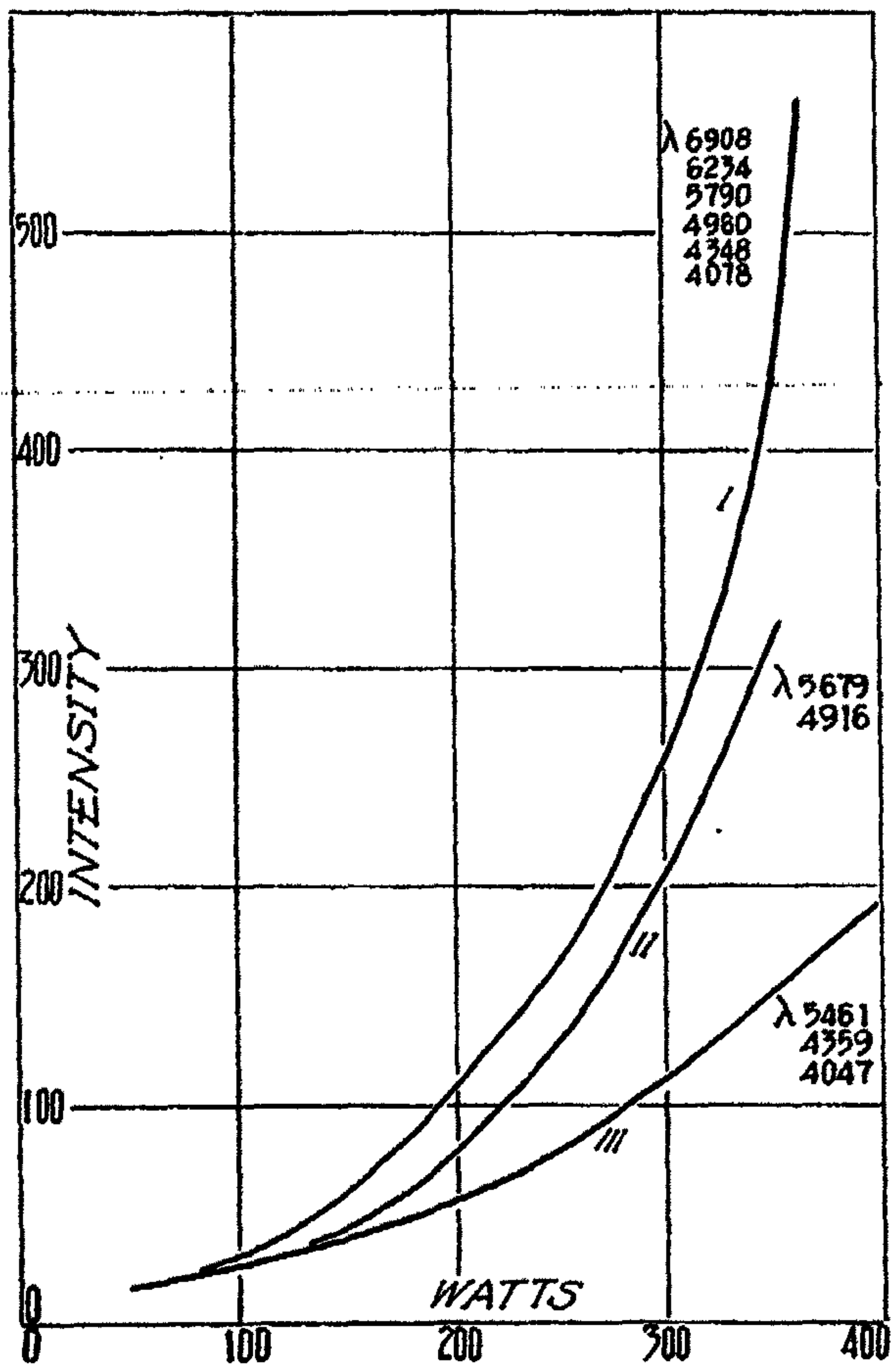

FIG. 5

Pflüger further found that, between 300 and 600 watts, the lines in the extreme ultra-violet grew more rapidly than those in the early ultraviolet. This, as already mentioned, has been pointed out by Coblentz and Kahler[1]; it has also been observed by Kuch and Retchinsky[2]. It is a result which agrees, qualitatively, with the laws of pure temperature radiation. Indeed, Pflüger's main thesis is that the growth of lines, at least of those within a

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[1] Coblentz and Kahler: loc. cit.

[2] Kuch and Retchinsky: Ann. Physik 22, 852 (1907).

series, is governed by these laws; i.e. increase of wattage, and therefore of temperature[1], favours short wave radiation. It must be said that the small number of measurements which Pflüger carried out seem hardly sufficient to support so general a thesis. That it cannot be entirely true, we have already seen from the work of Kuch and Retchinsky on the growth of the visible and that of Coblentz on the long visible and infra-red. The general tendency of growth is for the energy distribution to shift outwards into both the infra-red and extreme ultraviolet; the energy distribution in the visible and early ultraviolet remaining fairly constant.

Before we leave this question of the growth of lines with wattage one other investigation ought to be mentioned. This is the work of Boll[2] on the growth of the extreme ultraviolet line $\lambda 254\ \mu\mu$ from a Cooper Hewitt 220-volt lamp. He showed that the empirical equation:

$$\frac{E'}{E} = 0.84\left(\frac{W'}{W}\right) + 0.09\left(\frac{W'}{W}\right)^2$$

where E' = energy of the line at wattage W'
and E = energy of the line at wattage W

covered the growth of the line between 50 and 450 watts.

We must now turn to the next factor controlling the energy distribution in the radiation from a lamp, viz: its dimensions.

Absorption by Mercury Vapour

Assuming the electrical conditions (amperage and voltage drop per cm. of the burner) and the temperature of a lamp fixed, its dimensions will influence the energy distribution in its radiation by reason of the absorption of light within the lamp by the mercury vapour. Kuch and Retchinsky[3] and Pflüger[4] have measured this absorption by making use of two lamps, one behind the other and have shown that its magnitude is quite high. Thus, Pflüger, for an Haraeus lamp, has shown that for $\lambda 546\ \mu\mu$ it was 22.4% at 280 watts and 50.5% at 588 watts. It follows that given two lamps, burning under identical conditions, but one of greater depth than the other, a greater degradation of energy by absorption will occur in the lamp of greater depth. Further, Kuch and Retchinsky showed that, within a series, the lines of shorter wave length were absorbed less than the longer, and although Pflüger does not agree entirely with this conclusion, nevertheless, it still follows that the energy distribution in the above two lamps would be entirely different.

The Effect of the Age of the Lamp

It was noted quite early in the history of the mercury lamp that its emission, particularly in the U. V. fell off considerably with age. This was accompanied by a progressive discolouration of the inner walls of the burner.

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[1] See in this connection Kuch and Retchinsky: ibid p. 595.

[2] Boll: loc. cit.

[3] Kuch and Retchinsky: Ann. Physik **22**, 852 (1907).

[4] Pflüger: loc. cit.

Thus, Bordier[1] in the course of a paper on the use of quartz lamps in phototherapeutic work, showed, by use of a chemical actinometer, that a lamp two years old took seven times as long to produce the same effect as a new lamp, whilst one a year old took three times as long. He pointed out the danger of too great exposures when using new lamps and advised the use of his actinometer.

Again, Courmont and Nogier[2], using photographic, chemical and physiological tests, showed that there was a marked diminution in the ultraviolet component of a lamp after using it at excessively high loads; whilst Berthelot and Gaudechon[3] observed that all extreme ultraviolet had disappeared from a lamp whose inner walls had become discoloured.

Against these observations must be set those of Henri[4] and of Fabry and Buisson[5] that age has little effect upon the emission of lamps: a conclusion never since confirmed by other workers and, above all, not borne out by the thorough investigations on the subject by Coblentz, Long and Kahler[6].

These investigators examined the decrease in the total radiation and in its ultraviolet component from a number of mercury lamps and showed that a steady falling off in intensity occurred. Thus, for a 220 volt Cooper Hewitt lamp on 440 watts the following figures were obtained:

Decrease in Total Radiation with Age

Age of lamp in hours	0	97	177	343	450	522	640	783	959	1064	1140
Total energy below 1.4 μ (as galvo) deflection)	1611	1497	1503	1380	1033	910	1104	1107	1069	1025	1034

Decrease in Ultraviolet Radiation with Age

Age of lamp in hours	0	97	177	450	522	640	783	959	1140
Radiation shorter than 0.45 μ Percentage of Total	69.4%	67.8	60.4	59.9	58.2	54.9	52.3	50.8	49.1%

The above figures for age are for discontinuous burning over a period of a few months. The life of the lamp for continuous burning is longer. The authors suggest that, at the expense of luminous efficiency, there would be a marked increase in the useful life of mercury lamps by operating them at lower temperatures (i.e. lower wattages) since this would decrease devitrification of the quartz and disintegration of the tungsten electrodes, the two chief causes of the falling off in radiation.

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[1] Bordier: Arch. Elec. Med. (1910) 396.

[2] Courmont and Nogier: Compt. rend. 152 1746 (1911).

[3] Berthelot and Gaudechon, Soc. internat. des Electriciens, 5th June 1912.

[4] Henri: Compt. rend. 153, 426 (1911).

[5] Fabry and Buisson: loc. cit.

[6] Coblentz, Long and Kahler: loc. cit.

The figures for the falling off given by the authors must not be regarded as in any way absolute. The only general conclusion is that there is a steady decrease in intensity, but its extent, even in lamps of the same make, varies considerably. Thus, one R. U. V. lamp which was tested showed almost constant radiation for the period 300 to 1200 hours. On the other hand, another followed the behaviour of a Cooper Hewitt lamp (see above) almost exactly. Although no comparison was made amongst Cooper Hewitt lamps themselves a similar conclusion would undoubtedly apply to them; i.e. no general law can be laid down for the extent of falling off.

It will be seen that the above investigators examined the drop in radiation from large spectral regions without making a detailed examination of energy distribution. The writer has obtained some data on this latter point which may be reproduced here though a fuller account will be published elsewhere. A certain 110-volt Cooper Hewitt lamp after burning for about 500 hours was accidentally broken. After repair and renovation (which included reheating of the whole burner in an electric furnace) the energy distribution of the lamp was measured and it gave a curve very similar to that shown in Fig. 1, i.e. not differing much from that given by an almost new lamp. After another 500 hours of burning the energy distribution was redetermined and it was found that a considerable falling off in the intensity had occurred, chiefly in the ultraviolet. Assuming no reduction in the intensity of the green line λ546 μμ, (approximately true) the falling off for the other lines was as follows:

Falling Off in Intensity with Age

Line	Percentage Reduction	Line	Percentage Reduction
436 μμ	12.2%	290 μμ	(47%)
406 "	13.6 "	280.5 "	(36 ")
365 "	28 "	275 "	(23 ")
344 "	42 "	270 "	(50 ")
313 "	57.4 "	265.5 "	59 "
303 "	59.5 "	254 "	61 "
297 "	65 "	248.5 "	100 "

The figures shown in brackets are calculated from small deflections and are therefore not very reliable. It will be seen that, on the whole, a steady falling off in intensity has occurred, increasing from the blue into the ultraviolet until it reaches 100% at 248μμ; i.e. λ248.5 μμ has disappeared entirely. It was found by the writer that these extreme ultraviolet lines (below 254μμ) are extremely fugitive. λ248.5 μμ will sometimes disappear in as short a time as 100 hours, whilst λ230, 234, 237 and 240μμ, indications of which are given by the thermopile with perfectly new lamps, always disappear in less than 50 hours. This is confirmed by the fact that the amount of ozone given off by Cooper Hewitt lamps, formed photochemically by these very extreme ultraviolet lines, falls off very considerably within this time.

Some Practical Considerations

We have examined in some detail the various factors which control the energy characteristics of the quartz mercury lamp and it is now necessary to consider how they will affect the use of the lamp by the photochemist.

It is obvious that a constant voltage supply is practically essential for strictly quantitative work. It is true that corrections for voltage fluctuation could be applied by making use of empirical equations such as used by Coblentz for the total radiation and by Boll for each separate line. But, as we have seen, it would be necessary to determine such equations for every lamp in use, since their constants vary even for lamps of the same make. It would be far more convenient to keep the burner voltage constant. Assuming this done, (either by regulation at the mains or by the use of storage batteries) it would be possible to determine the energy distribution for a lamp with some accuracy; and this determination would apply to it for some time if burnt under the same conditions of load and cooling.

The latter precaution must be emphasised: a lamp, whose energy distribution had been determined whilst burning in the open air, could not be applied to quantitative photochemical reactions when burning in an enclosed box, even if the main voltage remained unchanged; for the burner voltage and amperage, and therefore the energy characteristics of the lamp would be entirely different.

The energy distribution of each lamp used must be determined separately; for even if of the same make and age and burning under exactly the same electrical conditions they may yet exhibit marked differences owing to differences in dimensions and to variations in the transparency of the quartz.

We are now confronted with the problem of the precautions which should be taken to correct for the diminution of radiation with age. In this connection, it is obvious that it would be practically useless to apply the quartz mercury lamp to quantitative photochemical work in the very extreme ultraviolet (below $\lambda 248\ \mu\mu$) unless the intensity of these rapidly weakening radiations were followed with the spectro-thermopile throughout the course of the reaction. Almost equally is this the case for $\lambda 248$ itself. When we come to the radiations of greater wave-length than $\lambda 248\ \mu\mu$, viz: $254\mu\mu$ and the whole of the remaining ultraviolet and the visible the solution of our problem is somewhat easier. Two courses are open to the investigator. One is to remeasure at suitable intervals the energy characteristics of the lamp. After the first complete energy distribution had been carried out, all that would be necessary for redeterminations would be the values of the deflections at the maxima of the lines (the heights of the "triangles"). The length of the intervals between each determination would depend upon the region of the spectrum which was being utilized in the reaction. For photochemical work between $\lambda 254$ and $\lambda 313\ \mu\mu$, intervals of not more than 200 hours would be advisable. In the spectral region above $\lambda 313$ and particularly in the visible much longer intervals would suffice: say 350 hours in the ultraviolet and 500 hours in the visible. During these intervals a steady falling off, between the limits indicated by the two energy distributions bounding them could be assumed.

The second method which might be used would be to take only two series of measurements of the lamps energy characteristics, one at 100 hours, the other at, say, 1500 hours and to obtain the intermediate values by means of periodic measurements of the intensity of radiation passing suitable light filters. Monochromatic filters would be best, but if unobtainable, a series of regional filters would give the desired measurements; (see in this connection Fabry and Buisson (Compt. rend. **152**, 1839 (1911)).

As a result of either of the above proceedures it would be possible to know the energy characteristics of the lamp used, at any time during the course of a photo-reaction, from which, as indicated at the beginning of this paper, the absolute energy absorbed by the substance under consideration could be calculated.

Summary

An account has been given of some of the problems which enter into the use of the quartz mercury lamp as a photochemical light source. The method of determining the energy distribution in its radiation has been described and the investigations upon this point have been mentioned. An examination of these has shown that, firstly, most of them are incomplete; secondly, that there are marked differences between them. These differences have been shown to be due, most probably, to differences in the following factors:

(i) the electrical conditions of the lamp
(ii) the dimensions of the lamp
(iii) the age of the lamp

each of which are then discussed in turn. The more important investigations upon the effect of electrical conditions upon radiation have shown that:

(1) The total radiation grows rapidly with increase of wattage. Empirical equations can be deduced to connect intensity of radiation with wattage, but the constants of these equations vary from lamp to lamp. Even for the same lamp they will depend greatly upon the degree of cooling.

(2) The intensities of various portions of the spectrum do not grow with wattage at the same rate. On the whole, the infra-red and the extreme ultraviolet grow the fastest. Careful examination of the growth of separate lines has shown that these can be divided into a number of groups, each of which grows at its own definite rate. The marked discrepancies between the relative intensities of the yellow and green lines, in particular, can be explained as a result. Empirical equations can be determined for the growth of each line.

Absorption of radiation by the luminous mercury vapour inside the lamp occurs. This absorption is quite marked, and varies with wave-length. Within a spectral series, the lines of shortest wave-length are absorbed least. It follows that the dimensions of a lamp will affect its energy characteristics.

An account is given of the various investigations which have shown the falling off in luminous efficiency of lamps with age. The extent of this falling off varies considerably even amongst lamps of the same make. It is less for lamps burning continuously than for those burning discontinuously. It is due to devitrification and discolouration of the quartz and is most marked in the extreme ultraviolet.

Finally, various practical considerations are discussed which follow as a result of the above conclusions.

The writer's thanks are due to Prof. A. J. Allmand for suggesting the writing of the above paper and for his unstinted help and encouragement during the course of work which led to it. He must also thank the Department of Scientific and Industrial Research for their grant whilst a Student in Training.

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THE BEHAVIOR OF SILVER IODIDE IN THE PHOTO-VOLTAIC CELL, II. A NEW TYPE OF SILVER IODIDE PHOTO-VOLTAIC CELL

BY ALLEN GARRISON[1]

This work on silver iodide is a continuation of an investigation of the cuprous oxide and silver halide photo-voltaic cells[2] and the related photo-chemical and photo-physical properties[3], which has been carried on under an appointment of the Research Fellowship Board of the National Research Council.

The light-sensitive electrodes used in the first experiments with silver iodide were prepared by depositing crystals of the salt in a thin layer over a plate of metallic silver. These electrodes were found to become either positive or negative on illumination depending on certain conditions of the electrode or electrolyte.

The experiments recorded in this report were performed on a different type of electrode, one whose properties was in some particulars better adapted to the discovery of the relation between the color or wave-length of the light rays and the extent and nature of the photo-chemical action. Therefore the experiments with this electrode have given results of importance bearing on a phase of the problem which has been only slightly developed.

Experimental Procedure

The complete photo-voltaic cell as well as the method of observation was the same as that described in the previous paper on silver iodide[4] with the exception of the light-sensitive electrode and its method of preparation. This consisted of a gold plate 2 cm. wide and 3 cm. long over which a thin film of molten silver iodide had been spread and permitted to solidify.

The gold acts only as an inert metallic support for the apparently amorphous silver iodide. Electrodes having the same properties were made on plates of both platinum and palladium. Silver can not be used since the molten iodide apparently reacts with the silver and does not solidify in a thin transparent layer as it does on the other metals.

The entire front surface of the electrode was covered uniformly with silver iodide and the entire back surface was covered with paraffin. Thus when the electrode was placed in an electrolyte an electric current could pass between the gold and the solution only through the thin layer of silver iodide. This layer was so thin that it was transparent, had a greenish yellow color

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[1] National Research Fellow in Chemistry.

[2] Garrison: J. Phys. Chem. 27, 601 (1923); 28, 333 (1924).

[3] Garrison: J. Phys. Chem. 28, 279 (1924).

[4] Garrison: J. Phys. Chem. 28, 333 (1924).

and was a good conductor of electricity. When current was passed into the electrode from the solution iodide ion was liberated into the solution and silver was deposited in dark spots over the surface of the gold.

The electrodes were mounted in the photo-voltaic cells and illuminated as has already been described in the previous paper.

Light of various colors was obtained by the use of light filters. A large assortment of these was at hand and a good variety of wide and narrow bands in all portions of the visible spectrum could be obtained by using the proper combination of filters. The range of wave-lengths admitted to the cell in each case was measured with a direct vision spectroscope.

Experimental Results

The light-sensitive electrode consisting of a thin continuous layer of silver iodide on gold in a solution of KI, $AgNO_3$ or NH_4NO_3 is obviously an entirely different electrochemical system from that consisting of a silver electrode covered with a layer of the halide in the state of fine crystals. Therefore it is not surprising that the electrode should have distinctly different properties.

In contrast to the silver-silver halide electrode the photo-potential of the gold-silver halide system was always positive provided the electrode did not have metallic silver deposited on it from long continued exposure to light. The changes in potential on illumination were slow, in case the light intensity was low it required several hours for the potential to reach its maximum value.

This suggested that the effect may be due to the heating power of the rays but this was found to be of much smaller magnitude than the photo-potentials obtained. Thus the temperature coefficient of one of the electrodes in a 0.1 normal solution of NH_4NO_3 was found to be +.0009 of a volt per degree while the photo-potential of this system in the light of a 500 candle power lamp at 25 centimeters was +.45 of a volt. The temperature did not rise more than 2°C.

The return of the electrode potential to its original value after the light was removed was also a very slow process requiring several hours. This property of the electrode made possible a very instructive experiment. An electrode in a 0.1 normal $AgNO_3$ solution was found to have a potential of +0.413 volts relative to the 0.1 normal calomel element in the dark. The light-sensitive electrode was then removed from the solution, dried and exposed to light in air behind a water screen for ten minutes. When the light was extinguished it was placed immediately in the solution again and its potential found to be +0.744 volts. After several hours this had fallen to +0.413 again. This demonstrates conclusively that the change in potential is not, like the Hallwachs effect, a result of electron emission. A change is produced in the silver iodide by the light and is only slowly reversed in the dark. This photo-chemical change has been shown to involve an increase in solubility.

Changes in the constitution of the electrolyte had little effect on the magnitude of the photo-potential. For example, an electrode in a 0.1 normal potassium iodide solution had a dark potential of +0.2587 volts relative to the calomel element and its photo-potential was +0.450 volts while the same electrode in 0.1 normal silver nitrate solution had a dark potential of +0.4110 volts and a photo-potential of +0.432 volts.

After continued illumination the silver iodide layer became discolored by small spots of silver. After this happened the properties of the electrode changed and it began to behave like the electrodes prepared on metallic silver. The original properties of the electrode were restored by simply melting the silver iodide and allowing it to solidify again.

The Relation between the Light Intensity and the Photo-Potential

It was found that the relation between the maximum values of the photo-potential and the intensity of the illuminating beam could not be measured as accurately as was possible in the case of electrodes which responded to the light more rapidly. When light of relatively low intensity was used it required as long as six hours for the electrode potential to rise to its equilibrium value and during this period of time enough permanent decomposition occurred to alter the nature of the electrode. The rough experiments which were possible indicate that the relation is the same form as was obtained for the silver-silver halide electrodes. For low intensities the maximum photo-potential was almost linear with the intensity and for higher intensities became nearly constant and independent of the intensity.

Since the relation for the maximum values could not be obtained accurately, measurements were made on the rate of rise of the photo-potential. If the values of the photo-potential were plotted against the time the points fell approximately on an exponential curve. The rate of the rise of the photo-potential was nearly constant and proportional to the light intensity immediately after the light was turned on but after some time had elapsed the rate became slower and approached zero when the potential was near its maximum value.

It was not necessary to solve this exponential curve for its constants for, by limiting the light intensity to moderate values and by confining the observations of rate to the first five minutes of illumination, the rate of rise of the photo-potential could be made to be linear with the light intensity. The slope of this line is therefore a constant which is characteristic of the rate of the photo-chemical reaction proceding in the electrode.

Table I contains some of the results which were obtained with a gold-silver iodide electrode in 0.1 normal NH_4NO_3 solution. The first column gives the color of the light and the range of wave-lengths included in the illuminating beam for each observation. The second column gives the intensity of the light as recorded by the thermopile.

When the light was turned on the potential was recorded at one minute intervals and an average rate of change in volts per minute was calculated for the first five minutes of illumination. This average rate of rise dE/dt is recorded in the third column. After each illumination the cell was left in the dark until the original potential was restored before another observation was made.

The values in the fourth column are the rates per unit intensity, that is,

$$K = \frac{dE}{dt} \cdot \frac{1}{I}$$

TABLE I

The Rate of Rise of Photo-potential and the Light Intensity

Wave-length	I	$\frac{dE}{dt}$	K
white	3.0	.0120	.0040
.406—.790	4.4	.0173	.0040
microns	5.0	.0200	.0040
	6.4	.0252	.0039
	7.0	.0278	.0039
	7.6	.0298	.0039
blue	3.7	.0036	.00091
.402—.495	5.2	.0048	.00092
microns	7.2	.0065	.00090
	15.8	.0150	.00095
	24.5	.0230	.00093
red	3.4	.0032	.00094
.602—.790	4.9	.0045	.00091
microns	7.8	.0071	.00091
	10.1	.0090	.00089
	19.8	.0181	.00091
red (narrow)	6.0	.0042	.00070
.645—.750	9.5	.0070	.00073
microns	14.6	.0106	.00072
	19.6	.0142	.00072
	24.8	.0180	.00072

The extent to which the values of dE/dt are linear with I and the relative values of the slope K may be seen by reference to Fig. 1 in which the light intensity is plotted on the X-axis and the rates on the Y-axis. I is the line obtained with the white light, II with blue light, III with the wide red band and IV with the narrow red band.

The Relation Between the Wave-Length and the Photo-Potential

It is apparent from Fig. 1 that the slope of the line for white light is several times as large as that for either the red or blue light. That is the amount of chemical action for a given intensity in a given time is several times as much in the white light. It sould naturally be concluded that the cause of this lies in the fact that there are certain wave-lengths admitted to the cell in white light which are shut out by the blue and red ray filters and that these wave-lengths produce a relatively rapid chemical action. One would expect to find lines or bands in the visible spectrum for which the value of K would be very large. However, this is not the case. There are no single wave-lengths in the visible spectrum having any particularly marked effect on silver iodide.

This fact was demonstrated by data which are summarized in Table II. A gold-silver iodide electrode in 0.1 normal NH_4NO_3 solution was used. The electrode was first illuminated with white light of wave-lengths extending from .406 to .790 microns and the rate of rise of the potential measured during the first five minutes of illumination. From this the average value of the slope was calculated and found to be .00395 volts per minute per unit intensity.

The white light was then subdivided into three divisions one blue, one green and one red such that no portion of the white light was omitted. The value of K was measured for each color separately as is recorded in the table.

The light was then further subdivided by different combinations of ray filters into six ranges of wave-length such that no color was omitted. The values of K were determined for each separate range in the same way.

Table II

The Rate of Rise of the Photo-potential and the Wave-length

Range of Wave-lengths	Slope of line(K)
.406 – .790	.00395
.406 – .495	.00012
.450 – .565	.00060
.516 – .790	.00076
	.00148
.406 – .450	.00005
.434 – .492	.00009
.500 – .565	.00010
.516 – .561	.00005
.556 – .606	.00014
.606 – .790	.00050
	.00093

Since the combination of the separate beams of light would produce the complete visible spectrum it might have been supposed that the chemical effects would be additive if each color contributed to the chemical action independently. The remarkable fact discovered is that this is not the case.

Although the light from the three filters if combined would give white light with no colors omitted and of intensity three times as large as the white light used, the addition of the slopes of the three lines gives .00148 a value less than one half of the slope of the line for white light. The division into six parts reduces even more the chemical action of the white light. The addition of the slopes of the six lines gives .00093 which represents a total intensity of six times the white light used but less than one fourth of the amount of chemical action.

We thus see that the photo-chemical action on silver iodide in any part of the visible spectrum diminishes as the light becomes more nearly monochromatic the light intensity being maintained at a constant value.

The rate of the chemical change was relatively larger in the long wavelength end of the spectrum. With the exception of the narrow band .516–.561 microns the values of K increased in every case in going from the blue to the red limit. The results are not quantitatively comparable on this point because the bands into which the white light was subdivided were not of exactly uniform width.

The Effect of Previous Illumination

The generalization concerning the greater activity of the red rays does not hold for newly prepared electrodes which have not been illuminated. Such electrodes are scarcely sensitive to red light at all until they have been exposed to the action of the short wave-length rays. A previous illumination to the blue region is sufficient to sensitize the electrode to the red.

A freshly prepared electrode in 0.1 normal NH_4NO_3 solution was exposed first to the red region .602 – .790 microns and the constant K determined to be .00015 volts per minute per unit intensity. A determination was then made in the blue region .402 – .495 microns and K found to be .00040 volts per minute per unit intensity. The experiment required about ten minutes exposure to the blue light. The potential of the electrode was then allowed to recover in the dark to its normal value and the value of K was redetermined in the red region. It was found to be .00130 volts per minute per unit intensity or almost ten times as large as before exposure to the blue light.

Theoretical Part

It has been known for some time that silver chloride, bromide and iodide as well as cuprous oxide and some other salts become better conductors of electricity when illuminated by visible light. Whether this is entirely electronic conduction or electrolytic in nature has not been proven in all cases but the phenomenon requires that a charged material either electrons or ions become loosened from the main structure of the solid to such an extent that it may be moved by an electric field.

Some experiments indicate that the visible light liberates free electrons which contribute to the conductivity. It has been found that there is also a separation or tendency toward a separation of the charged elements as ions under the influence of the light. This idea was first deduced from the experiments with photo-voltaic cells (1) and was later verified by the discovery that the salts when in equilibrium with the ions in water become more soluble on illumination. The increase in concentration of the ions in the presence of light was demonstrated by direct conductivity measurements (2).

The increase in tendency to dissolve and ionize when light is absorbed produces an increase in ionic concentrations and thus a change in equilibrium electrode potentials. The new type of electrode used in the above experiments differs from the others in that the silver was absent and the current must pass directly through the iodide. The simplest way to consider the decomposition in this case is as follows: The silver iodide in the thin layer discharges iodine ions into the solution and silver on the surface of the gold. This would result in a positive photo-potential until a little silver thus liberated came in contact with the solution. When this happened the electrode would behave like those described in the previous paper.

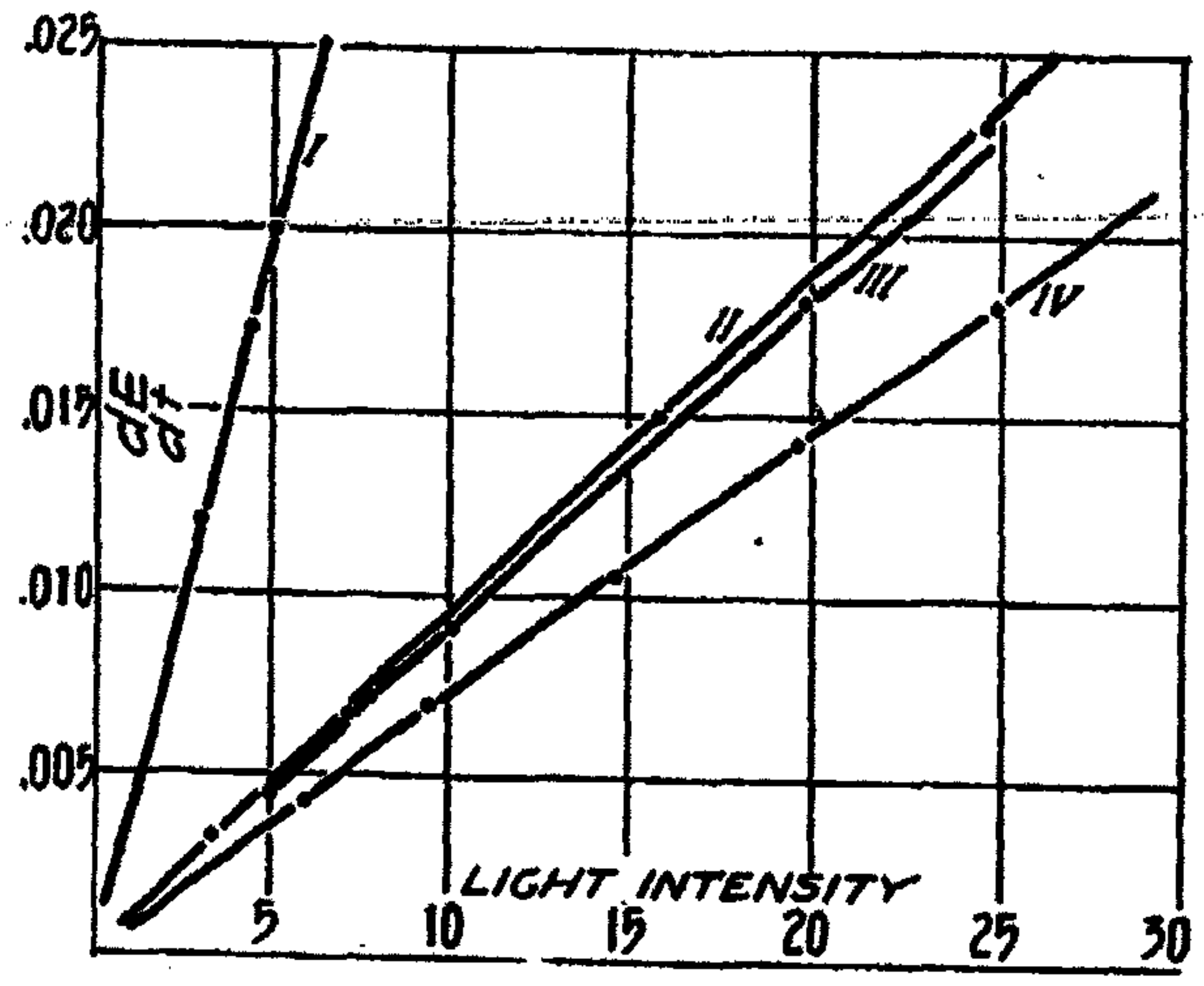

Fig. 1

The rate of rise of the positive photo-potential is therefore a measure of the rate of ionization of the silver iodide by the light. The slope K of the lines in Fig. 1 gives a quantitative measure of the rate of the reaction $\mathrm{AgI} + \text{light} \longrightarrow \mathrm{I}^- + \mathrm{Ag} + (+)$. Or the rise of potential may be considered a measure of the increased number of silver iodide molecules which have been made electrically polar by the light.

A picture of the atomic processes can best be drawn by using the molecular theory and notation of Prof. G. N. Lewis. The following theory of the photo-chemical processes based on Prof. Lewis' theory is suggested, not as a final solution but as a step toward the conciliation of some of the facts of experimental photo-chemistry with the modern concepts of molecular structure.[1]

The silver halides are represented by the formula, $\mathrm{Ag}:\overset{..}{\underset{..}{\mathrm{X}}}:$ where Ag is the silver kernel having the electron configuration 2, 8, 18, 18, and X the halogen

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[1] Lewis: "Valence and the Structure of Atoms and Molecules," (1923).

surrounded by its seven valence electrons and the one valence electron of silver. X has the electron configuration 2,8, for chlorine; 2,8,18, for bromine; 2,8,18,18, for iodine. A displacement of the electrons toward the halogen indicates polarity. The polarity of the silver halide bond is greater than the carbon-carbon bond in aliphatic compounds but much less than the bond between the sodium halides.

The following assumptions will be added to this molecular theory in order to explain the characteristics of the silver iodide photo-voltaic cells:

1. There is a probability distribution of polarity among the molecules of the salt. Most of the molecules are only slightly polar, a few more polar and a very few completely polar and in a condition to ionize in water as solvent.

2. The greater the degree of polarity of a molecule the longer the wave-length of the light which the valence electrons absorb. The silver iodide electrodes adsorbed more completely in the extreme blue but an increase in the polarity of the molecules would cause such a loosening of the electron structure that the valence electrons would absorb more in the green and red.[1]

3. The valence electrons absorb light in quanta and the energy of the light is stored in the molecule as increased polarization. Light absorption thus increases the number of molecules capable of ionization and thereby the apparent solubility in water.

4. A molecule having absorbed a quantum of energy and become polar may return to a less polar state giving its energy to several other molecules causing them to become partially polar. The absorption of a quantum of blue light in this way increases the number of molecules capable of absorbing green or red light and thus accounts for the fact that previous illumination intensifies the effect of the long wave-lengths and that the parts of the spectrum taken separately are not additive in their chemical effect.

The ideas may be summarized by writing the following reactions:

$$\text{LIGHT} + (\text{Ag}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:) \longrightarrow (\text{Ag}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:) \longrightarrow (\text{Ag}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:) \longrightarrow (\text{Ag}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:) \longrightarrow (\text{Ag}^+) + (\text{I}^-)$$

nonpolar partially polar polar ionized

$$\text{n}(\text{Ag}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:) + 1(\text{Ag}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:) \longrightarrow (\text{n} + 1)\ (\text{Ag}\ :\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{I}}}:)$$

nonpolar polar partially polar

The rate of the transformation from the nonpolar to the polar state in a given color of light is similar to a reaction of the second order in that the rate depends on the concentration of the silver iodide molecules which are in a state to absorb the color as well as on the concentration of the light quanta or the light intensity. At very low intensities the first factor is relatively a constant and the rate becomes nearly proportional to the light intensity. This is shown by the fact that the slope of the lines in Fig. 1 is nearly constant.

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[1] Lewis: "Valence and the Structure of Atoms and Molecules," p. 160, 160.

The concentration of the molecules which are in a state to absorb a given color depends on the rate at which they are formed and the rate at which they are destroyed. At very high intensities the rate of the chemical reaction is more nearly a constant determined by the rate of formation of the molecules which absorb the given color. The relation between the light intensity and the maximum photo-potential was given in the previous paper (page 344) where it was pointed out that the potential became more nearly constant at higher intensities of light. The quantity N_o was defined as "the amount of AgI present in the dark." This should now be defined as "the rate of formation of molecules capable of absorbing the light under consideration." $N = N_o - n$ then becoms the concentration of these molecules at intensity I. The magnitude of N_o for any particular color is increased by illuminating the salt with light of shorter wave-length. Thus the chemical effect of the entire spectrum is greater than that of the colors taken separately.

Some of the silver salt remains in the polar state for a long time after illumination. In fact the electrodes never completely recovered from the effect of the light. The electrodes were at first almost colorless but became greenish yellow in light and remained this way for an indefinite period in the dark. Only when the salt was remelted was the color destroyed.

It usually required twenty-four to thirty-six hours for the electrode potential of the electrode of the iodide on gold to return to its normal value in the dark. Less time was required for the electrode of the silver-silver iodide type. It is possible that the latent image on the photographic plate consists of the salt in the polar state for some time after the exposure.

The thermopile measured the light intensity in terms of energy per unit time per unit area. The number or concentration of light quanta is proportional to the light intensity only for a given wave-length. The magnitude of the light quanta is smaller in the long wave-length region and therefore the number of quanta for a given intensity is larger than in a region of shorter wave-length. If E is the total energy absorbed then

$$E = nh\nu$$

where n is the number of light quanta, h Planck's constant and ν the frequency.

The concentration of quanta being greater in the long wave-length region, the reaction velocity and the values of K will be proportionately greater in this region, provided the variation of the values of N_o from one color to another is taken into account.

Summary

A new type of silver iodide photo-voltaic cell has been described.

The maximum photo-potential was not proportional to the light intensity but became almost constant at high intensities. The rate of rise of the potential was proportional to the light intensity at the beginning of the illumination. This was true for light of any color.

An investigation of the effect of light of different colors in bands of various widths revealed the fact that white light has the largest effect. For a fixed intensity of light the rate of the chemical change decreased as the light was made more nearly monochromatic. This was true in any part of the visible spectrum.

A newly prepared electrode was more sensitive to the blue region but illumination in this region intensified the effect of the red and green light. After continued illumination the electrode was more sensitive to the red region.

A theory has been suggested to explain these facts.

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A NEW ENERGY RELATION GOVERNING LIQUIDS AND VAPORS

BY J. E. MILLS

Let V = Volume in cubic centimeters of one gram of vapor.
v = Volume in cubic centimeters of one gram of liquid.
v_0 = Volume in cubic centimeters of one gram of liquid at the absolute zero.
D = Density of vapor.
d = Density of liquid.
d_0 = Density of liquid at the absolute zero.
M = Molecular weight of substance.
N = Number of molecules in one gram molecular weight.
$m_1 = \frac{M}{N}$ = Mass in grams of one molecule.
$v_1 = \frac{MV}{N}$ = volume in cubic centimeters occupied by one molecule.
$s = \sqrt[3]{\frac{3v_1}{4\pi}}$ = Radius in centimeters of volume occupied by one molecule.
λ = Internal heat of vaporization in calories.

It has been shown in a series of papers previously published[1] that if the force of attraction between two molecules follows the law,

$$1.\quad f = \frac{-m_1 E}{s^2}$$

that the internal heat of vaporization for one gram is given by the equation

$$2.\quad \lambda = \mu' (\sqrt[3]{d} - \sqrt[3]{D}) \text{ calories.}$$

If the attractive force is expressed in millimeters of mercury per square centimeter than $E = 31414 \sqrt[3]{\frac{3}{4\pi}} \sqrt[3]{m_1}\mu'$.

In the papers cited, this equation was tested for twenty-five substances from 0°C. to the critical temperature and found to hold true within the limit of experimental error.

If a molecule starts with zero velocity at an infinite distance from a center of force supposed at rest, the molecule under the law of force given above will gain in velocity and in kinetic energy as it approaches the center of force. At a distance s from the center of force the energy acquired by the particle in approaching to this distance from infinity will be

$$3.\quad E_s = \frac{m_1 E.}{s}$$

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[1] J. Phys. Chem. 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132 594 (1907); 13, 512 (1909); 15, 417 (1911); 18, 101 (1914); 19, 257, 650 (1915); 21, 101, 345, 623 (1917); 27, 301 (1923); Phil. Mag. Oct. (1916); July (1911); Oct. (1912); J. Am. Chem. Soc. 31, 1099 (1909).

If the particle is to rotate in a stable circular orbit at this distance then one-half of this total energy must be given up and one-half must be retained.

We have shown[1], if s represents the major semi-axis of the orbit, that the average retained energy is always the same as for a circular orbit of radius s and equal to $\frac{m_1E.}{2s}$ Using one gram of substance the value in calories of this retained energy at density d_o becomes

$$\frac{\frac{N}{M}\,m_1\,31414\sqrt[3]{\frac{3}{4\pi}\mu'\sqrt[3]{m_1}}\ \sqrt[3]{\frac{4\pi d_o}{3\ m_1}}}{31414} = \mu'\sqrt[3]{d_o} \text{ calories.}$$

If the molecule when at an infinite distance apart had an energy of motion E_t equal to the temperature motion of the molecule as a perfect gas, then when these particles approached to density d their total average kinetic energy would be $2\mu'\sqrt[3]{d}+E_t$. If now one-half of this energy were retained in order that the molecules might continue in stable equilibrium at this temperature, then the retained energy would be $\mu'\sqrt[3]{d}+\frac{E_t}{2}$.

The energy required to change from d_o to d would be $\mu'\sqrt[3]{d_o}-\left(\mu'\sqrt[3]{d}+\frac{E_t}{2}\right)$.

Dieterici[2] showed that the internal heat of vaporization was given by the equation

4. $\lambda=CRT\ln\frac{V}{v}$, where C is a constant for any particular substance.

In the series of papers cited, the author has studied this equation of Dieterici with a view to throwing some light upon its theoretical meaning, but with slight success. Recently, however, it was decided to integrate the expression, $\frac{CRT}{v}\,dv$, which gives rise to the above equation of Dieterici, back to the absolute zero with the hope that the expression thus derived would also equal the energy required to change from d_o to d. We thus obtain

$$\mu'\sqrt[3]{d_o}-\left(\mu'\sqrt[3]{d}+\frac{E_t}{2}\right)=CRT\ln\frac{v}{v_o}=CRT\ln\frac{d_o}{d}.$$

By a transposition of terms, and remembering that the equation should hold equally as well for vapor as for liquid

$$5.\quad \mu'\sqrt[3]{d_o}=\mu'\sqrt[3]{d}+\frac{E_t}{2}+CRT\ln\frac{v}{v_o} \quad \text{For liquid}$$

$$=\mu'\sqrt[3]{D}+\frac{E_t}{2}+CRT\ln\frac{V}{v_o} \quad \text{For vapor.}$$

The test of this equation for twelve liquids is shown in Table I.

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[1] Phil. Mag. July (1911).

[2] Ann. Physik. (4), 35, 220 (1911).

TABLE I

Test of the Equation $\mu'\sqrt[3]{d_\circ}=\mu'\sqrt[3]{d}+\frac{E_t}{2}+CRT\ln\frac{V}{V_o}$

Temperature	Ethyl oxide		Di-isopropyl		Di-isobutyl		Isopentane		Normal Pentane		Normal Hexane		Normal Heptane		Normal Octane		Benzene		Iodo-benzene		Carbon Tetrachloride		Stannic Chloride	
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
0°K	104.8		95.0		85.6		101.6		106.1		100.0		96.3		91.1		115.7		57.0		56.9		38.1	
0°C	103.4	105.2	93.8	96.4	84.1	*91.9	100.8	101.7	104.9	106.4	98.4	*102.7	94.4	*101.8	89.3	*101.3	114.0	*120.6			56.1	57.8	37.4	*30.4
20	103.6	104.2					101.0	101.1																
40	103.8	103.7					101.2	101.0	105.3	105.2									30°C	30°C				
60	104.0	103.7	94.3	94.5			101.5	101.2	105.5	105.3	98.8	99.3							56.2	*61.7				
80	104.3	103.8	94.5	94.6			101.8	101.7	105.8	105.6	99.0	99.1	94.8	95.7			114.5	114.3			56.4	56.1		
100	104.5	104.2	94.7	94.7	84.4	85.1	102.1	102.2	106.1	106.0	99.2	99.1	94.9	95.3			114.7	114.2			56.5	56.2	37.6	37.8
120	104.8	104.6	95.0	95.0	84.6	84.7	102.4	102.7	106.4	106.5	99.4	99.3	95.1	95.0	89.7	91.0	115.0	114.3			56.6	56.3	37.6	37.7
140	105.1	105.0	95.3	95.4	84.7	84.5	102.8	103.2	106.8	106.8	99.6	99.5	95.2	95.0	89.9	90.6	115.2	114.7			56.8	56.5	37.7	37.6
160	105.4	105.4	95.6	95.8	84.9	84.6	103.2	103.5	107.1	107.2	99.9	99.8	95.4	95.1	90.0	90.5	115.5	115.3			56.9	56.8	37.7	37.7
180	105.7	105.6	95.8	96.1	85.1	84.8	103.5	103.6	107.4	107.5	100.2	100.1	95.6	95.3	90.1	90.4	115.8	115.9	56.5	56.6	57.1	57.1	37.8	37.8
200			96.2	96.4	85.2	85.0					100.4	100.4	95.8	95.5	90.3	90.5	116.1	116.4	56.6	56.5	57.3	57.4	37.9	37.9
220			96.4	96.4	85.4	85.2					100.6	100.4	96.0	95.7	90.5	90.5	116.4	116.8	56.7	56.6	57.4	57.7	38.0	38.0
240					85.6	85.3							96.2	95.8	90.6	90.5	116.8	117.2	56.8	56.6	57.6	57.9	38.1	38.1
260					85.7	85.3							96.2	95.7	90.8	90.6	117.1	117.4	56.9	56.7	57.8	58.0	38.2	38.2
280															90.9	90.5	117.4	117.4			58.0	58.0	38.3	38.3
T_c	105.3	105.3	96.1	96.1	85.2	85.2	103.3	103.3	107.2	107.2	100.3	100.3	95.6	95.6	90.4	90.4	117.1	117.1	57.6	57.6	57.8	57.8	38.3	38.3
Average	104.5	104.5	95.2	95.5	84.9	85.0	102.1	102.3	106.2	106.4	99.6	99.7	95.4	95.4	90.2	90.6	115.8	115.9	56.8	56.8	57.1	57.2	37.9	37.9
M× Average	7741	7741	8198	8224	9691	9702	7301	7375	7657	7671	8577	8585	9553	9553	10296	10341	9038	9040	11581	11581	8782	8797	9884	9884
T_c	193.8°		227.35°		276.8°		187.8°		197.2°		234.8°		266.85°		296.2°		288.5°		448.0°		283.15°		318.7°	
°Volume at 0°K	.9703		1.0837		1.0700		1.1176		1.1133		1.0867		1.0757		1.0684		.8426		.4399		.4640		.3362	
M	74.08		86.112		114.144		72.10		72.10		86.112		100.13		114.144		78.05		203.89		153.8		260.8	
μ'	103.76		97.53		87.58		105.46		109.94		102.80		98.64		93.16		109.26		43.37		44.01		26.51	
C	1.724		1.725		1.813		1.688		1.707		1.752		1.814		1.858		1.690		1.687		1.607		1.741	

The confirmation of the truth of the equation is most remarkable. The average value of the constant is given in the table. All values are included in this average except the seven values marked with an asterisk. Values marked with an asterisk differ from the average value by more than 2%. The values for the vapor at the lowest temperature tested are too high for seven of the substances tested because for these substances at this temperature the attraction between the molecule is not sufficient to produce closed curves and equation 5 does not hold.[1] With this exception, which was to be expected, out of a total of 254 values remaining, only two of the values differ from the average value shown for the substance by more than 1.5%. In other words, the remaining values are within the limit of experimental error all the way from 0° absolute to the critical temperature of the substance. With a good many of the substances there is an increase in the value of the constant from 0°C. to the critical temperature. Since for any particular substance this increase is within the limit of experimental error for the substance, and since the increase is not shown for all of the substances, it is not yet possible to say whether such increase is accidental or has some physical significance. Slight molecular association might cause such a slight change as that shown. Or the change might be due to the gradual loosening of the atomic attractions with increasing temperature, such loosening causing a minor change in the molecular attraction.

We are yet without knowledge of the significance of the constant C of Dieterici's equation. But the author has unpublished work showing that this constant is connected with the slant of the Cailletet and Mathias rectilinear diameter. It may be that this C is not always an exact constant but shows a minor variation as does the rectilinear diameter.

Speculation as to the possible significance of this minor increase in value of the constant can at least wait until such increase is more certainly established. *It is certainly true that equation 5 gives a new energy relation for both liquids and vapors that holds true from the absolute zero to the critical temperature either with absolute exactness or with such a close approach to accuracy that deviations are not larger than the present probable experimental errors.*

It should be pointed out also that the twelve substances tested were so chosen as to include a wide range in the type of the compounds. It is, therefore, probable that other organic non-associated liquids will show a similar agreement with the ideas advanced.

The critical temperature and molecular weight of the substances and the values for μ' and C are shown in Table I. Also, the value of the volume of one gram of the substance as a liquid at the absolute zero. This value was, of course, obtained by extrapolation. Also, there is given in Table I the value of the average constant obtained multiplied by the molecular weight.

The author would point out that the essential point of the argument advanced and finally expressed in equation 5 is that the average kinetic energy

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[1] J. Phys. Chem. 27, 301 (1923).

of a gram of liquid is given in calories by the expression $\mu'\sqrt[3]{d}+\frac{E_t}{2}$. The orbit followed by each individual molecule is probably highly variable and mathematically the balance among the millions of molecules and the attractive forces can probably be figured out in different ways with the same final result. Thus, the author is inclined to believe that the same mathematical balance between energy, pressure, and volume will follow from the assumption of linear orbits through a center of force, or elliptical orbits around a center of force, or a strictly circular orbit for the entire mass if the necessary adjustments are made in the calculation for the kind of orbit considered. Perhaps, therefore, it is immaterial mathematically as to the extent to which the attractive forces balance each other in the interior of the mass considered. It is hoped later to give a calculation showing how the external vapor pressure can be calculated by a detailed consideration of the orbit. At the present time the author's calculations of the pressure from a consideration of the orbit seem to hold for the vapor but not for the liquid.

However, a calculation of the pressure, energy, temperature balance at the critical temperature may be given here in order to show that the author is probably correct in assuming that $\mu'\sqrt[3]{d}+\frac{E_t}{2}$ represents the average energy in calories of a gram of liquid. It has been previously shown by the author[1] that the internal pressure p at the critical temperature can be calculated in a variety of ways.

$$6.\ p=\frac{31414\mu'}{3V^{4/3}}=\frac{CRT}{V}=\frac{dP}{dT}T\text{-}P=a.$$

$$=159{,}500\quad=157{,}700=161{,}800=159{,}924 \text{ for isopentane.}$$

Now the external pressure for isopentane at the critical temperature is 25,018 and $\mu'\sqrt[3]{d}+\frac{E_t}{2}$ is $65.01+9.52$ calories. Therefore, we have

$$P+p=159{,}500+25{,}018=\frac{31414\times 74.53}{3\times 4.268},\text{ or,}$$

$$=184{,}518=182{,}700$$

which is a sufficiently close check.

A remarkable feature of the constant given by equation 5 and shown in Table I is that the molecular volume at the absolute zero is an additive property of the atoms and atomic groupings. The relation, therefore, suggests strongly that molecular volume is a consequence of molecular energy and that molecular energy at the absolute zero may be the sum of the energy of the various atoms.

The author is well aware that the relation given in this article and expressed in equation 5 can be extended in various ways and that it can be

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[1] J. Phys. Chem. 19, 257 (1915).

combined with other known equations. Also, that the relation points towards a new conception of the nature of the balance between molecules and molecular forces. Therefore, a further discussion of this relation is in preparation.

Summary

A new energy relation holding for both liquids and vapors from the absolute zero to the critical temperature is derived and proved. This relation extends and confirms the previous work done by the author showing that the attractive force between molecules varies directly as a constant and inversely as the square of the distance apart of the molecules.

September 15, 1924.
Edgewood Arsenal,
Edgewood, Md.

19-864

THE ADSORPTION OF NITROGEN PEROXIDE BY SILICA GEL

BY RAMES C. RAY

1. Introduction

A considerable amount of work has been done on the adsorption of gases by porous substances and several theories have been proposed to explain the phenomena, but not one of them is applicable to all cases, or quite adequate from a practical point of view. This is mainly due to the fact that very little is known about the nature of the solid adsorbent, and any theory of adsorption which disregards the nature of both the adsorbent and the adsorbed substance must be incomplete from a theoretical standpoint. The specific and selective influence of the adsorbent on gaseous as well as liquid adsorption has been shown by several workers. In discussing a paper by Chaney,[1] Sheldon stated that he was successful in obtaining a charcoal which at liquid air temperatures took up relatively more hydrogen than nitrogen. The preferential adsorption from the gas phase, and the influence of the chemical composition of the adsorbent were confirmed quantitatively by Briggs,[2] who also studied the adsorption of nitrogen and hydrogen by charcoal and silica at liquid air temperatures. He found that the striking partiality of charcoal and carbonaceous adsorbents for hydrogen stood out in high relief when these substances were compared with silica gel. That the preference was not due to the state of porosity of the adsorbent was indicated by the fact that the non-porous graphite had, at −190°C, a H/N ratio almost the same as that of the very porous blood charcoal. One must assume the existence of high specific attraction between the two elements carbon and hydrogen. The selectivity of adsorption from liquids has been mentioned by Chaney, Ray, and St. John.[3] They state that the preferential adsorption can be readily demonstrated by shaking up a mixture of water and benzene with activated carbon and silica gel respectively. The carbon will adsorb the benzene, and if enough benzene be present to saturate the carbon, the water will be completely rejected. The silica gel, on the other hand, will take up the water and reject the benzene. These facts prove beyond doubt that every theory of adsorption must take into account the specific chemical nature of the adsorbent. The theory of capillary adsorption supported by Patrick and McGavack[4] must recognize the predominating influence of specific chemical factors, inasmuch as capillary phenomena exhibit certain sharply contrasting aspects depending upon whether the capillaries are wetted by the liquid or not. Such differences in the wetting action reveal

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[1] Trans. Am. Electrochem. Soc. 36, 91 (1919).

[2] Proc. Roy. Soc. 100 A, 88 (1921).

[3] Ind. Eng. Chem. 15, 1244 (1923).

[4] J. Am. Chem. Soc. 42, 946 (1920).

the operation of specific chemical or polar forces, which are not explicable on any simple mathematical concept of relative capillary diameters.

Langmuir's theory[1] of one layer adsorption appears to be well established for small amounts of gases which are held with extreme tenacity. The view that the maximum adsorption from the gas phase cannot exceed a monomolecular layer has, however, been much criticised. On the basis of their own measurements on the adsorption of gases on a known surface of glass wool, as well as of the data obtained by Mülfarth,[2] Evans and George[3] have shown that the adsorption layer may be many molecules thick. Further, Langmuir's equation, in its present form, deals with plane or smooth surfaces only, and is not applicable to contiguous surfaces and hence to the measurements of adsorption by porous bodies. Wilson[4] has demonstrated that although Langmuir's view explains the adsorption of small quantities of gases under very low pressures, and although capillary condensation may represent fairly adequately the slightly depressed vapour pressures in capillaries of moderate size, there is a wide intermediate range of adsorption in which neither theory seems to be satisfactory.

Of the several adsorption formulas, the one proposed by Freundlich[5] is the simplest and the most widely applicable. It is purely an empirical relation and is too elastic and pliable. But the greatest drawback of this equation is that, it is not possible to predict what the adsorption would be at a particular temperature, knowing the adsorption at another temperature. The isotherm has to be determined separately for each temperature in order to obtain the proper value of the constants to be used in the equation. In this respect the formulas proposed by Polanyi[6] and developed further by Berényi[7] as well as that by Williams[8] are more satisfactory, although they are still far from complete, and there is no means, at present, of calculating even roughly the amount of adsorption, at a given temperature and pressure, of a new substance for which the constants to be used in the equations are not known.

Patrick and McGavack[9] determined the adsorption of sulphur dioxide by silica gel at various temperatures and pressures. A small amount of water is always associated with silica gel. The water content of the gel can be lowered by heating it to increasingly higher temperatures. Only a definite quantity of water is removed at each temperature and when the percentages of water are plotted as a function of the temperature a straight line is obtained. The whole of the water is removed from the gel at about 700°, but a water-free gel obtained in this way loses almost entirely its adsorptive power. Patrick and McGavack found that a gel containing five to eight per cent. of

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[1] J. Am. Chem. Soc. 39, 1848 (1917); 40, 1361 (1918).

[2] Ann. Physik. 3, 328 (1900).

[3] Proc. Roy. Soc. 103 A, 190 (1923).

[4] Phys. Rev. (2) 16, 15 (1920).

[5] "Kapillarchemie," p. 127. Second edition.

[6] Ber. 16, 1012 (1914); 18, 55 (1916); Z. Elektrochem. 26, 307 (1920).

[7] Z. physik. Chem. 94, 628 (1920); 105, 55 (1923).

[8] Proc. Roy. Soc. Edin. 38, 23 (1918); 39, 48 (1919); Proc. Roy. Soc. 96A, 287, 298 (1919).

[9] Loc. cit.

water seemed to be the most active. The adsorption isotherms for sulphur dixoide with gels containing 8.01 and 4.85 per cent. of water lay practically on the same line, indicating that the maximum value of the adsorption would be possessed by a gel containing an amount of water lying between these two values. The fact that the gas was soluble in water appeared to make no difference. In a later paper, however, Patrick and Davidheiser[1], in order to bring the results of their work on the adsorption of ammonia by silica gel into conformity with the theory of capillary adsorption, assumed that the amount of adsorption of ammonia was considerably affected by the presence of even a very small quantity of water in the gel. The present investigation was undertaken in order to find out if the small amount of water in the gel, which possessed practically no vapour pressure almost up to the temperature to which it had been previously heated and did not suffer any appreciable diminution under a very high vacuum, really exerted any influence on the amount of adsorption. For this reason, nitrogen peroxide, which would react with the water, was selected. Moreover, a suitable medium for absorbing nitrogen peroxide is also important from a technical point of view.

2. Apparatus and Materials

As nitrogen peroxide attacks rubber, the different parts of the apparatus had either to be sealed together or connected by ground glass joints. Preliminary experiments showed that the amount of adsorption was fairly large, and as the gas attacks mercury and dissolves in or reacts with almost all liquids, it was found convenient to weigh the bulb containing the gel after each experiment; the increase in the weight of the bulb gave the amounts adsorbed. The arrangement of the apparatus is shown diagrammatically in Fig. 1. It may be divided into two parts, the first from A to J for the preparation and purification of nitrogen peroxide, and the second from K to N for determining the adsorption of the gas at different pressures and temperatures.

Large quantities of nitrogen peroxide can best be prepared by heating a mixture of finely powdered arsenious oxide, concentrated sulphuric acid and fuming nitric acid (sp.gr. 1.5) as described by Cundall[2]. The crude product, at first, contains nitrogen trioxide, but Cohen and Calvert[3] have shown that although liquid trioxide is practically unacted upon by oxygen, rapid combination takes place between oxygen and gaseous nitrogen trioxide which is thus oxidised to the peroxide. The tetroxide is not further attacked by oxygen; although it is oxidised by ozone. On the contrary, the pentoxide undergoes spontaneous decomposition into tetroxide and oxygen. The decomposition of the peroxide is negligible under the conditions of experiment. This

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[1] J. Am. Chem. Soc. **44**, 1 (1922).

[2] J. Chem. Soc. **59**, 1077 (1891).

[3] J. Chem. Soc. **71**, 1052 (1897).

method was used later by Frankland and Evans who[1] found it to be most satisfactory; all the lower oxides could be oxidised by prolonged treatment with oxygen.

The mixture recommended by Cundall[2] was heated in the distilling flask A. The evolved gases were first passed through the U-tube B filled with glass wool, then after passing through a series of tubes containing anhydrous calcium nitrate and phosphorus pentoxide, condensed in the glass spiral C packed in ice, and collected in the vessel D which was also kept cold with ice and water. The liquid was redistilled, at as low a temperature as possible, into the succeeding vessels F, H and J through phosphorus pentoxide tubes and the bulbs E, G and I where the gaseous oxide was mixed with a current of dry oxygen. The final product, when cooled with a freezing mixture, formed a perfectly white solid which melted at −10.2° (−10.8° according to Scheffer and Treub, −10.5° according to Egerton, and −9.6° according to Guye and Drouginine). The boiling point was found to be 22.4°. Finally, the pure nitrogen peroxide was distilled into the bulb L through a phosphorus pentoxide tube.

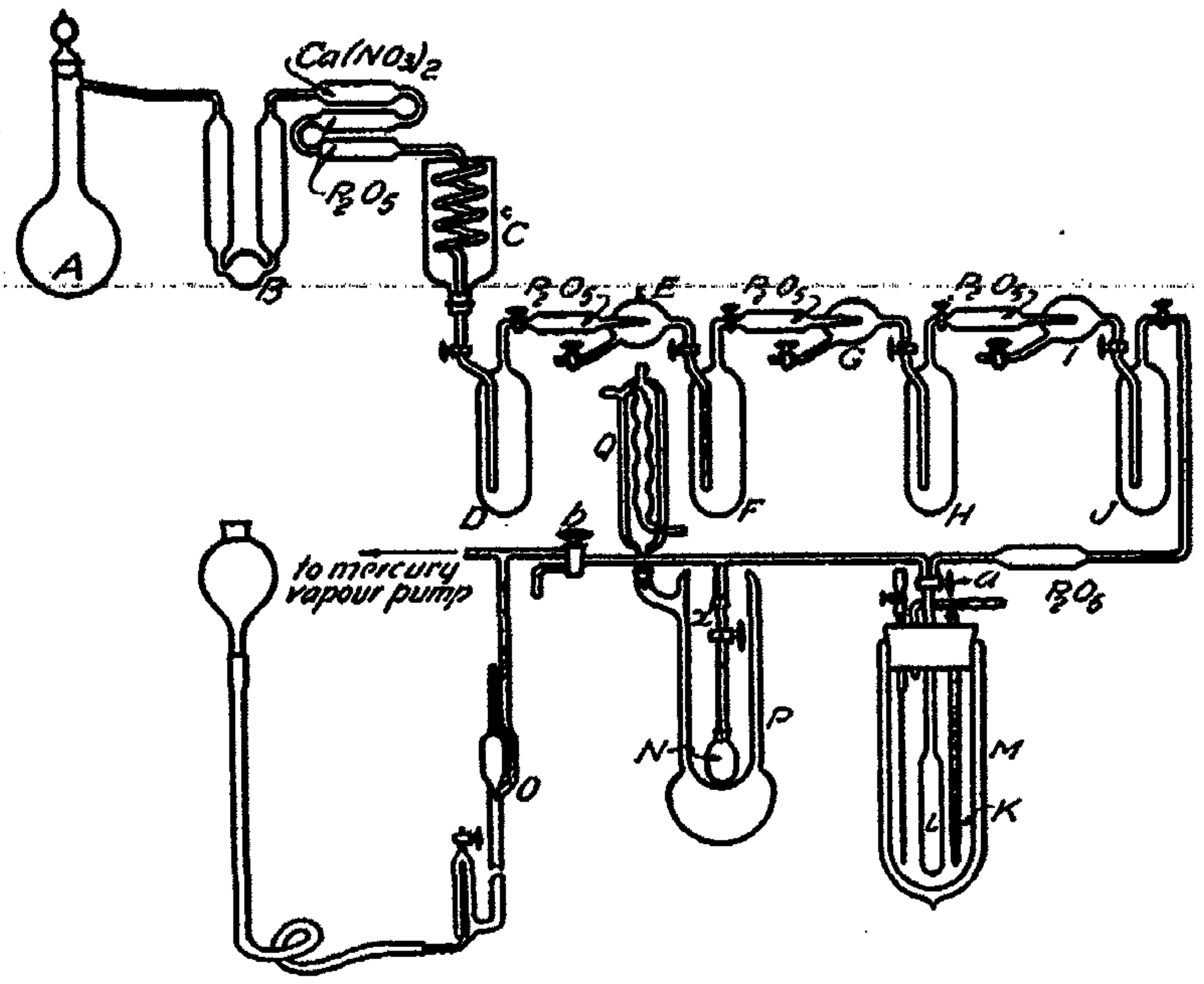

FIG. 1

The stem of the bulb L passed through a rubber cork which fitted closely the mouth of an unsilvered cylindrical Dewar vessel M of about three litres capacity. Besides the bulb the cork was bored to contain a normal pentane thermometer reading from +15° to −150°, a glass tube for making connection

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[1] J. Chem. Soc. 79, 1359 (1901).

[2] Loc. cit.

with a water pump, and a glass tube drawn to a capillary at its lower end which reached to the bottom of the vacuum vessel, the top being closed by a piece of rubber pressure tubing and a screw clip. The purpose of these will be explained later. The bulb L was provided with a three-way stopcock *a*, one arm of which was connected with the reservoir J containing pure nitrogen peroxide, the other arm to the adsorption bulb N, and then through another three-way stopcock *b*, to a McLeod gauge and a two unit Langmuir mercury vapour pump. A short piece of capillary tube carrying a stopcock *x* was ground to fit the neck of the adsorption bulb N. The other end of the capillary tubing served for connection with the rest of the apparatus through a ground glass joint, so that the adsorption bulb with the capillary stem could be detached when required and weighed.

Adsorption isotherms were determined at 15°, 57°, 80° and 100°. The vapours of briskly boiling acetone, benzene and water in the double-walled vessel P gave the last three temperatures. 15° was the air temperature which was kept constant by circulating, through the annular space of the vessel P a current of water, the rate of flow of which could be varied. The mouth of P was closed with cotton wool, and a thermometer was placed inside, the thermometer bulb being in contact with the adsorption bulb.

Different pressures of nitrogen peroxide were obtained by maintaining the bulb L at different temperatures, the vapour pressure being regulated by the coldest part of the apparatus. A large number of investigations have been published on the vapour pressure of nitrogen peroxide, notably by Ramsay and Young,[1] Guye and Drouginine,[2] Scheffer and Treub[3] and Egerton.[4] The results of Scheffer and Treub are in good agreement with those of Ramsay and Young. Those of Guye and Drouginine also agree well for the undercooled liquid at low temperatures but are somewhat higher than those of Scheffer and Treub and Ramsay and Young for temperatures above −20°. This fact is ascribed by Scheffer and Treub to the method employed by Guye and Drouginine for the measurement of statical vapour pressures. The experimental results of Egerton nearly agree with those of Scheffer and Treub for temperatures above −30° but the rate of decrease of vapour pressure is much greater. Guye and Drouginine's results decrease still less rapidly. However, by taking the mean of the closely agreeing results, it is possible to construct a smooth vapour pressure-temperature curve which probably represents the true values of the vapour pressure of nitrogen peroxide at different temperatures. From this curve, the vapour pressure at any temperature between +43° and −50° can be obtained. The vapour pressures of nitrogen peroxide can also be calculated approximately correctly from van der Waals' equation $\log \frac{\pi}{P} = a\left(\frac{\tau_c}{T} - 1\right)$, taking the mean value for a as 4.17 and for π and τ_c 147 atmospheres and 171.2° respectively.

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[1] Phil. Trans. **177**, 109 (1886).

[2] J. Chim. phys. **8**, 473 (1910).

[3] Proc. Akad. Wet. Amsterdam, **14**, 536 (1911); Z. physik. Chem. **81**, 308 (1919).

[4] J. Chem. Soc. **105**, 647 (1914).

The silica gel was obtained from the Kestner Evaporator and Engineering Co., Ltd. The gel was activated by heating it for about three hours at 200° in a U-tube contained in an oil bath at 200° through which was drawn a current of air, freed from carbon dioxide and moisture and, previously heated to the same temperature by passing through a glass spiral placed in the same bath. The water content of the gel was determined by blasting a weighed quantity of the activated substance in a platinum crucible to a constant weight. All taps were lubricated with viscous metaphosphoric acid except a short length of the ends exposed to the air; these were lubricated with a small amount of rubber greese. The pentane thermometer was calibrated by comparison with a tension-thermometer of the type described by Stock, Henning and Kuss.[1]

3. Method of Experiment

The bulb L, which contained nitrogen peroxide, was first cooled with liquid air and thoroughly evacuated. Solid nitrogen peroxide does not possess any appreciable vapour pressure at liquid air temperatures. The volume of the adsorption bulb N together with the capillary stem up to the stopcock *x* was accurately determined. A weighed quantity of the activated silica gel was then introduced into the adsorption bulb. Generally 12-15 grams of the gel were used for each experiment. The bulb was finally attached to the apparatus and connection was made with the pump. When the pressure, as indicated by the McLeod gauge, was of the order of 10^{-5}, the tap *x* was closed, air was introduced through the three way stopcock *b*, and the loss of weight of the adsorption bulb was determined. It was again connected with the apparatus and maintained at the desired temperature. The part of the apparatus between the taps *a*, *b* and *x* was then completely pumped out. In the meantime the bulb L was cooled to the required temperature. Temperatures below −10° were obtained by the method employed by Steele and Bagster.[2] Liquid sulphur dioxide or liquid ammonia was introduced into the unsilvered Dewar vessel M which was also connected with a water pump by a piece of pressure rubber tubing which could be more or less closed by means of a screw clip. To obtain any desired temperature below the boiling point of sulphur dioxide or ammonia, the pump was set in action and a regulated stream of air was admitted through the capillary reaching to the bottom of the Dewar vessel. The sulphur dioxide or ammonia boiled under the reduced pressure and its temperature fell. The stream of air served to prevent superheating and subsequent bumping, and also to stir the liquid and obtain uniform temperature throughout the bath. When the temperature was near the desired point, the pressure tubing was partly closed by means of the screw clip, thus checking the rate of withdrawal of the sulphur dioxide or the ammonia vapour, and consequently the rate of evaporation, so lessening the heat absorption and fall of temperature. In a short time a state of equili-

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[1] Ber. 54, 1119 (1921).

[2] J. Chem. Soc. 97, 2613 (1910).

brium was established, and by this means the temperature could be kept constant to 0.1°. If it varied occasionally, a slight turn of the screw clip sufficed to adjust it again. If the Dewar vessel was nearly filled at the beginning, it was possible to run from 2 to 3 hours without adding a fresh quantity of liquid. Filling the Dewar vessel with powdered ice gave 0°, and temperatures above 0° were obtained by placing the bulb L in a well-stirred mixture of ice and water in contact with a thermometer. When both the bulbs L and N were at the desired temperatures, the stopcock leading to the pump was closed and connection was made between the two bulbs. Adsorption took place very rapidly and was almost complete within a few minutes, but as the adsorption took place with the evolution of a large amount of heat, the bulbs were left in connection from 40 to 45 minutes in order to make sure that the gel had regained the temperature of the bath. The stopcocks *a* and *x* were then closed, and air was introduced through the three-way tap *b*. The adsorption bulb with the capillary stem was taken out and weighed. After allowing for the weight of nitrogen peroxide in the space not occupied by the gel, the increase in weight of the bulb gave the amounts of gas adsorbed.

4. Experimental Results

The experiments could be repeated, and the difference between the results of two determinations at the same temperature and pressure never exceeded 2.5 per cent. The results given below representt he mean of two or more experiments:—

TABLE I

Water content of the gel = 6.02 per cent. Amount of adsorption in grams of nitrogen peroxide per 100 grams of the gel

Temperature of the bath	Pressure of nitrogen peroxide in mm. of murcury	$\frac{x}{m}$ at 15°	$\frac{x}{m}$ at 57°	$\frac{x}{m}$ at 80°	$\frac{x}{m}$ at 100°
+12°	490	56.80	20.46	14.82	9.92
+10°	450	55.58	19.65	14.37	9.38
+ 5°	351	50.43	17.80	12.40	8.07
0°	270	45.64	15.78	10.69	6.85
−10°	150	37.27	12.17	8.05	4.89
−20°	88	30.16	9.59	5.92	3.56
−34°	30	20.85	6.42	3.38	1.84
−40°	11	14.49	4.14	1.99	1.02

The isotherms are plotted in Fig. 2. They agree well with Freundlich's equation, $\log \frac{x}{m} = \log a + \frac{1}{n} \log p$, except at pressures approaching saturation. The values of Freundlich's constants *a* and 1/n for different temperatures are tabulated below:—

TABLE II

Temperatures	15°	57°	80°	100°
a	14.00	3.98	1.89	0.96
1/n	0.358	0.418	0.529	0.602

5. Influence of the Water Content of the Gel on the Amount of Adsorption

In order to find out if there was really any connection between the amount of water present in the gel and the amount of adsorption, samples of gel were heated to increasingly higher temperatures in an electric heater. At each temperature, only a definite quantity of water appeared to be given up, no further loss of water seeming to take place even on prolonged heating at a particular temperature. In this way, gels containing different amounts of water were obtained. The water content was determined as before by heating, in the blow-pipe flame, a weighed quantity of the gel in a platinum crucible to constant weight. Adsorption isotherms were obtained at 15° in the manner previously described, using gels with 6.80, 5.16, 4.68 and 3.27 per cent. of water. The following results were obtained :—

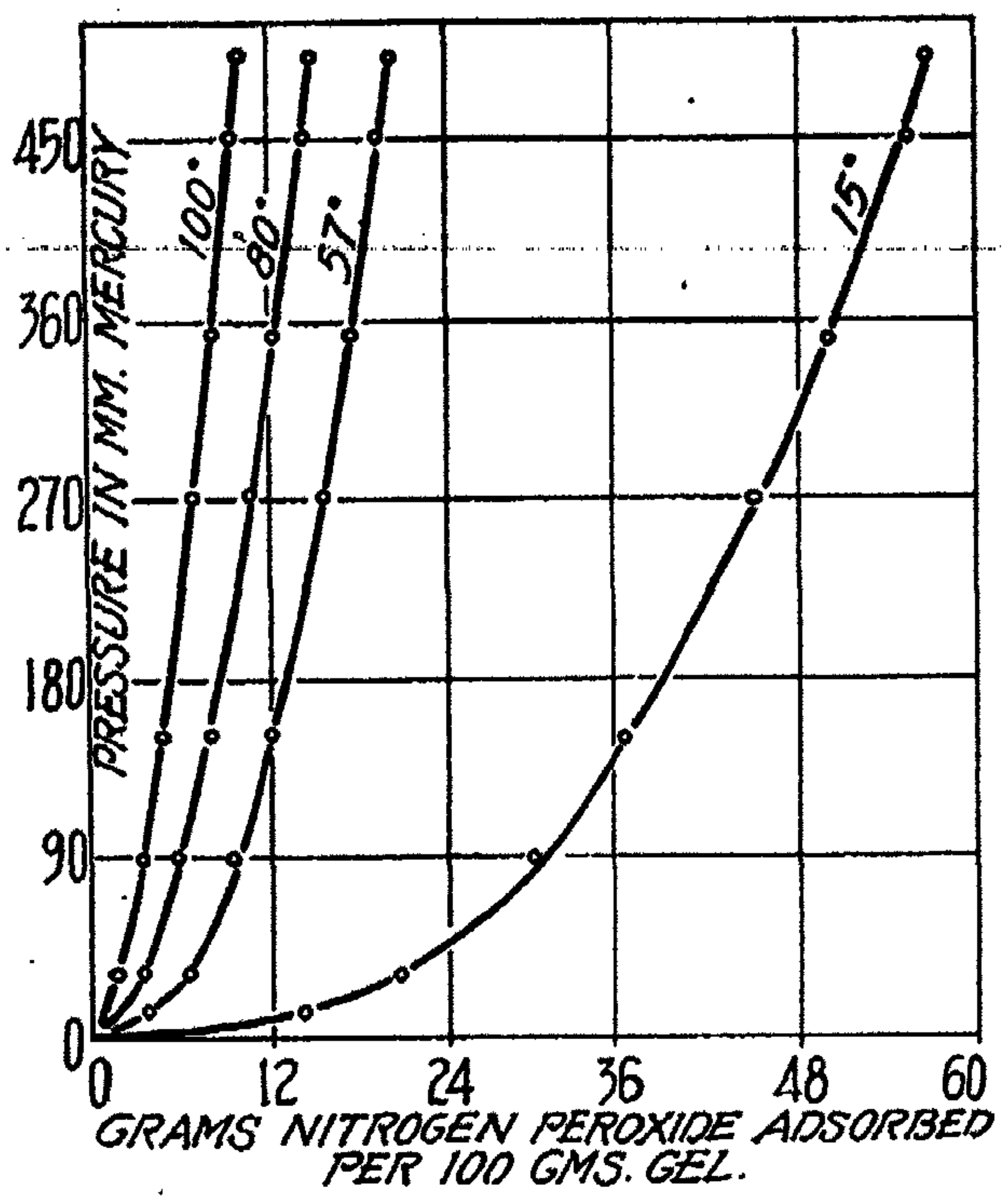

FIG. 2

Table III

Temperature of Adsorption:—15°

Amount of adsorption in grams of nitrogen peroxide per 100 grams of the gel (=x/m)

Temperature of the bath	Pressure of nitrogen perioxide in mm. of murcury	x/m with gel containing 6.80% of water	x/m with gel containing 5.16% of water	x/m with gel-containing 4.68% of water	x/m with gel containing 3.27% of water
+12°	490	57.22	56.12	— — —	44.26
+10°	450	55.64	— — —	54.30	— — —
+ 5°	351	51.29	50.48	— — —	37.70
0°	270	47.12	44.54	45.30	33.39
−10°	150	38.81	35.42	— — —	25.57
−12°	138	— — —	— — —	34.72	— — —
−20°	88	32.58	— — —	28.93	— — —
−34°	30	22.86	18.91	— — —	13.22
−35°	26	— — —	— — —	17.78	— — —
−40°	11	16.47	— — —	— — —	8.65
a....................		15.96	12.32	12.12	8.34
1/n..................		0.328	0.392	0.401	0.425

These results are also represented graphically in Fig. 3. It will be noticed that the isotherms with gels containing 6.80, 6.02, 5.16 and 4.68 per cent. of water lie practically on two lines quite close to each other, showing that the presence in the gel of an amount of water lying between these two values does not affect the amount of adsorption of nitrogen peroxide to any large extent. When the percentage of water in the gel falls to 3.27, however, the adsorptive capacity of the gel is considerably diminished. The loss of the adsorptive power is, no doubt, due to the reduction of the adsorptive space. In order to obtain a gel with very low water content, it has to be subjected to prolonged heating at a fairly high temperature, and in this process the gel undergoes incipient fusion which is revealed by the formation of a skin. Briggs[1] has suggested that the adsorptive power of any given material depends upon two factors, namely, (a) the degree of its porosity on the microscopic and ultramicroscopic scale, and (b) the degree of porosity on the molar scale. He believes that the heating, without destroying the coarser passages, vitrefies the silica and blots out the finest openings upon which adsorption so largely depends.

6. The Effect of Repeated Adsorption on the Same Sample of Gel

In all the experiments described so far, fresh quantities of gel were used for each experiment. The following experiments were undertaken in order to find out whether the adsorbed nitrogen peroxide could be completely

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[1] Loc. cit.

recovered, and whether the adsorptive capacity of the gel deteriorated by repeated adsorption. The experimental arrangement was the same as described previously with the exception that an adsorption bulb of a different type was used. The form of adsorption bulb employed in these experiments is shown in Fig. 4. At the bottom of the bulb was sealed a capillary tube which was bent in the form of a U and carried a stopcock. A weighed quantity of the gel was introduced into the bulb, and the amount of adsorption at a particular temperature and pressure was determined as before. In order to remove the adsorbed gases the bulb was detached from the rest of the apparatus, and a current of hot air, dried by passing through a series of tubes containing sodalime and phosphorus pentoxide, was drawn through the bulb until no more nitrogen peroxide came off. The bulb was again attached to the pump and thoroughly evacuated until the McLeod gauge indicated no pressure. After closing the taps, the bulb was taken out and weighed. It was found that a slight permanent increase in the weight of the gel took place. If the amount of adsorption was small at first, then a further increase in weight took place after the removal of the gases of the second adsorption, slightly more after that of the third, and so on until a stage was reached after which no further increase in weight occurred. On the other

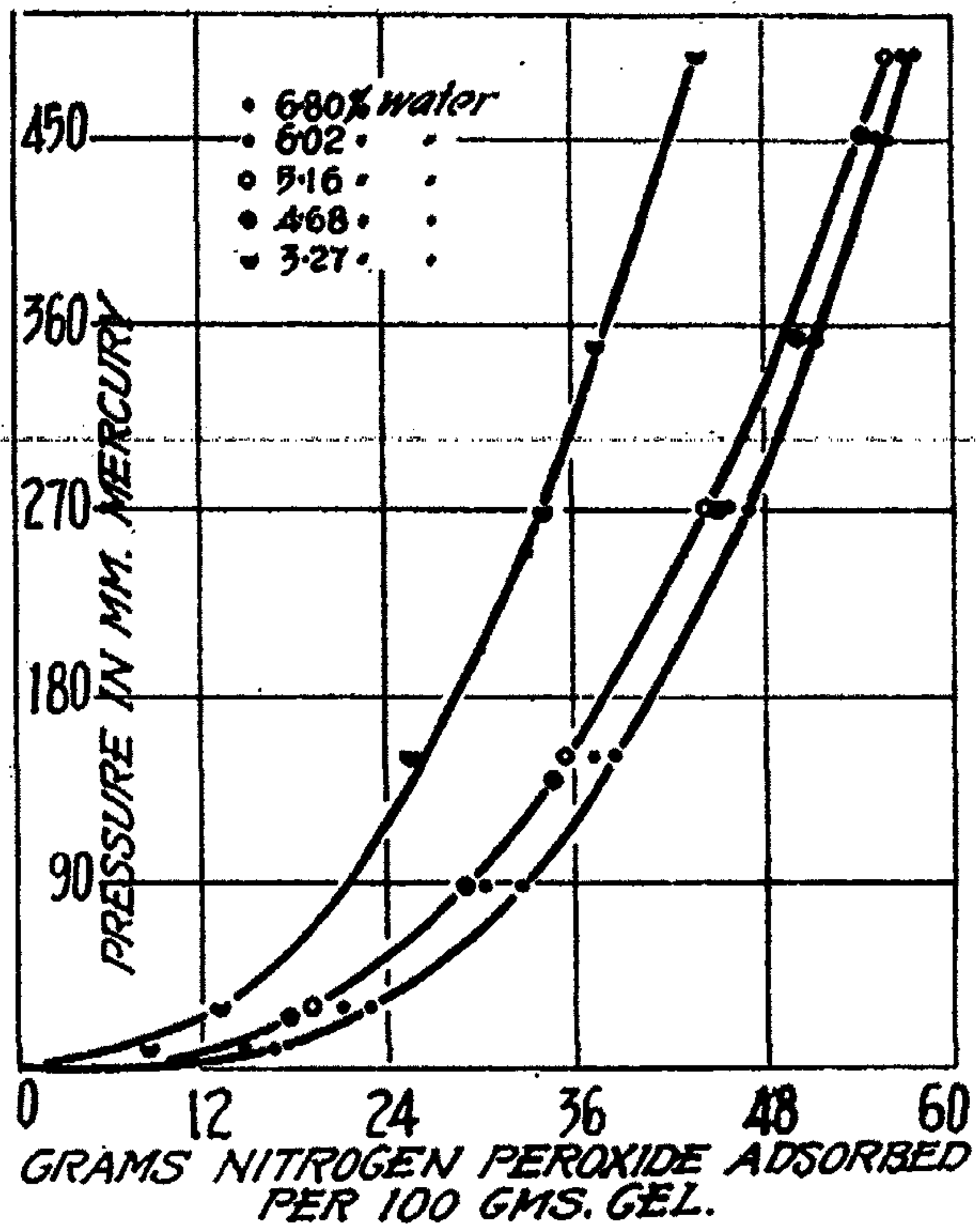

FIG. 3

hand, if the amount of adsorption was large at the first adsorption, after the preliminary increase in the weight of the gel, no further increase took place after subsequent adsorptions, and when the permanent increase in the weight of the gel was complete, the whole of the adsorbed nitrogen peroxide could be removed by passing a current of hot air for a sufficiently long time.

It should be mentioned in this connection that the gel turned bluish-green when it adsorbed nitrogen peroxide for the first time. When hot air was drawn through it for sometime the green colour disappeared and the gel assumed an orange-yellow colour and finally became quite colourless. The change of colour also occurred at subsequent adsorptions until the permanent increase in the weight of the gel was complete, after which the gel, although still capable of adsorbing fairly large amounts of nitrogen peroxide, did not turn green but acquired only an orange-yellow colour after adsorption. The production of the green colour was, no doubt, due to the formation of nitrogen trioxide. With small quantities of water nitrogen peroxide reacts according to the following equation:

$$2N_2O_4+H_2O=N_2O_3+2HNO_3.$$

When subsequently air was drawn through the gel the nitrogen trioxide was oxidised to peroxide nd finally removed[1]. Thus the water originally present in the gel was gradually completely replaced by nitric acid, when the gel no longer turned green on adsorption of nitrogen peroxide and there was no further increase in weight.

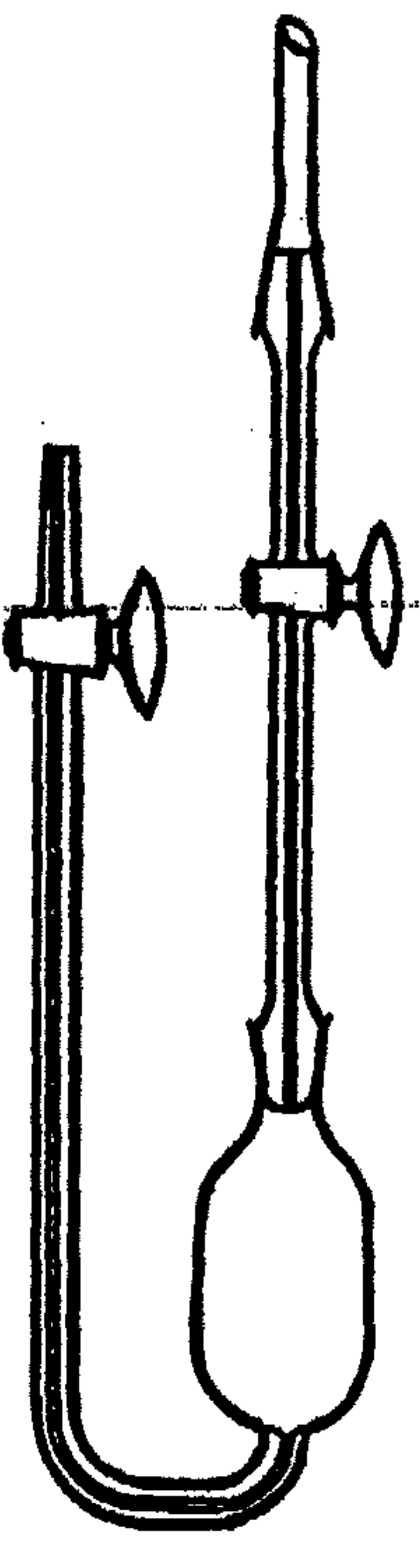

FIG. 4

McBain[2] has shown that the phenomenon of adsorption sometimes consists of two processes—namely, a surface condensation which takes place rapidly, followed by a slow diffusion into the interior of the solid with the formation of a true solid solution. In view of this fact, namely that ordinary adsorption of a gas by a porous solid may be a combination of both processes. McBain has proposed to employ the term *sorption* when referring to absorption as a whole, to call diffusion of the gas into the interior *absorption*, and to restrict the word *adsorption* to the first stage of sorption, namely surface condensation. The small amount of water, which cannot be removed by evacuation and only a definite amount of which comes off at each temperature when the gel is progressively heated, is possibly present either as a solid solution or in the interior of the gel. The water, however, does not exert any influence on the amount of adsorption. After the adsorption is complete, the adsorbed nitrogen peroxide slowly reacts with the water forming nitrogen trioxide and nitric acid, and producing the bluish-green colour. During the

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[1] Eng. Pat. 319 (1911); Eng. Pat. 1180061 (1916).

[2] Phil. Mag. (6) 18, 916 (1909).

reverse process of removing the adsorbed gases, the nitrogen trioxide becomes oxidised to tetroxide which, with the excess of the adsorbed nitrogen peroxide, is removed by the current of air. The water is thus gradually replaced by nitric acid. Finally, a gel is obtained in which the water is completely substituted by the acid. This gel no longer assumes a green colour when it adsorbs nitrogen peroxide, and it is possible to remove the whole of the adsorbed gas from it. There is also no increase in weight of the gel after the removal of the adsorbed gases as in the case when water is present.

An adsorption isotherm was determined at 15° with a gel in which the water had been wholly replaced by nitric acid. The results obtained are recorded in the following table:

TABLE IV

Temperature of the bath	+12°	+10°	+5°	0°	−10°	−20°	−34°	−40°
Pressure of nitrogen peroxide in mm. mercury	490	450	351	270	150	88	30	11
Amount of adsorption in grams ($\frac{x}{m}$) per 100 grams of the gel	54.26	52.31	48.70	43.38	34.43	27.08	16.69	10.61

$a = 10.18$ and $1/n = 0.446$

The above results are plotted in Fig. 5. An adsorption isotherm at the same temperature with a gel containing 6.02 per cent. of water is also given for comparison. It is evident from the curves that the adsorptive capacity of the gel, when the water is completely replaced by nitric acid, is only slightly diminished. It is interesting to note that there appears to be a definite relation between the amount of water originally present in the gel and the amount of nitric acid which takes the place of the water. Samples of gel which originally contained 6.02 and 4.68 per cent. of water underwent a permanent increase of weight of 3.23 and 2.52 per cent. respectively, i.e., 6.02 and 4.68 per cent. of water were replaced by 9.25 and 7.20 per cent. of nitric acid. The ratios of the percentage of nitric acid which takes the place of water to the percentage of water originally present in the gel are 1.54 and 1.52 in the two cases. As the ratio of the densities of the two substances is also approximately the same, it appears that the amount of water in the gel is replaced by nearly the same volume of nitric acid.

7. Summary

(1) The adsorption of nitrogen peroxide by silica gel has been determined at different temperatures and pressures. The results are given in Table I and adsorption isotherms at 15°, 57°, 80° and 100° are plotted in Fig. 2.

(2) The influence of the water content of the gel on the adsorption of nitrogen peroxide has been studied. The results are recorded in Table III. It was found that within certain limits the water content of the gel exerted no influence on the amount of adsorption. Isotherms with gels containing 5.16 and 4.68 per cent. of water lie practically on the same line. (Fig. 3).

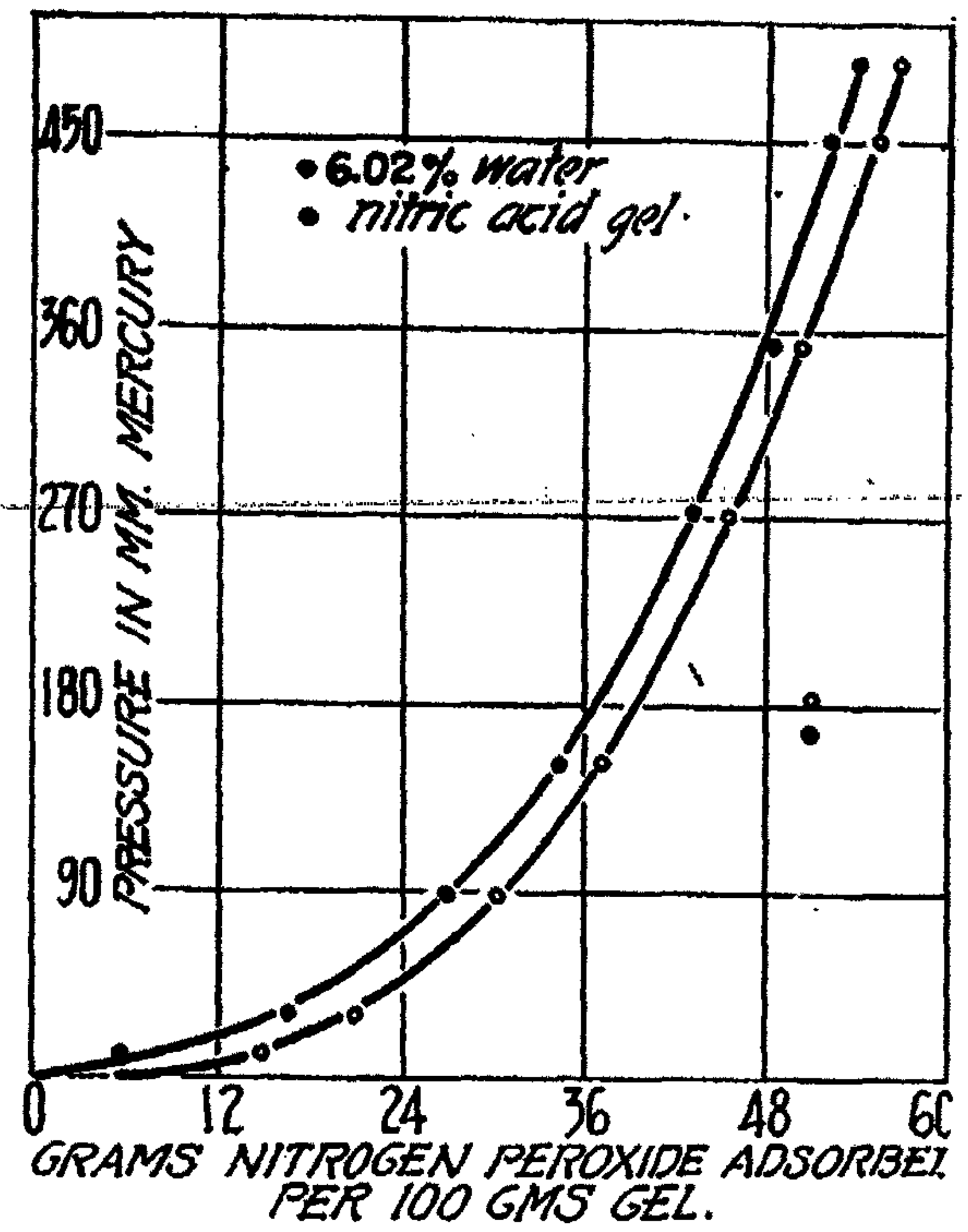

Fig. 5

(3) The effect of repeated adsorption of nitrogen peroxide on the same sample of gel has been investigated. It was found that by repeated adsorption the water in the gel was replaced by approximately the same volume of nitric acid. The adsorptive capacity of the gel is only slightly diminished when the water is replaced by nitric acid. (Table IV and Fig. 5). The adsorbed nitrogen peroxide could be removed from a gel containing nitric acid by drawing a current of hot and dry air through it.

(4) Freundlich's empirical equation was found to hold for all cases investigated, except when the saturation pressures were approached.

This investigation was undertaken at the suggestion of Prof. F. G. Donnan. My best thanks are due to him for procuring the silica gel, and for his kind interest and helpful criticisms. I must also express my thanks to Dr. D. C. Jones for his assistance in fixing up the apparatus.

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THE STRUCTURE OF SURFACE FILMS ON WATER

BY N. K. ADAM

In 1899 Rayleigh (4) came to the conclusion that the films formed by the spreading of fatty substances on water are one molecule thick. Later workers accepted this conclusion, (though in some cases with reserve); but prior to 1917 no serious discussion of the more detailed structure of the films was published. In 1917, Langmuir (12) accepted that the film was one molecule thick, and, expressing his results in terms of the average area in the surface occupied by each *molecule* of the film, was led to the conclusion that the molecules in the film possessed approximately the shape indicated by their organic structural formulae, and also that they were *oriented* perpendicular to the surface, in much the same manner as that which Hardy (Proc. Roy. Soc. **88** A, 303 (1913)) had previously discovered from the study of the properties of interfaces between two liquids. In this way a most important and direct connection was established between organic chemistry and capillarity, and the relation between chemical constitution and capillary properties has from the adoption of a new point of view, become most satisfactorily clear.

The development of experimental methods for the study of these surface films began with Miss Pockels' observation (1) that the surface of water can be cleaned from contamination, even of molecular dimensions, by sweeping with a solid barrier. Such barriers may be used to confine a film within a known area of a surface, and have been employed by Rayleigh and Hardy, and by Devaux, Marcelin, and other workers in France. Barriers of the type employed by earlier workers are not, however, efficient means of keeping a film confined within a given area of surface, but allow it to leak slowly. Mainly for this reason it has been necessary to modify the apparatus, in order to obtain accurate results.

Langmuir was the first to measure *directly* the force which acts on the film, in the plane of the surface, although Rayleigh and others studied the relation between free surface energy and surface concentration. By a modification of Langmuir's apparatus, I have succeeded in eliminating leaks past the barriers practically completely, and in conducting experiments of fairly long duration. In this paper the present method of experiment will be described, and an attempt will be made to arrange the results so that the argument leading to conclusions regarding the molecular force-fields is developed more consistently than has been possible in the original papers. The experiments cover some ground already investigated by Langmuir, but are probably more accurate. The portions of the theory for which I am indebted to others are generally indicated in the preceding remarks. The theory, it will be noticed, is based on Langmuir's, but is, in some respects, carried further.[1]

The apparatus[2] (Fig. 1) consists of a rectangular trough filled to the brim with water and levelled. Glass strips, CD, are used as barriers. The sides of the trough are at least 3/8-inch thick and are flat on the top. A brass trough built up of rectangular section brass on a plate has been used for most of the experiments.

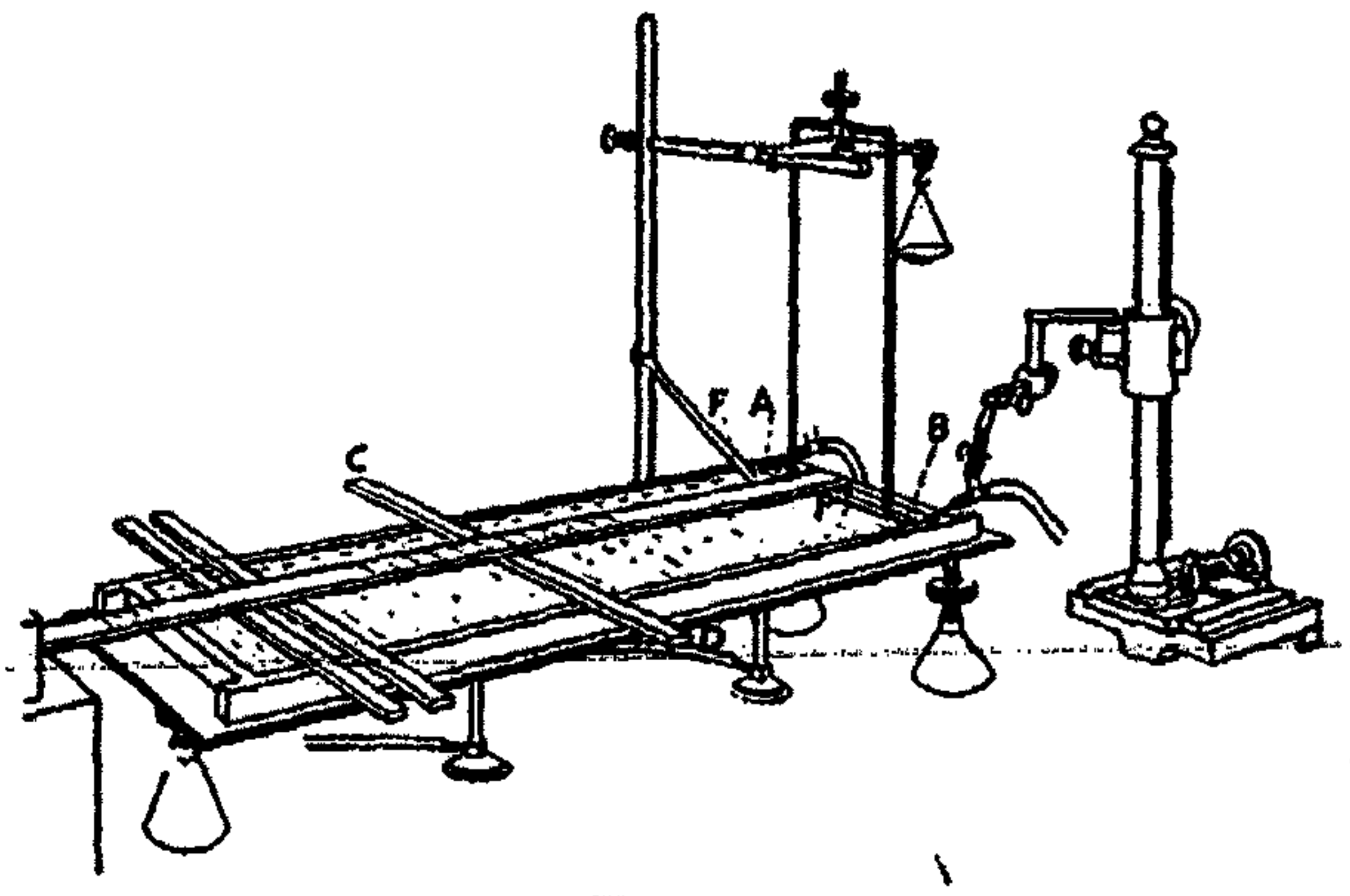

FIG. 1

The trough and barriers must be clean so as to avoid contamination of the water, but since water spreads over clean surfaces, a perfectly clean trough is in a state in which the barriers cannot confine the film, since there is a pool of water round the point where the barriers touch the sides of the trough, and the film can move freely along the surface of these pools from one side of the barriers to the other. This difficulty is overcome by coating the barriers and the sides of the trough with good paraffin wax, which prevents spreading, but does not contaminate the water surfaces.

The surface is first cleaned by sweeping up all contamination to the left hand end of the trough by the barriers. The film is then deposited on the cleaned surface, by dropping a known number of drops of a solution of the desired substance in *clean* benzene or toluene, from a calibrated pipette. Using a fine pipette the error can be reduced to about 2%. The solvent must be purified till it leaves practically no trace on the surface after evaporation of a few drops.

One end of the film is bounded by the barrier CD; at the other there is a strip AB (usually of thin copper, paraffined), floating on the surface. The horizontal force on this strip is measured by the balance, the vertical arms of which pass loosely through holes in the floating strip. The strip is about 1 ½ mm. shorter than the width of the trough, to allow for free movement, and

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[1] References to my own papers will be made simply to the number of the part. Part I, Proc. Roy. Soc., 99A, 356 (1921); Parts II and III, 101A, 452, 516; Parts IV and V, 103A, 676, 687. Several figures are reproduced from these papers, by kind permission of the Council.

[2] For full details see Part I, 337, Part II, 469.

the escape of the film through the narrow channels at its ends is prevented by a current of air from the jets shewn in the figure.

The weight of the substance put on the surface being known, and its molecular weight, the number of molecules put on is deduced, assuming the number of molecules in a gramme molecule to be 6.06×10^{23}. The principal results have been obtained by considering the curves relating the force exerted by the float AB on the film, to the area *per molecule*.

Weights in the balance pan obviously cause the float AB to exert a compressive force on any continuous film of floating objects between AB and CD. The films for this work are necessarily of substances so insoluble in water that they do not leave the surface appreciably during an experiment. Being confined to the surface, the molecules composing the film may correctly be considered as floating objects; hence the float AB exerts a *compressive* force on the film ABCD.

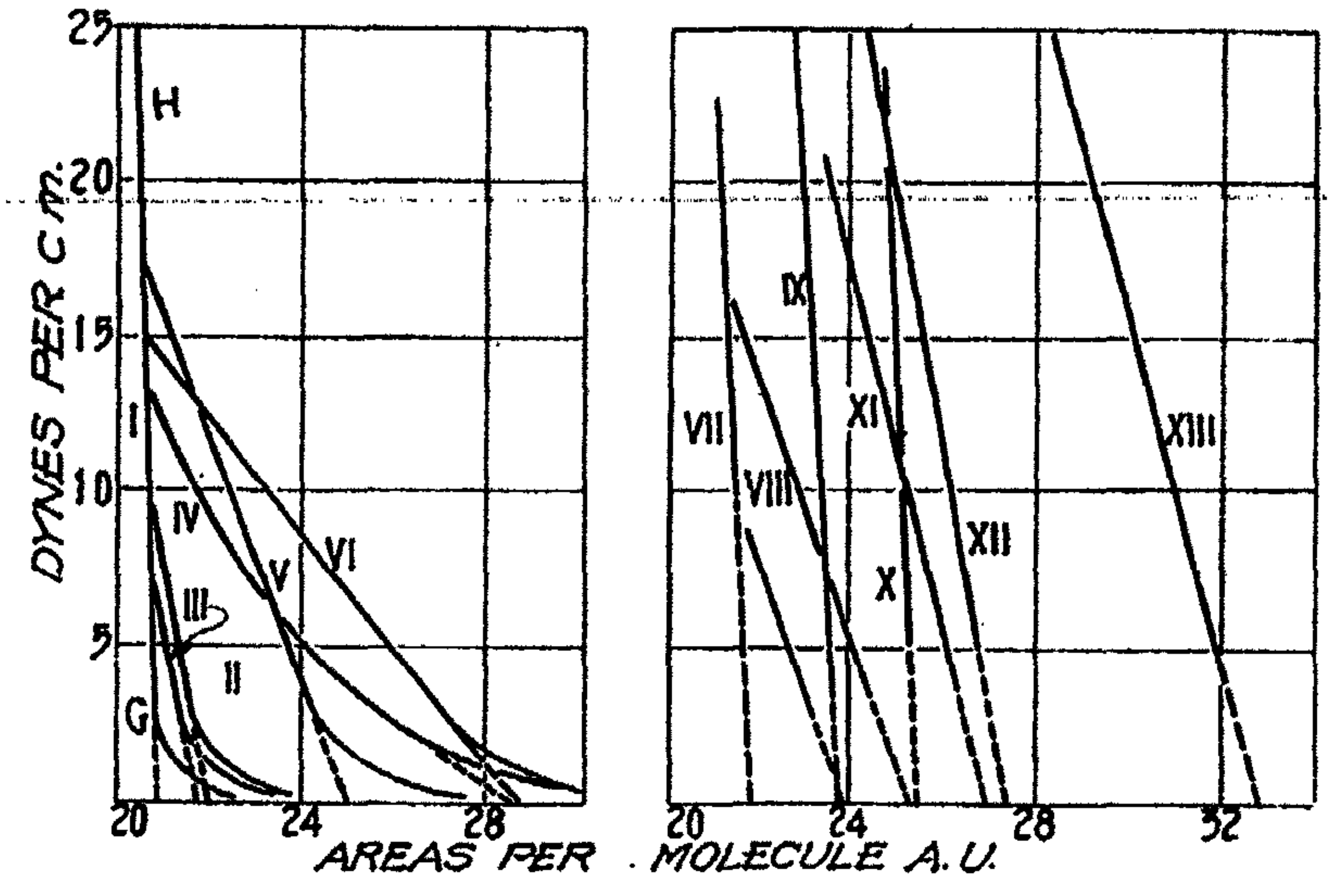

FIG. 2

Curve I	Fatty acids on distilled water (final curve); amides; triglycerides; ureas above the transition temperature.
II	Alcohols on water, acid, and alkaline solutions.
III	Ethyl, methyl, and allyl esters of saturated acids, on water and acid solutions.
IV	Ethyl iso-oleate.
V	Fatty acids on dilute HCl.
VII	Iso-oleic acid on dilute HCl.
VII	C_{16} aldoxime.
VIII	C_{16} and C_{14} aldoximes.
IX	Hexadecyl phenol and allied substances.
X	Ureas above the transition temperature.
XI	Nitriles.
XII	Final curves of the longer chain α bromo-acids, on dilute HCl.
XIII	Bromo-palmitic and bromo-margaric acids, on dilute HCl.

Before putting on the film, the barrier CD is moved so as to allow more room than is found by experience to be necessary to accommodate the film.

Next, the barrier is moved up until the float begins to move away to the right, indicating a compressive force on the film. At this point the film must be complete, and since it is the point at which the floating molecules first transmit a thrust, at this point the film is *one molecule thick*. By the study of the variation in compression as the area is still further reduced, it has been found that the films always remain one molecule thick, until they finally buckle up altogether. Not one case has been found, in thousands of experiments, in which a film could be considered as two or more molecules thick.

The Measurements of Molecules

The curves of Fig. 2 shew the relation between the area per molecule, plotted horizontally, and the compressive force on the film, plotted vertically, for a number of different substances.

In the first six of these curves, which have been obtained on a fairly large range of substances having nothing in common except the long hydrocarbon chain, in their constitution, the same line GH is found. It is exceedingly steep, cuts the abscissa at about 20.7 A.U.,[1] and is found in the most accurate experiments to be slightly steeper in the upper part than in the lower.

If the density of the film be assumed to be not far removed from that of the substance in bulk, the thickness of a film of stearic acid can be calculated from the area and is about 26 A.U. This thickness is of the same order of magnitude as, though somewhat greater than, that found for the length of this molecule in the crystal, by Muller (J. Chem. Soc. **123**, 2043 (1923)). Using this value as the thickness of the film, the slope of the line GH indicates that the compressibility of the surface film is about the same as that of a higher liquid paraffin in bulk. (Part II, p. 458.) Now when a liquid is compressed in bulk, the molecules cannot rearrange themselves under compression so as to occupy less space. Therefore the low compressibility in GH shews that, in this condition of the film, lateral compression does not alter the packing arrangement of the molecules.

The line GH occurs with many different long chain substances, and areas smaller than GH have never been found with stable films. Clearly long chain compounds cannot pack together closer than the area required by the chain will allow; so that the state of packing where the line GH is found is probably that in which the hydrocarbon chains are closely packed. Thus the cross section of a hydrocarbon chain as packed in the films is 20.7 A.U., within a few tenths of a unit.

The orientation of the molecules follows from the fact that in almost all these curves the shape of the curve is entirely unaffected by the length of the hydrocarbon chain, provided this is greater than a certain minimum. One curve is characteristic of the acids, others of the alcohols, the nitriles, esters, and so on. This constancy of the area per molecule, for molecules of different lengths, shews that the molecules must be oriented in the films, at a definite and constant angle to the vertical. A force-field, however, which would

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[1] The unit of length used is 1 A.U. $= 10^{-8}$ cm., and of area 1 A.U. $= 10^{-16}$ sq. cm.

orient a molecule of one length of chain, say of the series of alcohols, at a certain angle to the vertical, would be most unlikely to orient longer and shorter members of the same series also at the same angle, as well as molecules of other series of compounds. The evidence seems therefore conclusive that the molecules are oriented *perpendicular* to the surface.

The polar end of the molecule must moreover be directed towards the water; it is found that those groups which confer solubility on aliphatic substances of low molecular weight also confer the property of forming stable films on long chain compounds (Langmuir, 12, p. 1863). Also it will be seen later that a stable film may be rendered unstable by methylating, or otherwise modifying, the end group, so as to diminish its attraction for the water.

All the curves in Fig. 2 shew, at the lowest compressions, a part which tends to become horizontal and to depart from the general direction of the curve (these portions have been omitted, for clearness, from curves VII to XIII). The meaning of these lower portions is not at present clear. But apart from these, in curves II and VI, there is a definite lower portion, below GH, which in the case of each group of compounds cuts the abscissa at a definite area. This is 22 A.U. for the ethyl, methyl, and allyl esters; 21.7 for the alcohols, 27.5 for the nitriles, 25.1 for the acids on dilute HCl. These areas are characteristic of definite end groups in the molecule, and must be due to a different packing in the films from that of close packed chains. These areas must be the cross sections of the end groups as packed in the films. The structure of the films in this state may be represented diagrammatically as in Fig. 3, the chains being not quite in contact. If the heads of the molecules are not too bulky, they may be expected to be capable, under constraint, of fitting into recesses in the chains of neighbouring molecules, and from the curves II to VI it is seen that often simple lateral compression causes the films to change their structure from the state of close packed heads into close packed chains. If the heads, as seems perhaps most probable, do not change their proper cross sectional area much on compression, then there must be a gradual change from the packing of Fig. 3 to that of Fig. 4, as the compression is increased from that at the lowest portion of the curves II to VI, to the point at which these curves join the line GH. This change is found to be reversible, for on removing the compression the area increases along the original curve of compression.

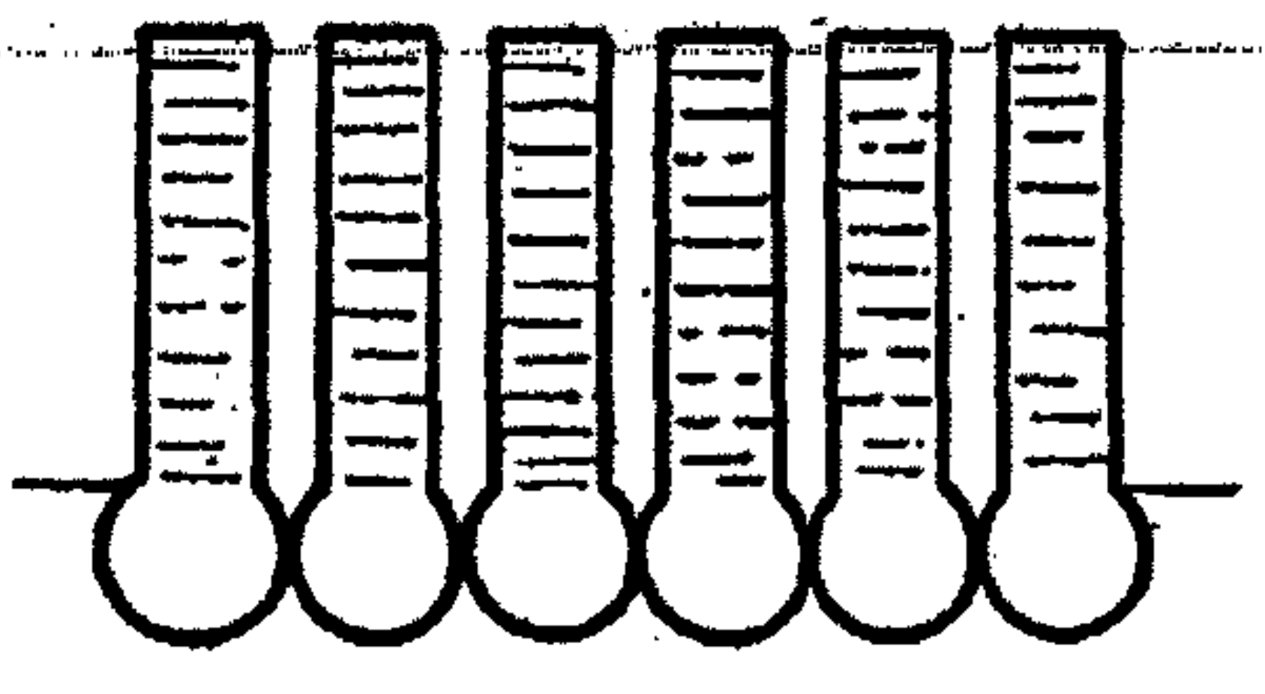


FIG. 3

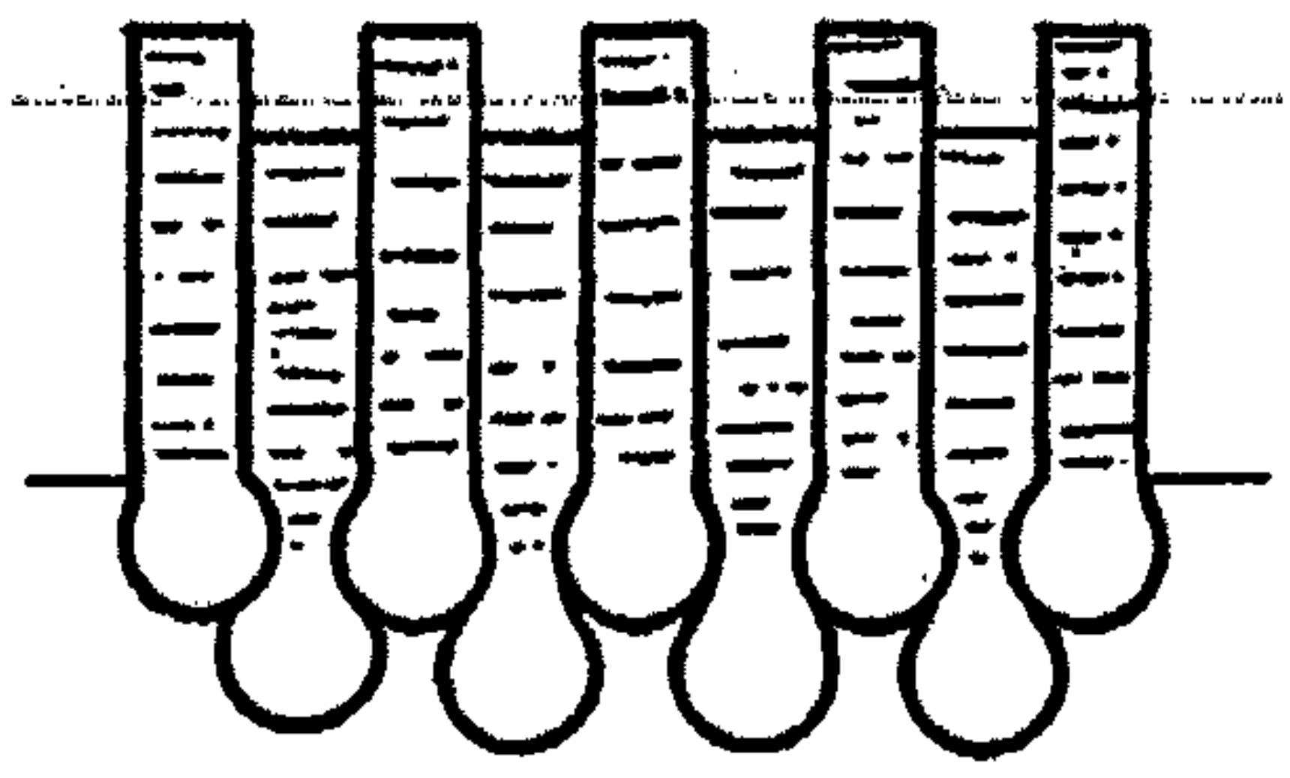
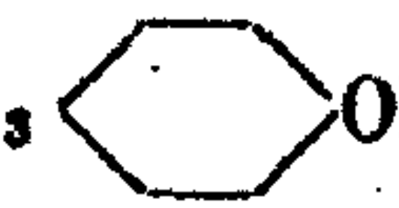


FIG. 4

Naturally, if the head of the molecule is too large, or fits accurately into the heads of the neighbouring molecules, simple compression will not alter the structure to that of close packed chains. Curves XI, XII, and XIII, obtained on the nitriles and α bromo-acids, illustrate this point. The bulky bromine atom not only increases the size of the head of the molecule, but, possibly because it renders the head very unsymmetrical, makes quite a number of different packings possible. Actually it was found on a series of bromo-acids that the heads packed into areas from 26 to 32 A.U., according to circumstances (Part V, p. 687).

In other cases, as with benzene derivatives of the type $C_{16}H_{33}$ OH, the head has not a very large cross section, but it appears to have too much length to fit into recesses in the chains. Here the arrangement of close packed heads shewn in Fig. 3, appears to be stable against compression. The observed curve (IX) shews a compressibility which is actually of the same order of magnitude as that of benzene in bulk, which agrees with the supposition that the benzene rings are taking the whole of the strain of the compression, without rearrangement. In these films the molecules appear to be packed with the hydroxyl group to the water, the benzene rings closely packed in one plane, and the long chains vertically above the rings. The structure of the layer formed by the benzene rings in this film appears to be identical with that of the monomolecular layer which would result from a series of cleavages of the crystal of an aromatic hydrocarbon. The area, 23.8 A.U., is in very good agreement with 23.3 A.U., the best value that can be deduced at present for the corresponding cross section of the benzene ring, from the X-ray measurements (Part IV, p. 677).

An interesting effect on the cross section of the head is produced by introducing an ethylenic linkage in the α position to the carboxyl group. Curves IV and VI shew the cross section of the heads of iso-oleic acid and its ester to be 28.7 A.U., and these are considerably greater than the cross sections of the heads of the saturated acid (25.1) and the saturated esters (22). It seems probable that the chain of the molecule is bent into an elbow at the region of the double bond, and this makes packing more difficult than with the saturated compounds. Where the double linkage is in the middle of the chain, as with elaidic, erucic, and brassidic acids, there is no such enlargement of the head of the molecule in the films. In the middle of the chain, a double bond does not seem to alter the area of packing of the molecule (Part II, p. 457).

Table I gives the principal measurements of the cross section of groups which have been made. These are of course the cross sections to which the groups pack in the films, and are not necessarily the cross sections in free space, of a single molecule.

TABLE I

Group	Cross section, A.U.
Hydrocarbon chain	20.7
$-CH_2\,CH_2\,COOH$	25.1
$-CH{=}CH\,COOH$	28.7
$-CH_2\,CH_2\,COO\,C_2H_5$[1]	22
$-CH{=}CH\,COO\,C_2CH_5$	28.7
$-CH_2OH$	21.7
$-CONH_2$	less than 21
$-CN$	27.5
$-CH_2\,NH^2CO\,NH_2$	25.5
$-C_6H_4\,OH$	23.8
$-C_6H_4\,NH\,CO\,CH_3$	28.2 or 25.8[2]
Triglycerides	63
Glycol dipalmitate	42
Cholesterol	39
Hydrolecithin	53

Two instances have been found of a kind of two-dimensional allotropy in the films, in which the packings change at a definite transition temperature which is altered by compression. The substituted ureas, $RNHCONH_2$, give the arrangement of Fig. 3 below about 30° (for octadecyl urea), and that of Fig. 4 above this temperature (Part II, p. 464). Hexadecyl acetanilide gives two packings like Fig. 3, but of different closeness, one stable above 29°, the other below 24° (Part IV, p. 681). Such phenomena are natural when the heads of the molecules reach a sufficient degree of complexity, and seem to be precisely analogous to the changes in crystalline structure of many solids at a definite temperature, usually called allotropy.

The thickness of the films is frequently given, but it must be remembered that what is always measured is the area of the film, and the thickness can only be calculated from this by an assumption as to the density. This can as a rule be considered correct only as to order of magnitude.

The Forces on Individual Molecules

The two-dimensional and oriented state of matter in these films not only allows of the calculation of the size and shape of molecules, that is of the contour of their repulsive force fields, but it is one of the most favourable cases which can be found for the study of the attractive fields of force round the molecules. The problem of reducing observed forces to the actual forces on the individual molecules is enormously simplified when, as in the films, there is no need to allow for more than one orientation of the molecules or more than one position in a vertical direction. Up to the present, however, only qualitative information has been obtained.

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[1] Ethyl, methyl, and allyl esters pack into the same area.

[2] According to temperature.

Considering first the stability of the films, it is possible to compress them frequently to some 30 dynes per cm, which on a usual thickness of the films is of the order 100 atmospheres compression. It is at once clear that the film molecules have a very strong adhesion to the surface of the water, for no isolated thin film could stand a compression of this amount without buckling. If the intensity of the attraction of the end group near the water is diminished, the film often becomes less stable under compression. For instance, a film of hexadecyl phenol (Fig. 5 (I)) is quite stable, but if the hydroxyl group which adheres to the water is methylated as in II, the film is found to diminish slowly in area, and patches of the substance in bulk appear on the surface. Numerous other instances of films being unstable, where the polar group at the end of the molecule is partly blocked, have been found (Part IV, p. 682).

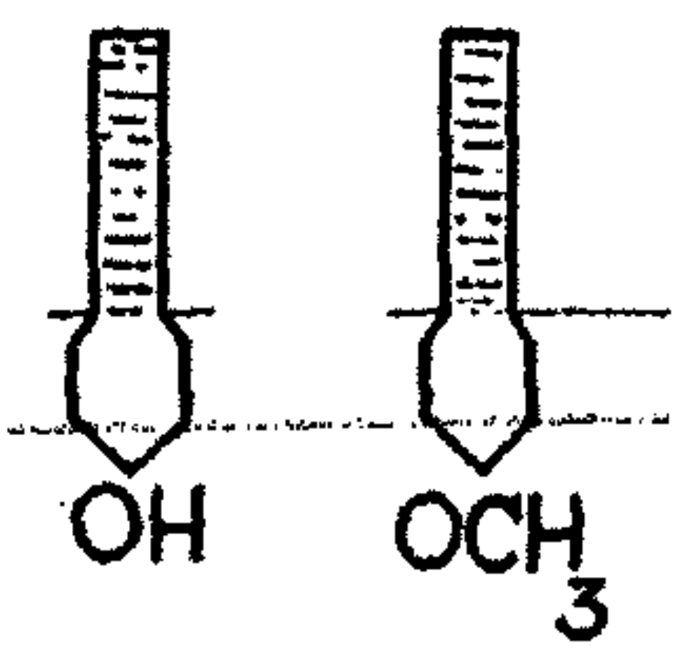

Fig. 5

If the compression is increased sufficiently, eventually some of the molecules must be forced out even from a stable film. It would be expected from the fact that hydrocarbons possess cohesion, that the chains packed parallel to each other in the films should have a mutual lateral attraction. To expel a single molecule from the film would mean doing work against these lateral attractions as well as against the normal attraction of the end group for the water. But if an area containing a considerable number of molecules is buckled at one time, it becomes only necessary to overcome the attraction of the end groups on the water. Indeed in practice probably the work required to buckle a film is even smaller than this, for the film of Fig. 3 can fold up into one or more double layers as in Fig. 6, *work being gained* by the approach of the polar end groups to one another. Double layers of this nature probably form the fundamental laminae out of which are built up the thin flakes in which most of these long chain compounds crystallise.

Raising the temperature has also given information as to the attractive forces. The heads of the molecules are in a sense dissolved in the water, and are in intimate contact with the water molecules. They therefore partake of the thermal movement. Actually it is found that increasing the temperature may affect the film in one of two ways. The less common way is for the vertical component of the thermal movement to help the molecules to leave the surface film, and collapse as in Fig. 6. This effect of the molecular motion only predominates when the film is, at any temperature, rather unstable, that is, when the attraction of the end group for the water is only just sufficient to hold the molecules there temporarily. In such cases, usually a rise of temperature increases the rate at which the films collapse.

Much more frequently, the effect of the horizontal components of the motion breaks up the lateral cohesion of the film, long before the vertical agitation assists the molecules to leave the film altogether. The films at a certain temperature increase greatly in area, a phenomenon first observed by Labrouste; the explanation of its meaning was given almost simultaneously by Marcelin (10) and myself (Part III). Fig. 7 shews the general course of the change in area, under a constant small compression. The changes in the curves relating compression with area, as the temperature rises, are shewn in Fig. 8. As the temperature rises, with myristic acid on HCl, from 3.5° to 32.5°, the compression curves change from the general compression curve of Fig. 2 for the condensed films of fatty acids on HCl, to one shewing much more compressibility, which resembles the isothermal of a gas. Marcelin (11) claims to have detected a compression on a film of oleic acid at an area which he does not state in definite measure, but which must have been of the order of magnitude of 200 A.U., using a very delicate means of detecting compressive forces.

The curves intermediate between 3.5° and 32.5° bear some resemblance to the isothermals of a vapour near the critical point. The main difference is that the area increase in the expanded films is not so great as the volume increase when a liquid vaporises. Above the temperature at which the inflexions first disappear from the curves, further rise of temperature only has the effect of moving the curves slightly to the right and upwards; at constant compression there is a gradual further increase in area as the temperature rises above that at which the main expansion is complete (Parts III, p. 519, and V, p. 689).

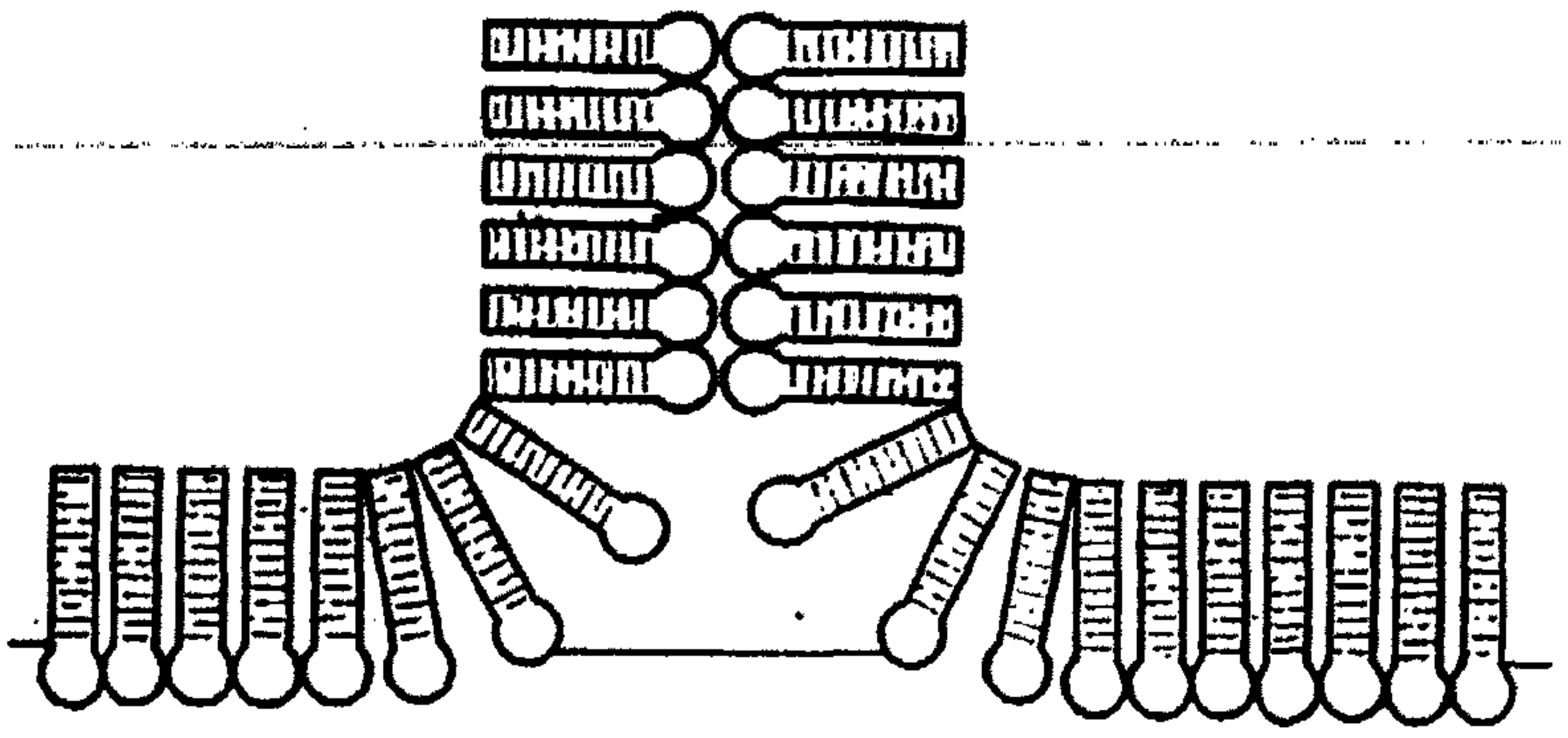

Fig. 6

This expansion of the films at a definite temperature is a general phenomenon; it has been observed in every case, except when collapse of the film set in before expansion, or when it was experimentally impossible to reach the temperature of expansion on account of its being too high or too low. It takes a slightly different form with some substances; for instance the corresponding curves to Figs. 7 and 8 for the esters of fatty acids are given in Fig. 9, and the area of an expanded film of a fatty acid under given compression depends on the solution on which it is examined (Part III, p. 521).

The temperature of expansion however rises regularly with the length of the chain, in each homologous series. On ten different homologous series, the fatty acids, alcohols and their acetates amides, nitriles, ureas, methyl and ethyl esters, aldoximes, and bromo-acids, the same law has been found for the variation of the temperature of expansion as a given number of CH_2

groups is added to the chain; the addition of one CH_2 raises the temperature of expansion by about ten degrees near 0° and about seven degrees near 60°C (Part III, Tables I and II, and Part V.). As, on the foregoing theory, the expansion is an overcoming of the lateral attractions between the chains, it is to be expected that lengthening the chains will increase the temperature requisite for expansion; and also that where the disruption of the film is into similar units (single chains) the influence on the temperature of expansion caused by an equal lengthening of the chains should be the independent of the nature of the end group. The only exception yet found to the rule just given for the influence of the addition of one CH_2 to the chain on the expansion temperature, is with the triglycerides, where the expansion temperature only increased about half the usual amount on passing from tripalmitin to tristearin (Part III p. 523). This is to be expected from the fact of these substances having the chains linked permanently together in groups of three.

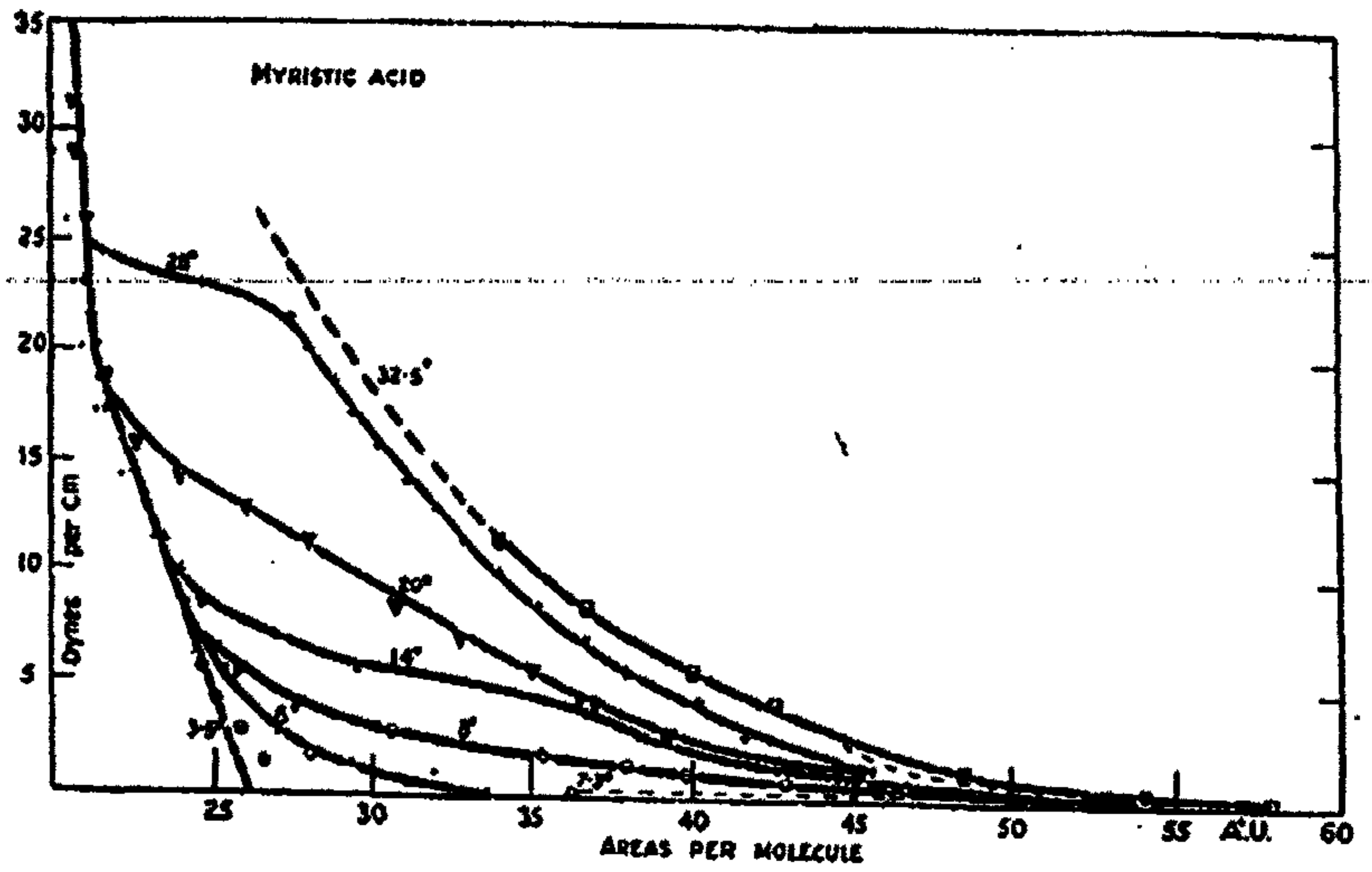

Fig. 7

The expanded films are two-dimensional gases. In the condensed films an impulse is transmitted from one end to the other by actual contact between the molecules. In the expanded films there appears to be considerable space vacant in the surface; the molecules are in constant motion along the surface, and exert pressure on the barriers by reason of their momentum. An impulse is transmitted in such a film by the transfer of momentum from one molecule to another in collisions. The film is not however to be treated as an isolated two-dimensional gaseous system, for the film molecules are in constant contact with the close packed water molecules, and are influenced by their motions. Hence the problem of working out the kinetic theory of these two-dimensional gases is not easy. It is a problem which is related closely to the theory of the interactions of solvent and solute molecules, for the ends of the film molecules are in much the same relation to the water as are dissolved molecules to a solvent. It is already clear that there are differences in the motions of the film molecules according to the nature of the end groups of the film molecules and the substance dissolved in the water (Parts III and V).

It is probable that in the expanded films, as in the condensed, the molecules are oriented perpendicular to the water surface. The area of the expanded films does not increase with lengthening chains, as it would do if the molecules were not vertical; on the contrary, it is often found that the area of an expanded film is actually less (at the same temperature) for a longer chain compound than for a shorter one of the same series (Part III, p. 525). This effect seems to be due to the greater attraction of the long chains in the expanded films causing a correction to the "simple gas laws" which is greater with longer than with shorter chains.

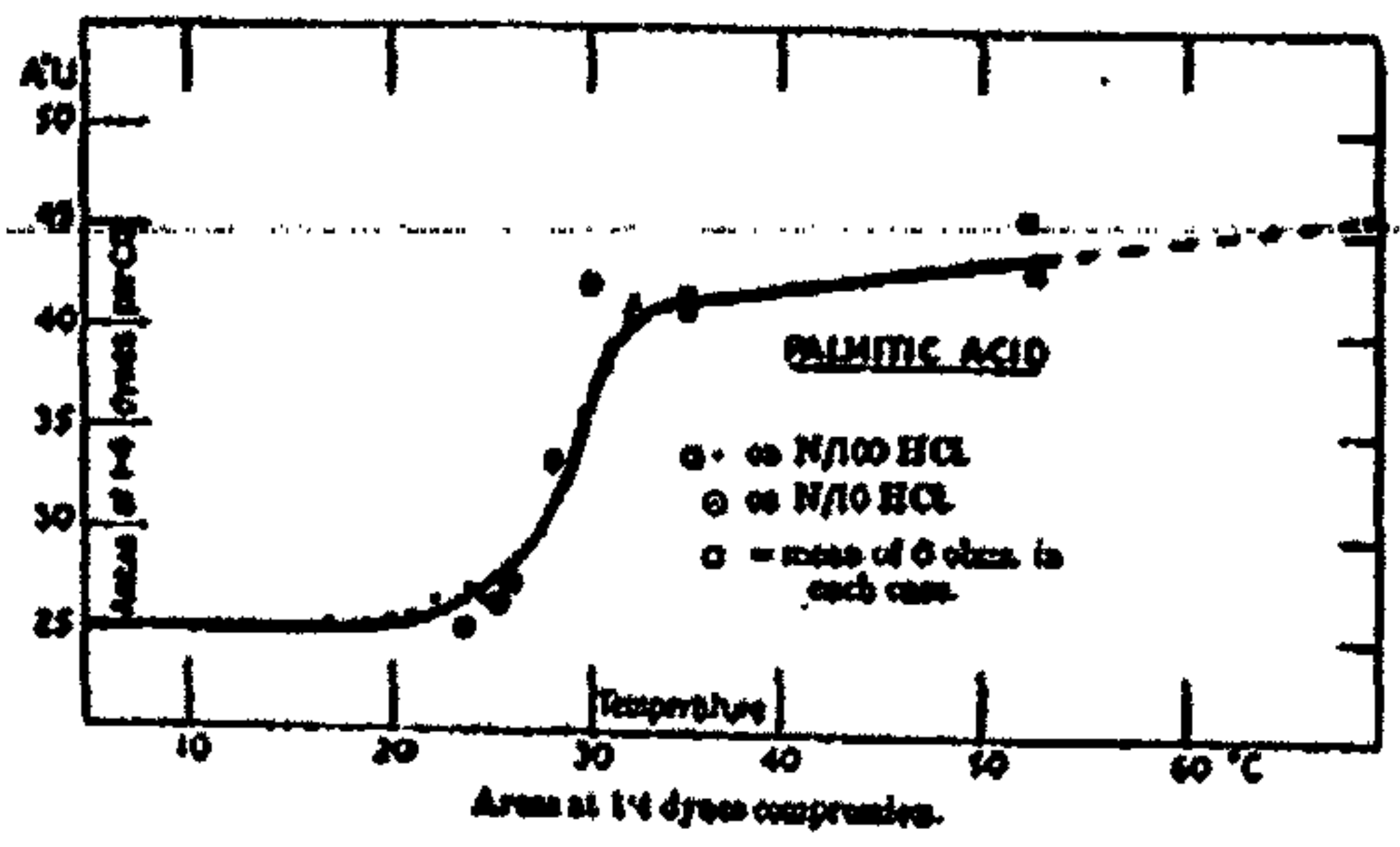

Fig. 8

An ethylenic linkage in the molecule in the middle of the chain is found to diminish the lateral attraction between the chains, and the attraction is considerably less if the stereochemical configuration of the double bond is as in oleic and erucic acids, than if it is as in elaidic and brassidic. The double bond of the oleic type lowers the expansion temperature by nearly 70°C, that of the elaidic type only by about 40°, comparison being made with the saturated acid. In Langmuir's paper, the suggestion was made that because oleic acid occupied a greater area on the surface than the saturated acids he examined, it was therefore doubled up with the double linkage in the water; unfortunately this most interesting suggestion is found to be incorrect now that it is known that both saturated and unsaturated acids can exist in the condensed and expanded states, at suitable temperatures, and that there is very little difference, except in the temperature of expansion, between films of saturated and unsaturated acids.[1]

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[1] Note added, November, 1924. Dr. Langmuir has pointed out to me that the expanded films consist of molecules oriented vertically and projecting from the surface, these molecules will have a high potential energy, and may tend to lie down flat on the water surface. If this is so, they must overlap, as there is not room for the whole area of all the molecules lying flat. There is the more probable alternative, however, that as soon as the molecules have separated, through expansion of the films, they sink in among the water molecules so as to satisfy the attractive forces of the chains. If this is so, they will probably remain vertical. Nevertheless it must be remembered that the pressure in two dimensions in the surface is only about one sixth of that expected from the gas laws, and no satisfactory explanation of this fact is at present available.

Applications of the Foregoing Theory

A few examples of the way in which the ideas gained as to the force-fields about long molecules are useful in explaining different phenomena may be of some interest. A strong tendency of the long chains to pack closely together side by side has been revealed; this lateral adhesion being overcome when a suitable temperature is reached, which is higher, the longer the chains. There is also a strong attraction between such groups as OH, COOH, $COOCH_3$ CN, etc., and water.

These properties, considered together with the melting points of the crystals, sufficed to predict some of the principal points of the structure of crystals of the fatty acids and their esters, which have since been shewn, by the X-ray investigations of Muller and Shearer, to exist in these crystals (Part III, p. 528). In the acids, the melting points rise with increasing length of the chains, shewing probably a lateral close packing of the chains. But the esterification of the COOH group immediately lowers the melting point, shewing that in the esters the COOH groups of adjacent molecules attract each other and help to stabilize the crystal. Hence the crystal is probably composed of laminae made up of pairs of monomolecular films like those which form on the surface of water, the COOH groups being placed together in the centre of such a lamina. The esters containing *long* chains in both acidic and alcoholic groups rise in melting point as the alcoholic chains are lengthened, so that in these probably both sets of chains lie side by side, and therefore there is probably not any juxtaposition of the oxygen-containing groups of several molecules in the centre of the laminae, as there is with the acids. In the unit cell, the acids have two molecules end to end: the higher esters only one molecule.

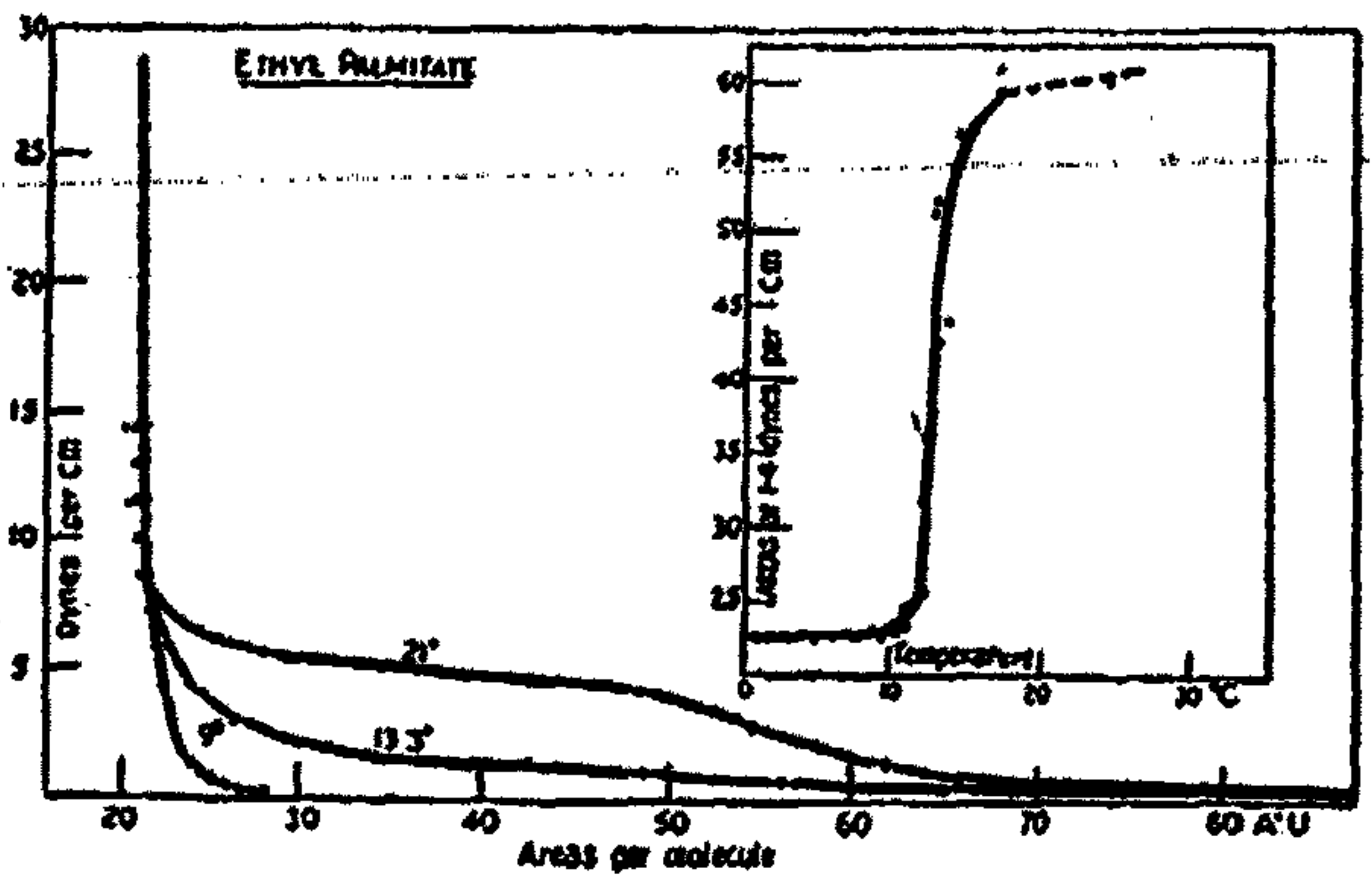

Fig. 9

It becomes easy to see why the salts of the higher fatty acids have a tendency to form colloidal ions of high molecular weight and mobility, and to suggest a possible structure for these colloidal ions or "Micelles." A single anion of a soap of a monovalent metal may exist temporarily in the free state in a liquid, but if it comes into contact with another will naturally pack close to it, the chains side by side; and the final result of the close packing of soap anions in this manner will be an aggregate having the chains packed together in the centre, and the carboxyl groups all presented outwards to the water, Fig. 10. These carboxyl groups, being free to dissociate, will confer a considerable charge on the colloidal particle, and thus the soap molecules naturally build themselves up into aggregates possessing the known properties of the colloidal ions of soap solutions. That the fatty acids with chains shorter than a certain minimum do not form these aggregated ions is probably due to the thermal agitation of the water molecules disrupting the aggregates, as it does the condensed films, when the lateral attraction between the chains is not sufficient.

Harkins (J. Am. Chem. Soc. 39, 592 (1917)), has suggested that in the formation of the layer of soap at an interface between aqueous and hydrocarbon phases, a layer which is most important in determining the stability of emulsions, the "orientation and the form of the molecules together with adsorbed ions" may be of importance in determining the curvature of the interface. With the reservation that, since there is not yet any actual knowledge of the shapes of the soap molecules nor of their mode of packing, the suggestion must be revised when such knowledge is obtained, it can now be suggested that a calcium soap, or soap of a divalent metal, may have the polar end of less cross section than the two chains, while the monovalent soaps may have their polar ends larger than the chains, since with them there is one metallic atom to each chain instead of one to two chains. Molecules larger at their polar ends will naturally pack into a curved film having the hydrocarbon side concave and the water attracting side convex, and such a film will fit the surface of an emulsion of *oil dispersed in water*. On the other hand molecules such as soaps of the divalent metals will be tapered in the opposite sense and so will tend to fit the curvature of, and to stablize, emulsions of water in oil. These are well known to be the effects of mono- and divalent soaps.[1]

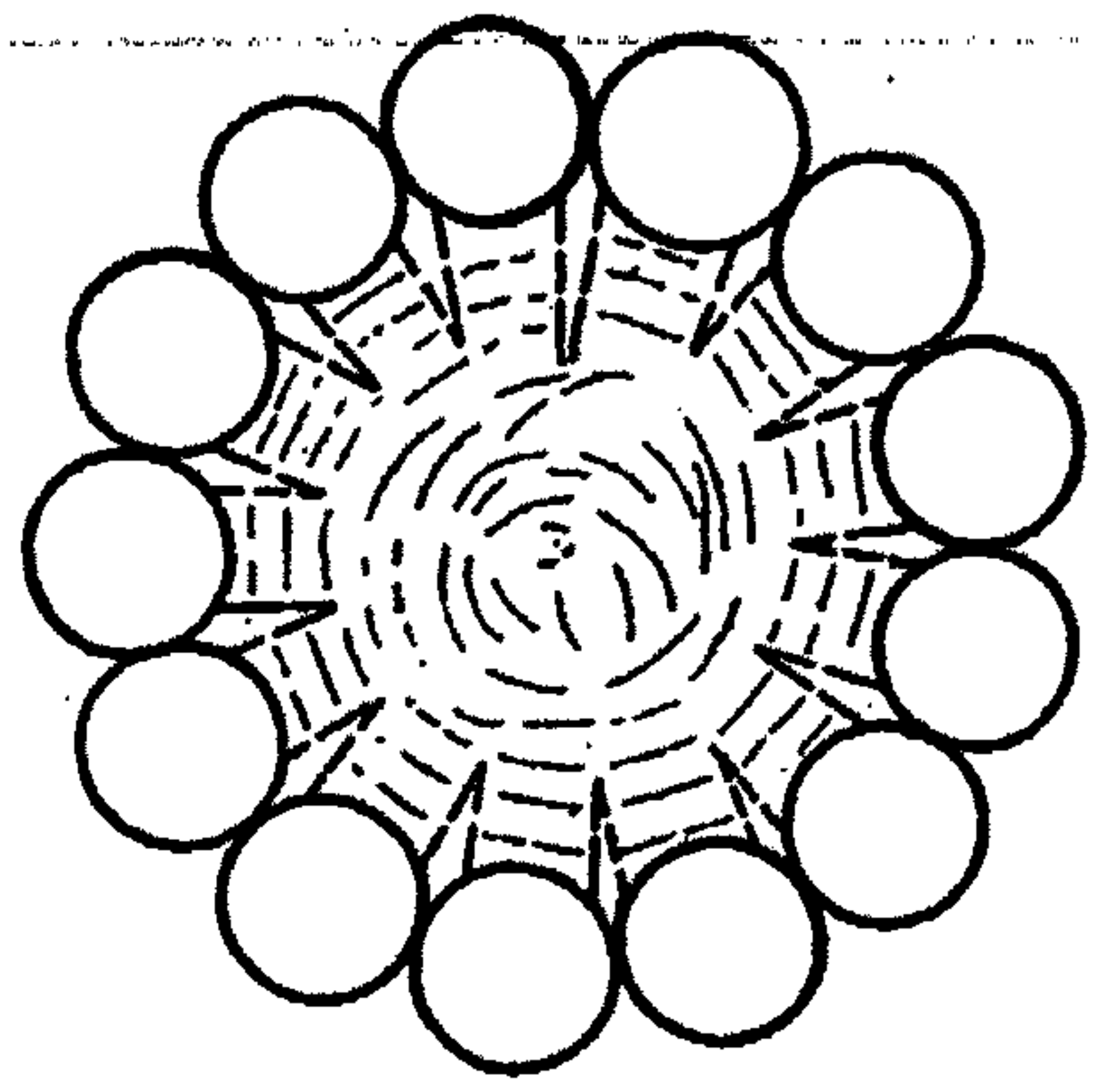

FIG. 10

Moreover the molecules which are narrower at their polar ends than at their hydrocarbon ends will not probably form such stable aggregates of the type of Fig. 10, as the monovalent soaps which do form these colloidal ions.

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[1] These remarks were written before reading the interesting paper of Finkle, Draper, and Hildebrand (J. Am. Chem. Soc. 45, 2780, (1923)), which presents almost identical ideas.

It is perhaps however worth allowing my presentation to stand, as it brings out more clearly the relation with the information deduced from the study of mono-molecular films, with the explanation of phase reversal given by Bancroft, and with the solubility of the different classes of soaps.

Taking into consideration only the ease of packing of molecules of the shape we are now assuming the divalent soaps to be, it is probable that these molecules will pack with their metallic ends in the centre and hydrocarbon chains outwards; and under certain circumstances of precipitation the insolubility of the group formed by the divalent metal and the COO groups may assist this packing of the polar groups within. Such an aggregate as this will present nothing but hydrocarbon groups outwards to the water, and therefore will probably be soluble in hydrocarbon solvents, not in water. Actually it is sometimes found that the soaps of the divalent metals form colloidal solutions in benzene and oil. It would seem therefore to be possible that the shapes of molecules may, under favourable circumstances, play a deciding part in determining the solubility of substances in different solvents. In this instance the shapes cause packing into aggregates, in the one case packed so as to present a water attracting face outwards; in the other, the packing produces a surface which attracts hydrocarbons.

In the explanation of the forces on the floating copper strip, at the beginning of this paper, it has been shewn that the simplest way of regarding the force is as a thrust from the molecules of the surface film. But these molecules reduce the free surface energy, or "surface tension," of the surface; so that what is commonly called "diminution of surface tension" appears, in a complicated surface like this, to be really an effect of the crowding of the molecules together laterally in the film, with compression. In the case of the tapered molecules, the crowding may be considered as greatest at the wider end of the molecules, so that we may regard the curvature of the interface as being taken up in order to counteract the effect of the greater crowding at one end of the molecules. Bancroft (Applied Colloid Chemistry, p. 261 (1921), has suggested that the reason for the curvature is that the surface tends to become convex towards that phase in which the surface tension is most diminished by the adsorption of the soap. If we read, as we may, "greatest crowding of the film molecules," for "greatest diminution of surface tension," we see that Bancroft's explanation and mine are identical, although at first sight they might have appeared utterly different.

The detergent action of soap also receives a simple explanation on this theory. Nearly all foreign matter which is insoluble in water, and therefore requires soap to remove it is of an oily nature, or at least has a less attraction for water than for hydrocarbons. Therefore, in a solution of soap, the soap molecules will be adsorbed on the surface with their hydrocarbon ends to the dirt, and their water attracting ends to the water. Hence the surface of the particle is rendered strongly water attracting, and, if the particle is small enough, it will go into colloidal solution. Pickering (J. Chem. Soc. 111, 86, (1917)) has shewn that small amounts of paraffin can be incorporated with soap and caused to dissolve in water.[1]

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(2) Rayleigh: Proc. Roy. Soc. **47**, 364 (1890).
(3) Rayleigh: Proc. Roy. Soc. **48**, 127 (1890).
(4) Rayleigh: Phil. Mag. **48**, 331 (1899).
(5) Devaux: "Ann. Rep. Smithsonian Institution," 261 (1913).
(6) Hardy: Proc. Roy. Soc. **86A**, 610 (1912).
(7) Hardy: Proc. Roy. Soc. **88A**, 313 (1913).
(8) Marcelin: Ann. Phys. **1**, 19 (1914).
(9) Marcelin: Compt. rend. **173**, 38, 79 (1921).
(10) Marcelin: Compt. rend. **175**, 346 (1922).
(11) Marcelin: Compt. rend. **176**, 502 (1923).
(12) Langmuir: J. Am. Chem. Soc. **39**, 1848 (1917).
(13) Langmuir: Met. Chem. Eng. **15**, 468 (1916).
(14) Labrouste: Ann. Phys. **14**, 164 (1920).
(15) Adam: Proc. Roy. Soc. **99A**, 336 (1921).
(16) Adam: Proc. Roy. Soc. **101A**, 452, 516 (1922).
(17) Adam: Proc. Roy. Soc. **103A**, 676, 687 (1923).
(18) Ehrenfest: Rec. Trav. chim. **42**, 784 (1923).
(19) Leathes: Proc. Physiol. Soc. Nov. (1923).

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[1] This explanation of detergent action has been suggested by Zsigmondy (Kolloidchemie, 314 (1920)), though apparently without the author recognizing the evidence, from other sources, for the orientation of the soap molecules at the surface.

THE PROPERTIES OF PHOSGENE SOLUTIONS: VAPOR TENSION CURVES OF ALUMINUM CHLORIDE SOLUTION AT 0° AND AT 25°

BY ALBERT F. O. GERMANN AND GLENN H. MCINTYRE

The unusual chemical properties of the solution of aluminum chloride in liquid phosgene recently recorded in this JOURNAL have led to studies in which a knowledge of some of the physical constants of the solution is necessary. The data recorded in this and in succeeding papers were obtained to fill this need.

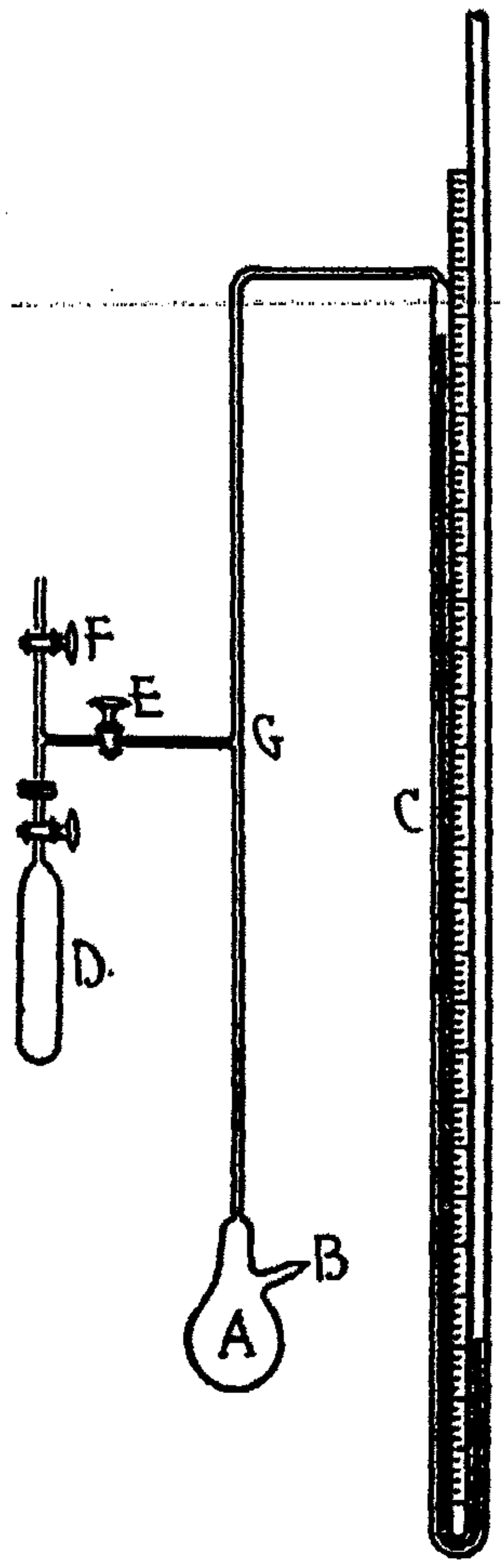

FIG. 1

Two series of measurements of the vapor tension of solutions of aluminum chloride in liquid carbonyl chloride were made by a gravimetric method at each of two temperatures, 25° and 0°, designated series A and series B, and one series of measurements at 25°, designated series C, by the volumetric method described by Germann and Gagos,[1] in which a weighed sample of aluminum chloride was dissolved in a weighed sample of phosgene, and the composition of the solution changed by withdrawing phosgene vapor from the system by means of a mercury pump, and measuring the volume of the vapor in a gas burette. The apparatus used in the measurements made by the gravimetric method is sketched in Fig. 1. The solution bulb A was sealed to one end of a T-tube G, the mercury manometer C to another end, and a stop-cock E communicating with a weighing tube D to the third end. The dead space between the stop-cock G and the weighing tube was provided with means of evacuation through stop-cock F. Samples of the solid solute were introduced into A through the filling tube B, which was then sealed off. By this method, the composition of the solution was altered by distilling phosgene from the solution into the weighing tube, using liquid ammonia as refrigerant, and making a correction for the weight of phosgene left in the dead space above

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[1] J. Phys. Chem. 28, 965 (1924).

the weighing tube because of the vapor tension of phosgene at the temperature of the liquid ammonia bath, about 65 mm. at −45°; the value of this correction, 5.8 mg., was ascertained by direct measurement.

The aluminum chloride used was the purest obtainable, and was further purified by mixing with powdered aluminum, and distilling under a pressure of about three atmospheres, or above the triple point, in a specially constructed pyrex still. The product obtained in this way had only a slight color, and dissolved in phosgene to form a clear colorless solution; on evaporating off most of the phosgene, the concentrated solution remaining had a light amber color, due to traces of iron chloride; but on crystallization the solution yielded pure white crystals of a phosgenate of aluminum chloride.

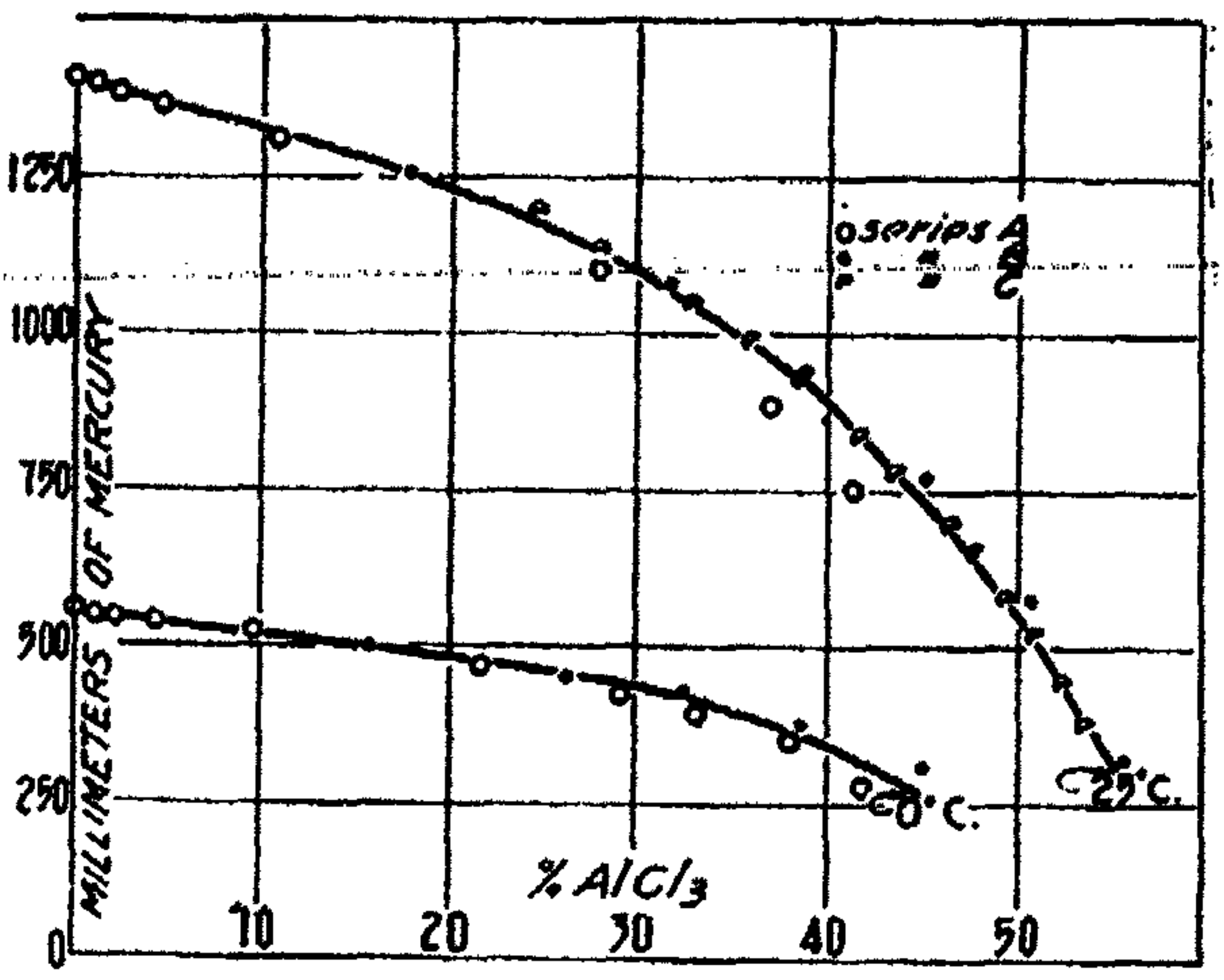

Fig. 2

The phosgene used was a sample supplied by Edgewood Arsenal, and was purified in the usual way. The purity of the samples used was judged by the constancy of the vapor tension: the first fraction showed a vapor tension at 0° of 556 mm., and at 25° of 1407.5 mm.; while the last fraction gave at zero 555 mm., and at 25° 1404.5 mm.

Constant temperatures were maintained at the lower temperature by a large ice bath, and at the higher temperature by a large thermostat, the temperature of which fluctuated no more than one hundredth of a degree.

Calculation of Results

It is evident that, due to the high vapor tension of phosgene, a certain part of the solvent introduced into the apparatus will not be in the liquid phase, and this will vary with the concentration and consequent change in vapor tension, and with the volume of the apparatus, which in turn will depend on the position of the mercury in the manometer (internal diameter about 10 mm.), and on the volume of the solution. This large correction factor is the principal objection to the method; the weight of the vapor filling the solution vessel, the manometer above the mercury, and the communicating tubes must be estimated, and subtracted from the total weight of phosgene in the system. The weight of vapor filling the system under a known pressure (observed on the manometer) and at a known temperature was determined by condensing it in the weighing tube and weighing. Using as a basis of calculation the value found by Germann and Jersey[1] for the weight of the liter of purified technical phosgene vapor, 4.53, which leads to the number 4.15 as the weight of one liter of phosgene vapor at normal pressure at 25°, the basic volume of the system was calculated. The basic volume of the system in series A was 330 cc.; in series B, 205 cc.; and in series C, 100 cc. At each concentration, the volume of vapor was estimated, taking into account the volume of solution and the position of the mercury in the manometer, and its weight under the existing conditions of temperature and pressure calculated. Obviously, the error committed on the percentage composition of the solution due to any uncertainty in the value of the correction would be very small for high concentrations of phosgene, but relatively large when the size of the correction approaches the weight of phosgene in the solution.

TABLE I

Series A at 0°	
% $AlCl_3$	V. T.
0.00	555 mm.
1.20	551
2.41	547
4.56	541
9.52	524
21.64	473
29.18	429
33.36	398
37.72	343
41.94	281

Series A at 250°	
% $AlCl_3$	V. T.
0.00	1406 mm.
1.22	1397
2.49	1380
4.86	1364
10.90	1308
27.97	1105
37.15	888
41.40	756
44.50	600
47.70	457

Series C at 25°	
% $AlCl_3$	V. T.
24.6	1200mm.
28.0	1139
33.1	1052
36.1	991
38.65	931
41.8	842
43.7	786
46.3	703
47.7	658
49.4	578
50.8	522
52.4	445
53.7	380

Series B at 0°	
% $AlCl_3$	V. T.
15.66	505 mm.
26.43	458
32.47	432
38.65	381
45.05	311
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Series B at 25°	
% $AlCl_3$	V.T.
17.86	1263 mm.
31.82	1087
38.91	945
45.31	776
50.65	578
55.81	323

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[1] Chem. Abs. 16, 3795 (1922).

Results

As a result, the three series of measurements check each other very well up to about 30% of the solute; but for higher concentrations there are greater deviations, particularly in the case of series A; series B and C give very concordant results, when it is remembered that these series involved the use of different methods. It thus seems logical to attach greater confidence to the results obtained in them; hence, the curves are drawn (see Fig. 2) with this in mind, and the vapor tensions given in Table II are taken from these curves, drawn on a large scale. Table I gives the results given by direct experiment.

TABLE II

Vapor Tensions of Phosgene Solutions

% $AlCl_3$	V. T. at 0°	V. T. at 25°
0.0 %	555 mm.	1406 mm.
5.0	540	1372
10.0	525	1335
15.0	508	1293
20.0	490	1243
25.0	462	1180
30.0	430	1107
35.0	394	1015
40.0	354	897
45.0	308	748
50.0	260	551
55.0	crystals	328

Acknowledgment

Thanks are due the Chemical Warfare Service, for the generous supply of phosgene provided for this research.

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NEW BOOKS

General Cytology. *Edited by E. V. Cowdry.* 25×17 *cm, pp.* vii+754. *Chicago: The University of Chicago Press, 1924. Price: $7.75.* This is "a co-operative attempt to state in general terms what is known or conjectured regarding the principles which govern cellular structure and function; or, in other words, to present briefly for the first time within the scope of a single volume data concerning the cell fundamental, alike, to the sciences of botany, zoölogy, physiology, and pathology." After an introduction by Edmund B. Wilson, the individual chapters are: some general aspects of the chemistry of the cells, by Albert P. Mathews; permeability of the cell to diffusing substances, by Merle H. Jacobs; reactivity of the cell, by Ralph S. Lillie; the physical structure of protoplasm as determined by micro-dissertation and injection, by Robert Chambers; mitochondria, Golgi apparatus, and chromidial substance, by Edmund V. Cowdry; behavior of cells in tissue cultures, by Warren H. Lewis and Margaret R. Lewis; fertilization, by Frank R. Lillie and E. E. Just; cellular differentiation, by Edwin G. Conklin; the chromosome theory of heredity, by Clarence E. McClung; Mendelian heredity in relation to cytology by Thomas H. Morgan.

"The word cytology denotes the study of cells, and in its widest sense this study might be said to extend into every branch of biology that is directly concerned with cell phenomena. In practice, however, cytologists have not made for their subject so ambitious a claim. They have commonly employed the word in a much narrower sense to denote the microscopical study of cells with especial reference to their structure and structural transformations. As thus limited cytology, evidently, is nearly related to the older histology, a subject treated as a branch of anatomy dealing with the structure of the tissues, and often designated as microscopical anatomy. Such a restriction of the subject, however, would no longer be possible even were it desirable; for cytology long since outgrew the limits of merely morphological inquiry. In respect to its relation to histology, we are struck by the fact that the earlier investigators of the cell did not clearly distinguish between the two subjects. Cytology first received recognition as a distinct subject when later researches served more and more to focus attention upon the *individual cell considered as an organic unit.* Even now the boundary line between cytology and histology cannot, and need not, be very strictly drawn. It stands for no more than convenient practical usage," p. 3.

"The history of cell research since the promulgation of the cell theory may conveniently be divided into three periods, the first beginning approximately in 1840, the second in 1870, and the third in 1900. The first of these includes the early development of the cell theory and the second that of modern cytology and cellular embryology. In the course of these two periods our general conceptions concerning the mechanism of development and heredity began to take on definite form. The third period, opening with the rediscovery of the Mendelian phenomena of heredity, includes the detailed genetic and cytological analysis of these phenomena; the minute cytological analysis of nucleus and cytosome; and the modern experimental study of cell physiology. These periods are separated by no sharply marked lines of demarcation; they are distinguished merely as a matter of convenience. Without attempting to review them in detail we may briefly indicate a few of the outstanding results which they have brought forth," p. 5.

It is of course impossible to expect all the articles to reach the same high level, and, unfortunately, the weakest one is that on the general chemistry of cells. The following paragraph, p. 28, will make clear the truth of this statement.

"We will begin with the simplest atom, hydrogen. The work of Bohr permits the conclusion that this atom can exist in various states containing different amounts of energy. The energy content differs according to the size of the orbit of the negative electron which is revolving about the central positive nucleus. There are various possible orbits, and when the electron drops from an external to an orbit nearer the nucleus the atom radiates light. The different lines of the spectrum of hydrogen are due to the dropping of the electron from various exterior to more interior orbits. When the electron is in the orbit closest to the center, it has the least energy. The absorption of energy by the atom is accompanied by the electron moving from an interior to an exterior orbit. Now, of these various hydrogen atoms the most stable is of course the commonest; but the least common will be the one with the largest orbit as it is the least stable and most reactive form of hydrogen. In accordance with the suggestion already made, that form with the more energy would be the *anakinetomere;* and that with the less or the least, the *katakinetomere.* The anakinetomere form is the living form; the katakinetomere form is the dead. It is perfectly correct, therefore, from this point of view to speak of living and dead hydrogen atoms. We can even go farther with the simile if we wish and say that when the living highly reactive form of the atom passes to the dead, unreactive form, the soul of the atom escapes at the moment of its death, for a ray of light leaves the dying atom and travels onward in space, until perhaps it encounters and is absorbed by some other dead hydrogen atom, which it again raises to life by thus giving it a soul. What is this soul? It is a minute portion of the luminiferous ether; of time and space; of eternity and infinity."

This sort of speculative metaphysics may be justifiable in a popular article; but it should not have been allowed in a book like this. If anybody thinks that this criticism is too severe, let him read the paragraphs on the living cell as a battery, pp. 68-73.

The next three chapters are naturally the other ones of most interest to the chemist, and he will find much in them which will appeal to him.

"Of all known substances, water is the one which on *a priori* grounds would be expected to show the most universal ability to enter living cells. Over 80 percent of the weight and over 99 percent of the total number of molecules of most active protoplasm are accounted for by this substance, while living cells, with few exceptions, are bathed in an aqueous medium of some sort with which their relation is a most intimate one. The fact that on the average between one and two liters of water enter and leave the human body every day or that, according to Babcock (1912), an annual plant in the production of one pound of dry material requires 200 to 400 pounds of water are indications of the magnitude of the penetration in the aggregate where many cells are concerned.

"Nevertheless, the rapidity with which water enters cells is not so great as is often supposed. In plasmolytic experiments with plant cells, the time required to reach equilibrium is frequently as long as an hour or more, while the swelling and shrinking of many animal cells in anisotonic solutions may be surprisingly slow. The very fact that protoplasm in general is not miscible with water would make it seem unlikely that the interchange of this substance through the surface of the cell should be entirely unimpeded. It appears probable, therefore, that while cells in general are permeable to water, the permeability is a somewhat restricted one.

"In the case of certain cells, at certain times, the permeability to water is practically zero. Thus, *Fundulus* eggs will develop equally well in distilled water, normal sea water, or sea water concentrated to one-half its original volume, showing during many days no evidence of osmotic effects, provided that the external medium is not physiologically unbalanced with respect to its electrolytes (Loeb, 1912). Facts such as these can be accounted for only by the assumption of an impermeability to water, which, however, may be destroyed under certain conditions," p. 130.

"It would be convenient for the physiologist if he could remember as a general principle that Na, etc., increase, and Ca, etc., decrease cell permeability under all circumstances; however, conditions are not so simple as this. For example, Loeb (1922) has recently investigated the effect of various salts on the penetration of *Fundulus* eggs by acids, and has found that the effect of Na is qualitatively similar to, though quantitatively less than, that of Ca and La, all of these ions to varying extents hindering the entrance of the acids. The same ions, however, favor the entrance of alkalies, so it is evident that 'permeability' must not be looked upon as a simple property of the cell membrane which applies to all substances in the same manner," p. 147.

"With so many of the facts regarding the penetration of the cell by diffusing substances still in uncertainty, the time is not yet ripe for attempting a comprehensive theoretical explanation of the process itself. Nevertheless, hypotheses are so necessarily and so inextricably connected with the acquisition of new facts that a review such as the present one would not be complete without some mention of several of the chief theories of cell permeability which have been suggested in the past, together with the brief criticism of some of the deficiencies of each. In general, it may be said that no single theory is entirely satisfactory, as indeed would be expected from the complicated nature of the facts which they attempt to explain. At the same time, there are probably elements of truth in most of them, and if each were regarded by its supporters merely as an attempt to deal with a limited number of the factors concerned in a very complex process rather than as a complete explanation of the behavior of the cell, there would be far less occasion for criticism than actually exists.

"The majority, though not all, of the theories of cell permeability presuppose a plasma membrane of some sort, which exhibits a differential permeability, permitting some substances to enter the cell with ease (alcohol, ether); others with difficulty (most salts, sugars, etc.); and still others not at all (most colloids). Such a membrane was postulated by Pfeffer (1887) to account for his osmotic results, and has been accepted as a matter of course by most subsequent workers. However, there have not been lacking those who have attempted to explain cell behavior in other ways. For example, Moore and Roaf (1907, 1908) and Moore, Roaf, and Webster (1912), as the result of observations on blood corpuscles and on the behavior of various artificial membranes, came to the conclusion that the distribution of salts inside and outside of cells could be explained better by an adsorption hypothesis than by the usual membrane theory. M. Fischer (1915) also, in connection with his studies on oedema, has supported the view that the volume changes which occur when living cells are placed in various solutions are to be considered as cases of colloidal swelling, having nothing to do with semi-permeable membranes, the importance of which in such processes he denies," p. 149.

"The acceleration of chemical reactions by contact with finely divided solid materials (charcoal, platinum, etc.) is well known in inorganic chemistry and constitutes the phenomenon of heterogeneous catalysis. There is every evidence that the structural surfaces in living cells exercise a catalytic influence of the same kind, although other factors (especially electrical factors and factors dependent on specific chemical relationships) also enter and render the conditions more variable and complex than in inorganic systems. There can be no doubt, however, that the high velocity of the more characteristic chemical reactions of protoplasm (e. g., the oxidation of sugars and amino acids) is chiefly determined, directly and indirectly, by the polyphasic structure of the living system. This condition implies the presence of a large surface of contact between the solid or structural elements of the cell system and the aqueous solution, containing the oxidizable compounds, which forms its continuous phase. Warburg's recent investigations on the oxidation of organic compounds under the influence of finely divided animal charcoal show many striking parallels with the protoplasmic oxidations, although the parallelism is not complete, e. g., the rapid oxidation of sugar has not yet been accomplished by this means. Amino acids, however (cystin, leucin, tyrosin), are rapidly oxidized; the same is true of other organic compounds, e. g., oxalic acid and alcohol (Warburg, 1914, 1921). When charcoal is added to a aqueous solution of cystin (the sulphur-containing amino acid of proteins) and shaken with air at room temperature, the oxygen dissappears simultaneously with the cystin, while CO_2, H_2SO_4, and NH_3 are formed; i. e., the cystin is oxidized to the same end products as in the living cell. The rate of oxidation is also closely similar; e. g., a suspension of charcoal containing a solution of cystin (M/500) was found to consume as much oxygen in a given time as an equal weight of mammalian liver (Warburg, 1921, 1922). Charcoal may thus accelerate certain oxidations to the same degree as actively metabolizing living cells. Since amino acids in aqueous solution at neutral reactions are typically stable compounds, the fact that in a heterogeneous system of such simple composition they undergo rapid oxidation is a very clear indication of the important part which surface conditions play in the metabolic reactions of protoplasm. The suspension of charcoal may be regarded as a simple model illustrating the part played by surface conditions in cell metabolism. The resemblance becomes still more striking when the acting of surface-active or narcotizing compounds on these oxidations is studied; small quantities of alcohols, nitriles, amides, and similar compounds retard the oxidations in charcoal suspensions to about the same degree as they retard oxygen consumption in living cells (e. g., blood corpuscles). Another remarkable parallel is that slight traces of iron salts greatly accelerate the catalytic oxidation of amino acids by charcoal, just as they accelerate oxygen consumption in certain animal cells, e. g., sea-urchin eggs. Cyanide, on the other hand, depresses oxidations both in the charcoal system and in living cells (Warburg, 1921, 1922)," p. 174.

"As already mentioned, the presence of thin films with semi-permeable properties can readily be demonstrated in certain regions of the cells, e. g., at the external surface (plasma membranes), or at the surfaces of cell structures, such as nuclei, vacuoles, spheres, or alveoli. The chief, physiologically important, property of these films is their semi-permeability, or resistance to the diffusion of dissolved substances. It is well known that the semi-permeability of the plasma membranes disappears on death; semi-permeability thus appears to be a special feature of the living state; in all dead or dying cells the membranes become permeable to substances to which formerly they were difficultly permeable or impermeable. Conversely all permeability-increasing substances are destructive to living protoplasm (cytolytic substances). There is also evidence that this increase of permeability at death affects not only the most external protoplasmic film or plasma membrane, but also the film structure in the cell interior. The coagulative changes in dying cells, the changes then occurring in the physical consistency and tensile strength, and the phenomena of death rigor are evidence of profound structural changes in the protoplasm. Apparently the intracellular partitions undergo increase of permeability or breakdown at death; this is indicated by the fact that many chemical reactions which are absent or inappreciable during life proceed rapidly in dead cells; examples are the oxidase reactions which cause browning in fruits, potatoes, and leaves, the production of large quantities of acid (like lactic acid), and the hydrolysis of proteins and glycogen in autolysis. All these reactions are promoted by cytolytic substances. The indications are that compounds which during life are kept apart by barriers of some kind become free to interact when the protoplasmic structure alters at death. Apparently the type of structure characteristic of living protoplasm is one by which free diffusion is prevented or restricted," p. 178.

"A single brief mechanical or electrical stimulus may have no apparent effect upon an irritable cell or tissue, while two or more such stimuli in sufficiently rapid succession will stimulate. This is the phenomenon called summation; evidently the effect produced at the end of a succession of subminimal stimuli is an additive one; each member of the series produces some latent effect, but the physiological response does not appear until the end of the series is reached.

"In all summation phenomena the time factor is of primary importance. We have seen that too brief closure of a current of threshold intensity will not excite a nerve or muscle; a succession of two or more such brief currents will also have no effect unless they follow one another by less than a certain interval. This interval is called the "summation interval"; its duration varies for different tissues, and has a definite relation to the characteristic chronaxie, being brief for rapidly reacting tissues and vice-versa (Lucas, 1910). In general the interval is shorter than the minimal duration of the current of threshold intensity," p. 199.

"It is impossible to give all the quotations which the reviewer would like to from the chapter on the physical structure of protoplasm; but there are some which cannot be omitted.

"Bütschli, from 1876, had always maintained that protoplasm obeys the fundamental laws of a fluid mass. He experimented with oil emulsions and became convinced (1892) that protoplasm possesses an alveolar or foam structure similar to that seen in artificially produced oil lather. He attributed the lack of visible structure in hyaline protoplasm to the extreme attenuation of its alveolar walls.

"Although, from a purely observational point of view, Bütschli's theory stands on no firmer basis than Altmann's granular theory (e. g., granules in hyaline protoplasm may be invisible in the same way as colorless glass beads in oil), it has been the more generally accepted because of its close analogy to our present conceptions regarding the structure of hydrophilic colloids. The great service rendered by Bütschli is in his having firmly established the fact that protoplasm is essentially a fluid.

"By the application of newer methods we have since learned that the alveolar structure observed by Bütschli is due, in most cases, to microscopically gross inclusions which may be eliminated without affecting the viability of the protoplasmic matrix. The microscope thus far has revealed no structure within this matrix—its colloidal nature is indicated not so much by its appearance, as by its behavior. On the other hand, protoplasm is a cellular unit which cannot exist without its nucleus and its cortex and, therefore, must be regarded not as a 'stuff' but as a mechanism consisting of visibly differentiated and essentially interrelated parts," p. 238.

"In order to obtain anything like a correct notion of what protoplasm is, we must realize that it exists only within the confines of a cell. In plants the cell is usually separated from its neighbors by a rigid wall of cellulose. On the other hand, animal cells are not as a rule confined within rigid walls. This allows them in most cases to be packed together more closely than is possible in plant cells. It is, however, wrong to consider the typical animal cell as actually naked. If it does not possess an extraneous membrane of some kind, it is usually surrounded by a cement-like substance which may serve to hold contiguous cells together. It is a question whether protoplasmic bridges between contiguous cells, a feature well known in plants, are common in animals," p. 241.

"It is extremely difficult if not impossible to speak at present of the viscosity of protoplasm except in relative terms. Owing to the microscopic dimensions in which protoplasm exists we have as yet no means of securing any absolute value of its viscosity. Seifriz (1920) has made some conjectural analogies by comparing the viscosity of the interior of a sea-urchin egg to glycerine and that of the cortex to bread dough," p. 246.

"An extraordinary feature of protoplasm is the fact that, although it consists largely of substances which are soluble or are suspended in water, nevertheless it maintains itself perfectly within an aqueous environment. The question is whether its maintenance depends upon the existence of a differentiated surface or whether protoplasm may be regarded as a substance whose essential properties exist throughout its entire mass," p. 251.

"The readiness with which surface films in protoplasm can be formed only to disappear again by fusion of the protoplasm is strikingly shown in the plasmodium of the Myxomycetes, *Badhamia*, which can flow through wet cotton wool. Lister (1888) used this method to filter out the contained spores in order to obtain clear protoplasm. Indeed, the plasmodium normally creeps through and permeates rotting wood, coming to the surface only just prior to sporulation. In order to obtain a proper conception of the nature of a true protoplasmic film, one must realize that the protoplasm of most cells also possesses a more or less solid cortex of an appreciable thickness. In addition to this, many cells are either completely or partially invested in extraneous membranes or pellicles which are probably products of secretion or precipitation (cf. Seifriz, 1921)," p. 252.

"The results of micro-dissection prove the presence of a viscid cortical layer in the unfertilized mature eggs of some echinoderms, especially the starfish. The extraneous egg membrane must first be removed. The cortex may then be seized with a micro-needle and pulled out into long strands which, on being released, slowly draw back into the egg. If the cortex be torn through and the egg brought under compression the more fluid interior flows out, on the surface of which a film quickly appears. This new surface is more fluid than the original cortex, for a strand pulled out from it will rapidly flow back when released. In the echinoderm egg there is no visible difference between the cortex and the interior. In an egg which has been torn, one also cannot distinguish the new surface from the original cortex except by their reactions to the needle," p. 255.

"The film which forms on the surface of protoplasm cannot be considered as being strictly analogous to an interfacial film. The facts that a time factor is involved in its production, that it protects the underlying cytoplasm from disintegration, that its durability depends not only upon the environing medium but also upon the specific constitution of the protoplasm from which it forms, and, finally, its semi-permeable properties, all point to its being a definite organized structure.

"The protoplasmic film is in all probability a combination of both passive and chemicophysically active parts. The passive part may be composed of certain cell constituents both organized and unorganized which collect on the surface and which may give to it an appreciable thickness. We must distinguish from this an active film whose instability is such that it can be maintained only in the presence of the passive part," p. 261.

Chambers sums up his results on injection experiments, p. 264, as follows:—

"1. Aqueous solutions can be injected into the protoplasm of the amoeba and the echinoderm egg without producing an interfacial film between the injected liquid and the protoplasm.

"2. The oils injected (olive oil, paraffin oil, sperm oil, starfish oil, chloroform, xylene) immediately round up into drops.

"3. Chlorides of basic dyes coagulate whereas the salts of acid dyes liquefy protoplasm, an effect probably attributable to free acid and free base.

"4. Dyes which do not penetrate the living amoeba from outside (e. g., eosin) rapidly diffuse through the cytoplasm when injected.

"5. The injection of aqueous solutions into the cytoplasm of echinoderm eggs is apt to cause a disintegration of the cytoplasm whereupon a protoplasmic film forms and converts the disintegrated area into a vacuole.

"From these results we may conclude that the internal protoplasm is freely permeable to water whereas it is not to the oils which have been injected. It is also shown that the protoplasmic surface film possesses porperties of impermeability which the protoplasm within the film does not possess."

These quotations will give some idea of the importance of this book to chemists. It is obvious that the volume is of even greater interest to those for whom it was written, the botanists, zoölogists, physiologists, and pathologists. A special feature of the book is the extensive bibliography at the end of each chapter.

Wilder D. Bancroft

Introduction to Organic Research. *By E. Emmet Reid. 23×16 cm; pp. viii+343. New York: D. Van Nostrand Company, 1924. Price: $5.00.* In the preface the author says that "research as a vocation, or even as an avocation, offers alluring joys to the individual as well as benefits to the race. This book is put forth with the hope of assisting those beginning research and of aiding some now not engaged in it to take it up. In its preparation free use has been made of the publications of many, and not a few distinguished chemists have honored it with specially prepared contributions."

The chapters are entitled: on research, concerning researchers; incentives to research; problems; chemical literature; secondary publications; libraries; literature searches; patent searches (by W. W. Ammen); study of known compounds; preparation of known substances; preparation of new compounds; synthesis of new medicinals (by A. D. Hirschfelder); study of structure; study of reactions (by F. O. Rice); organic analysis (including identification of organic compounds and quantitative analysis of mixtures of organic compounds by Louis E. Wise); plant processes (by C. M. Stine); writing up results.

"Some place poets and scientists far apart, crediting the poet with a wonderful imagination and the scientist with none at all. Of the two, the poet can get along with less imagination, or at least with a less definite one. The architect builds his cathedral first in his imagination and must see the bridge spanning the river before the blue prints are made. Chemists must see things that are doubly invisible, for cathedrals and bridges are constructed of stone and girders that we can see and the structures are visible to anyone after they materialize while the molecules with which the chemist conjures are invisible structures built of invisible materials and are just as invisible after they are realized as before. The chemist requires a super-imagination. Dalton owed his atomic theory to a vivid and materialistic imagination that insisted in seeing atoms singly and in pairs, trios and quartets, combining with each other and changing places. While Kekulé "nodded, nearly napping" he visioned the carbon atoms linked in chains till one of these turned serpent, swallowed his tail and rolled off as a ring. This dream did more for the science of chemistry than the labor of scores of men.

"The imagination can be used to great advantage in materializing the properties of substances so that we may see the relationships between them to the end that our mathematical calculations represent realities and are not simply juggling with symbols," p. 16.

"Life in the great world outside the laboratory is in verity research, new situations and unsolved problems await one every morning and follow one home at dusk, so of all parts of one's training, research is that which best fits one for the life into which one is to plunge on graduation. It has often been noted that many who win all honors in examinations during their college course sink into oblivion soon after, while their less brilliant classmates forge steadily ahead and ultimately reach high positions. High examination grades may frequently be made by a retentive memory and judicious cramming, with little actual grasp of the subject. Independence of thought and self reliance in the face of unforeseen difficulties, resourcefulness in surmounting obstacles, and perseverance when things look most hopeless are qualities that make for success alike in research and in one's subsequent work.

"It does not follow that one who does well in research will make money in business: it is frequently quite the reverse, since one who concentrates his whole attention on the scientific side of a problem may fail to see the practical side. The mistake is, however, not in the research method but in the failure to apply research to the practical as well as to the scientific part of the problems," p. 43.

"If old age begins when the crest is passed, when the mind ceases to expand and produce, then it is within the power of every man to postpone old age, perhaps not indefinitely since the tissues of our bodies and our brain cells do get old in time and cease to function, but at least till he is well stricken in years. . . . A teacher is prone to settle down into a rut and start to grow old long before the age set for his retirement. To one so circumstanced, the means of staving off old age, of keeping alive, is the finding of some interest, some endeavor, into which energy and effort can be put, to the quickening of the intellectual pulse. Research supplies this need better than almost anything else and keeps one thinking, working and growing, thus maintaining the upward slope of the curves; the publication of the results of the research is tangible evidence to the world that life is not extinct. Would that all teachers were like Nef and Emil Fischer, from whose laboratories papers appeared regularly right to the end—some being published after the obituaries!", p. 44.

"Finding a problem is a serious difficulty to many, and all the more troublesome because it is imaginary. It is a difficulty until one gets started and then the trouble is how to dodge problems, they come from the east and from the west, from within and from without, they come in droves like the locusts came to afflict Pharaoh, they disturb one's reveries in church, pop into one's head during one's bath, they start every page one reads and even one's dreams. The thing is to get started on some piece of research—then every experiment performed suggests two more, and each of these, two more and so on: they multiply like flies, but the multiplication process does not start till one begins to work. One who begins to work and think will never lack for something on which to work and think, the only difficulty is in getting the first "think". The process is auto-catalytic, the products of the reaction accelerating it," p. 51.

This is a very interesting book and can be read with profit by everybody. The reviewer would have liked to see a whole chapter on the methods of research; but that happens to be his private hobby. *Wilder D. Bancroft*

The Fitness of the Environment. *By Lawrence J. Henderson. 20×14 cm; pp. xv+317. New York: The Macmillan Company, 1924. Price: $2.00.* So far as the reviewer can judge from a superficial examination, this is the same book that was reviewed over eleven years ago (17, 707), except for the 1924 date on the title-page. How far this is ethical is a matter which the publishers have evidently decided for themselves. As the book itself is a good one, it is rather a pity that the publishers should have done this thing. The author, of course, is not to blame. *Wilder D. Bancroft*

SORPTION OF AMMONIA AND CARBON DIOXIDE BY GLASS

Time and Pressure Relationships

BY D. H. BANGHAM AND F. P. BURT

In a previous paper[1] we have described an apparatus for measuring the rate of sorption of carbon dioxide by a known surface of glass wool under approximately constant pressure conditions at a temperature of 0°C.

It was *found that the sorption-value* (*s*) *was related to the time* (*t*) by the equation $S^m = kt$, where *m* is a number varying from 10 at low pressures to 14 at pressures approaching atmospheric. Although the sorption-values exhibited by carbon dioxide were relatively small, the fall of pressure in the sorption-vessel, due to removal of gas, introduced serious complications when the initial pressure was low. Experiments with ammonia, yielding sorption-values some five times greater than for carbon dioxide under similar conditions, indicated the necessity of devising some means of correcting the results to constant-pressure conditions, as an alternative to designing a constant-pressure apparatus.

The present communication, while presenting further data obtained with our original apparatus, deals in the main with an attempt to solve this problem by expressing the sorption as a function of a variable involving both pressure and time.

The Sorption Apparatus

The apparatus described in the previous paper consisted essentially of a gas pipette A connected by a tap to a sorption-vessel B: A and B were calibrated and provided with manometers so that their gas-content could be determined. The system was kept at 0°C. After measurement of an initial quantity of gas in A the tap between A and B was opened for a few seconds and the disappearance of gas in the sorption-vessel noted at different intervals. By reversal of the operations just described it was possible at the end of any sorption experiment to examine the gas-content of the glass wool as the pressure was reduced in successive stages. Sufficiently long intervals were allowed to elapse between each pressure-reduction to enable the time-effects to be examined. For sorption experiments at pressures greater than half an atmosphere a special device was adopted whereby the whole of the gas in A was transferred to B. In such experiments, however, the admission of gas to the sorbent occupied an appreciable time[2] (some minutes).

At the end of each experiment the glass wool was out-gassed by heating for several hours at a constant temperature in the neighbourhood of 200°C. As the gases examined were readily condensible and carefuly freed from permanent gas a high vacuum was achieved during this process by immersing a

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[1] Proc. Roy. Soc. 105 A, 481 (1924).

[2] Proc. Roy. Soc. 105 A, 482 (1924).

portion of the system in liquid air. As already discussed in the previous paper this treatment was successful in recovering quantitatively the activity of the glass towards carbon dioxide. It was also successful in the case of all other gases examined with the single exception of sulphur dioxide.

Experiments with Ammonia

In actual chronological order these experiments preceded those with carbon dioxide.

Ammonia was prepared from a very pure specimen of ammonium chloride made at Messrs Brunner Mond's works at Winnington. The gas evolved on decomposing this salt with aqueous caustic potash was partially dried by passage over quick-lime and then solidified at liquid air temperature. After removal of permanent gas by the mercury pump the solid was allowed to melt and the first fractions passed over potash and phosphoric oxide. The highly desiccated gas obtained in this way was again solidified and freed from the last traces of permanent gas. A middle fraction of the ammonia so purified was introduced into an exhausted storage-bulb. The melting-pressure of this ammonia was 45.6 mm.

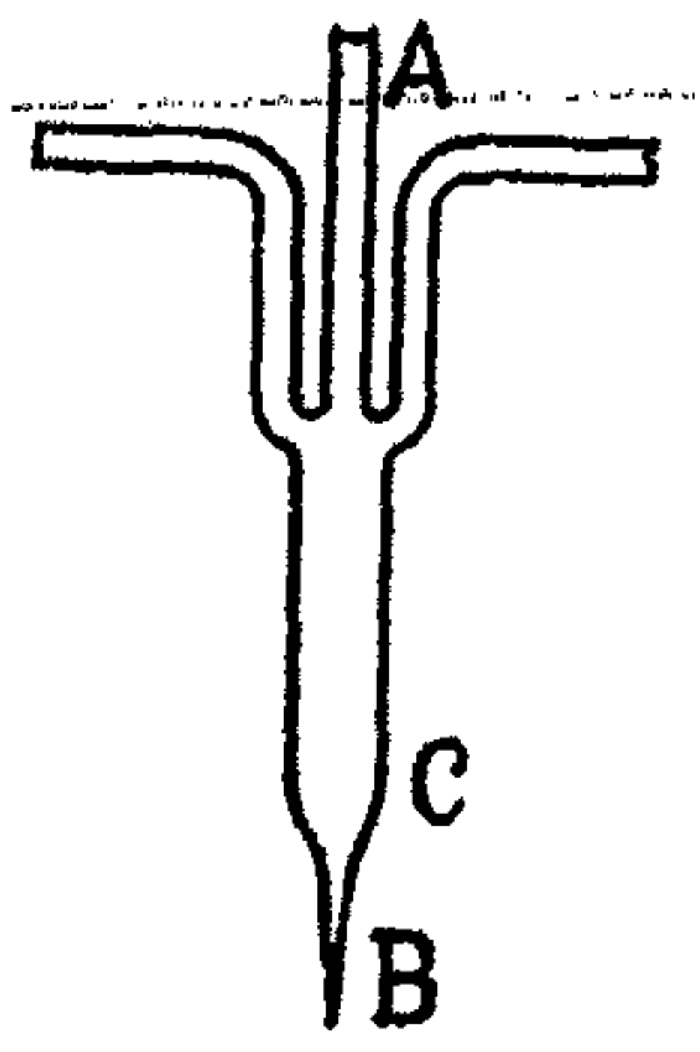

FIG. 1

Before being admitted to the measuring pipette of the sorption apparatus the gas from the storage-bulb was condensed in a small tube which formed part of the fractionating train. Into this tube (illustrated in Fig. I) phosphoric oxide had been distilled in a stream of oxygen. The oxygen entered by the centre tube A and escaped by the capillary tube B at the bottom, the accompanying pentoxide being retained by a plug of glass wool at C. The tubes A and B were sealed off when sufficient pentoxide had been collected. The liquefied gas, therefore, was brought into intimate contact with finely divided pentoxide and, since liquid phase always remained after charging the pipette, we believe that very efficient desiccation of the ammonia was achieved.

A sorption experiment with ammonia was carried out at an initial pressure of 360 mm. and continued for a period of 35 days. At the end of this time the rate of sorption, though small was still detectable. Table I gives the reduced pressures and sorption-values observed at different times.

In Fig. 2 the results are represented by plotting log s against log t, where s is the sorption-value at time t. It will be noticed that the graph remains linear up to $t = 400$ mins., but thereafter becomes concave to the log t axis. The value of m in the equation $s^m = kt$ is 12.8. Too much weight cannot be attached to the exact form of the latter part of this graph; not only had the pressure fallen very considerably below its initial value but, owing to a slight melting of the ice near the top of the wool tube that was occasionally noticed, the temperature of this part of the system may have risen temporarily

TABLE I

Time (mins)	s (cc.@ N.T.P)	p_0 (mm.of Hg)	Time (mins)	s (cc@N.T.P)	p_0 (mmof Hg)	Time (days)	s (cc.@ N.T.P)	p_0 (mm.of Hg)
2	6.552	360.33	70	8.700	340.33	1.05	10.949	318.85
4	6.976	356.42	75	8.746	339.91	1.13	11.011	318.27
6	7.195	354.39	80	8.786	339.50	4.04	12.031	309.76
8	7.350	352.92	85	8.832	339.07	4.12	12.062	309.33
11	7.501	351.52	90	8.879	338.63	4.94	12.187	308.20
12	7.584	350.73	95	8.911	338.32	5.14	12.213	307.56
14	7.670	349.98	100	8.938	338.07	7.07	12.328	306.47
16	7.767	349.04	110	9.007	337.45	8.11	12.388	306.35
18	7.840	348.38	125	9.104	336.51	9.13	12.441	306.00
20	7.885	347.97	135	9.158	336.00	12.10	12.519	304.85
22	7.938	347.47	145	9.213	335.50	14.10	12.585	304.41
26	8.044	346.47	155	9.270	335.00	15.15	12.604	304.26
28	8.097	345.98	165	9.308	334.60	16.13	12.624	303.08
32	8.181	345.19	204	9.461	333.07	17.18	12.644	302.69
36	8.261	344.43	212	9.486	332.87	18.05	12.675	302.50
38	8.288	344.18	220	9.519	332.55	18.96	12.678	303.57
40	8.327	343.86	240	9.579	331.98	21.10	12.705	303.11
46	8.415	343.04	322	9.802	329.84	22.04	12.710	303.12
49	8.458	342.65	330	9.821	329.66	24.03	12.732	302.92
55	8.539	341.88	335	9.831	329.57	28.11	12.765	302.45
59	8.581	341.47	364	9.886	329.05	34.99	12.786	302.32
65	8.651	340.82	367	9.891	329.02			

a few degrees above zero. In the light of independent evidence, however, there is little reason to doubt that a similar departure from the linear would have been observed under ideal conditions.

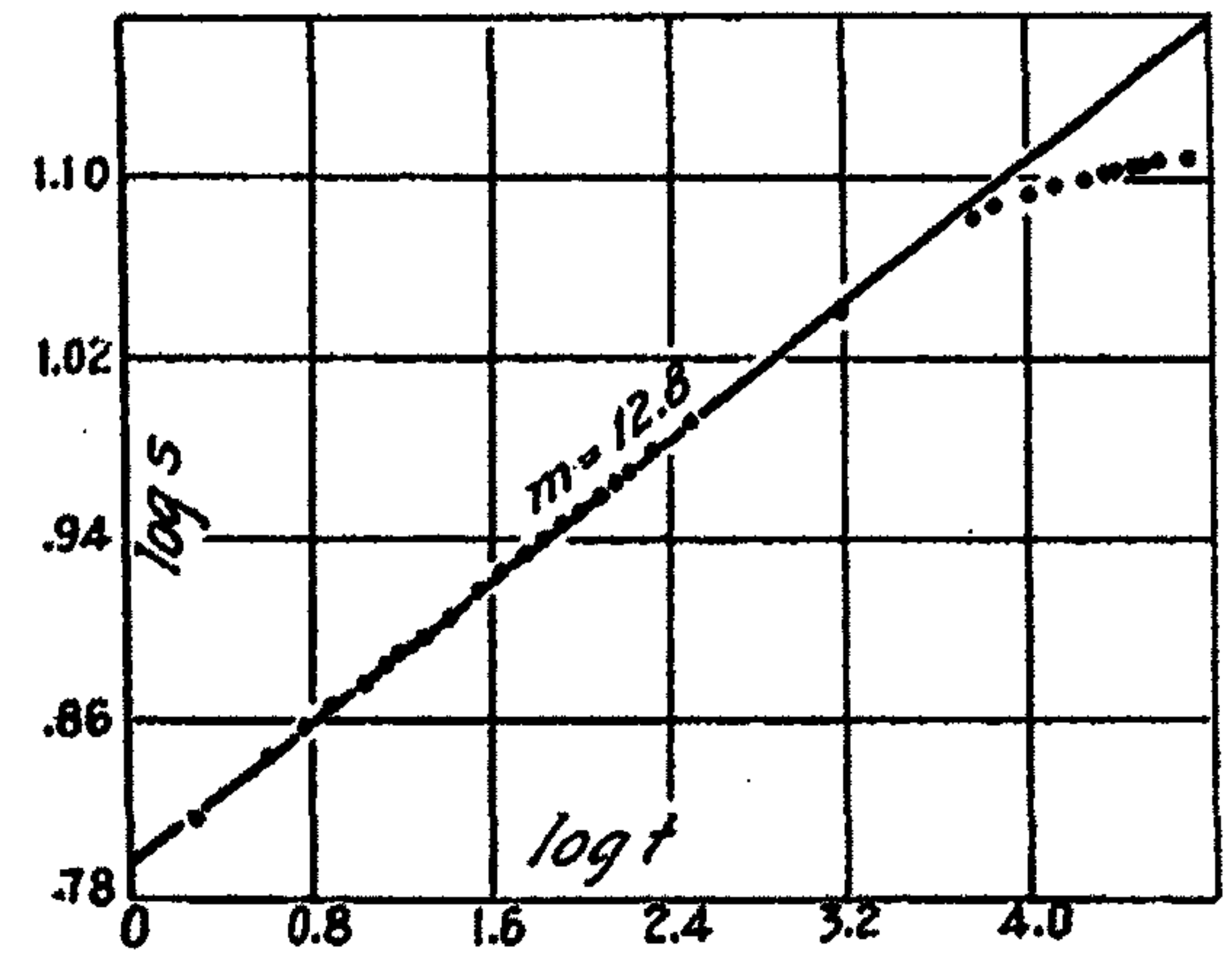

FIG. 2

Desorption

The sorption run was extended for the long period of five weeks in the hope that the change of sorption with pressure could afterwards be examined under equilibrium conditions. It is clear from the foregoing that this was not actually realized, but on the thirty-fifth day, the rate of sorption, though still detectable, was so far reduced that it could be neglected without involving serious error. The procedure consisted in repeatedly distributing the gas in the wool tube to the evacuated gas-pipette. The pressure was thus in the course of some hours reduced to about 5 mm. Fig. 3 shows the course of the desorption process as carried out. Both the sorption-value (s) and the pressure (p) are shown plotted against the time, the zero of time coinciding with the moment of the first distribution. The graphs indicate that an instantaneous or very rapid evolution of gas accompanied each fall of pressure, and was followed by a slow further desorption. The evolution of gas was in no case complete when the next step was made, and this is indicated by the course of the extrapolation of each line beyond the experimental region. The desorption at each stage is thus a composite quantity representing the cumulative effect of the pressure history. In order to elucidate any relationships existing between *s* and *p* it seemed best to select for comparison values corresponding to equal times after each distribution; and further, to isolate the specific effect due to each individual fall of pressure from the surviving effects on which it was superimposed.

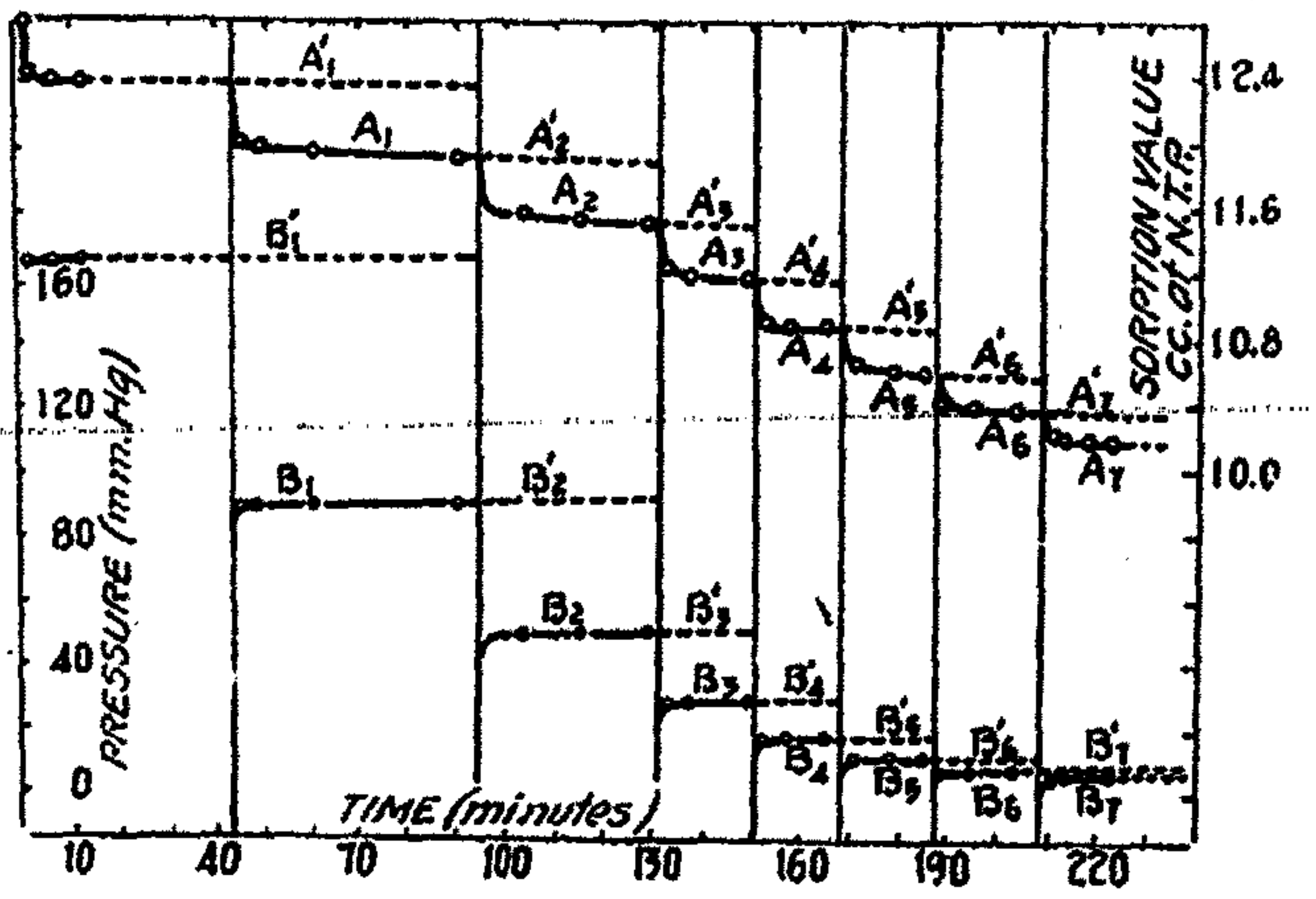

Fig. 3

In the following table (Table II) the logarithms of the 2- and 10-minute values of *s* and *p* as read (in the latter case) from the graph at A_1, A_2, A_3 . . . and B_1, B_2, B_3, . . . are shown in comparison with those of the corresponding values of s′ and p′, taken from the overlying extrapolated sections of the graph at A'_1, A'_2, A'_3 . . . and B'_1, B'_2, B'_3 . . . The vertical lines across the diagram indicate the times at which the successive pressure reductions were made.

The constancy of the quotient $\Delta \log p/\Delta \log s$ (which is the index of *s* in the Freundlich equation $s^n/p = \text{constant}$) implies the validity of this expression over the range of *s* covered by the experiment. Although this range was small the agreement is surprising in view of the wide departure from equilibrium conditions. On account of the difficulty of obtaining accurate early readings it was to be expected that the deviations would be greater in the 2-minute table; but, even here, the two most discrepant values are those in-

TABLE II

	log s′	log s	log p′	log p	n*
		t = 2 mins.			
1st distribution	1.1067	1.0945	2.479	2.219	21.3
2nd ”	1.0931	1.0799	2.220	1.951	20.4
3rd ”	1.0766	1.0661	1.957	1.687	25.7
4th ”	1.0615	1.0510	1.699	1.446	24.1
5th ”	1.0484	1.0380	1.459	1.230	22.1
6th ”	1.0364	1.0276	1.243	1.023	25.0
7th ”	1.0249	1.0170	1.059	1.875	23.3
8th ”	1.0154	1.0090	0.903	0.740	25.4
		t = 10 mins.			
1st distribution	1.1067	1.0938	2.479	2.220	20.1
2nd ”	1.0930	1.0788	2.220	1.952	18.9
3rd ”	1.0763	1.0634	1.957	1.693	20.3
4th ”	1.0611	1.0489	1.701	1.455	20.2
5th ”	1.0481	1.0367	1.462	1.236	19.8
6th ”	1.0361	1.0256	1.248	1.049	19.0
7th ”	1.0244	1.0162	1.061	0.892	20.6
8th ”	1.0149	1.0079	0.908	0.778	18.7

$$^{*}\mathrm{n} = \frac{\Delta \log \mathrm{p}}{\Delta \log \mathrm{s}} = \frac{\log \mathrm{p}' - \log \mathrm{p}}{\log \mathrm{s}' - \log \mathrm{s}}$$

volving the most serious extrapolations. It is further evident that *n* is a decreasing function of the time, tending towards a final lower limit. In attempting to arrive at this value we extended the observations after the eighth distribution for a period of two days at the end of which the rate of desorption was barely detectable. The final values of log s and log p were:—

$\log s = 0.9919 \qquad \log p = 1.029$

and these, taken in conjunction with the initial values

$\log s = 1.1067 \qquad \log p = 2.479$

lead to the value $n = 12.6$, which is remarkably close to the constant of the time equation for the sorption process, viz: $m = 12.8$.

Other Sorption Experiments with Ammonia

As a first attempt to interpret the empirical time equation and at the same time to introduce the pressure as a variable, the assumption was made that a controlling influence in the sorption process was the number of molecular impacts received by the wool. Under constant pressure this number would be proportional to the product pt, and under varying pressure to $\int p.dt$ which could be evaluated from our data.[1] This idea proved of great service

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[1] The use of this integral expression enabled us to evade the difficulty of assigning a time origin to the high pressure experiments, in which the gas was introduced to the wool by the necessarily slow process of evaporation. During this process frequent observations of pressure and time were made and the value of $\int p.dt$ determined by a graphical method.

since it enabled us to impose conditions resulting in a much wider variation in the sorption than would have otherwise have been possible. While we have found it convenient to apply the same treatment to the data for other gases it should be remarked that the results leave it an open question whether the above kinetic assumption is entirely justifiable.

Three further experiments were carried out at initial pressures of 16, 20, and 600 mm. respectively. As a result of these experiments the following regularities became apparent:—

(1) log s plotted against log $\int p.dt$ yielded in each case lines which were initially straight and parallel, with slopes leading to values of *m* not very different from 12.

(2) The Freundlich expression when applied to *s*, *p* values for times equidistant from the beginning of each experiment led to a value of about 6 for the index constant.

(3) The Freundlich expression when applied to *s*, *p* values for times corresponding to equal values of $\int p.dt$ led to a value of about 12 for the index constant.

(4) For equal values of the product $p_t \int_0^t p.dt$, where p_t represents the momentary pressure, the value of *s* was found constant.

These four relationships are summarised in the equation $\frac{s^m}{p_t} = k \int_0^t p.dt$, where the value of *m* is about 12.

This equation implied:—

(1) That in experiments carried out at constant pressure the values of log s and log t would be related by a linear equation. The effect of the falling pressure would be twofold, and while the device of plotting log $\int p.dt$ in place of log t would eliminate one cause of deviation, that due to desorption known to accompany fall in the value of the momentary pressure, p_t, would still remain.

(2) That if a number of sorption experiments were carried out at different constant pressures, then for equal times $s^{2/m}$ should be directly proportional to those pressures.

(3) That the equation $s^n/p = \text{constant}$ ($n = 12$ approx.) found to hold in the desorption experiment described, was a necessary consequence of the absence of any further significant increase in the value of $\int p.dt$ while desorption was proceeding.

(4) That if the values of log s from all four sorption experiments were collected and plotted against (log p_t + log $\int_0^t p.dt$), a single straight line should result.

Fig. 4 shows how nearly this last requirement is fulfilled. To avoid confusion only typical points from each experiment are shown, these being indicated by different symbols for each of the four series; but in actual fact (neglecting the latter part of the half atmosphere experiment) every single one of the 140 observations taken yields a point lying between the boundary lines drawn. The ranges of time and pressure covered in these experiments are given in the following table which is arranged in the order of decreasing pressures.

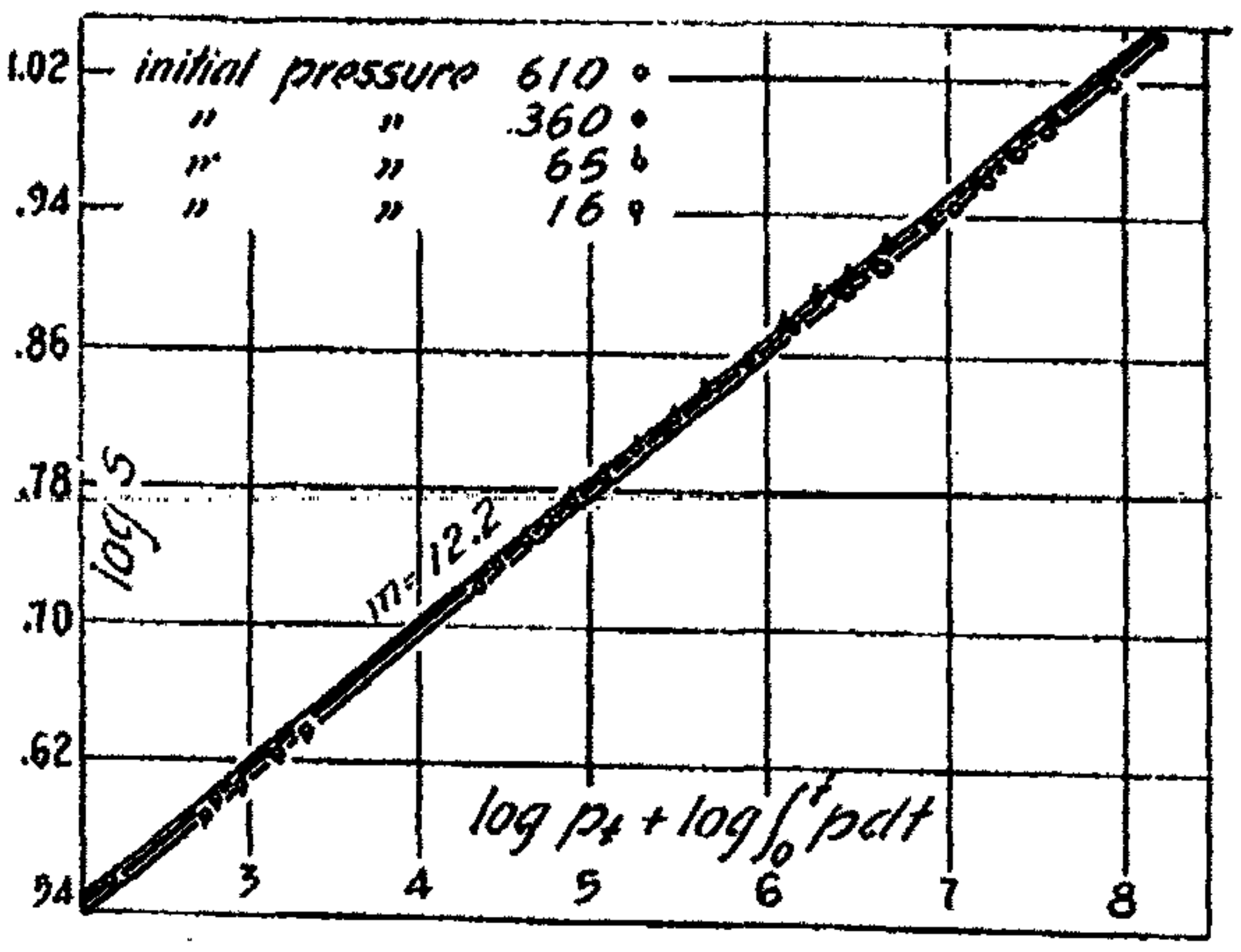

Fig. 4

TABLE III

Experiment		Pressure (mm. of Hg)	Time (mins)
1 (25 Jan. 1922)	initial	610.45	3.5
	final	588.20	236.5
2 (25 Nov. 1921)	initial	360.33	2.0
	final	318.27	1627
3 (10 Jan. 1922)	initial	64.97	4.0
	final	25.92	5760
4 (20 Feb. 1922)	initial	16.25	0.5
	final	5.47	57

While the points referring to each separate experiment are in better alignment than the series considered as a whole, the deviations are throughout small enough to warrant the conclusion that the initial condition of the wool was closely comparable in the four cases[1].

In order to apply still more crucial tests to the general applicability of the equation $\frac{s^m}{p_t} = k\int_0^t p.dt$, the form of which was somewhat surprising, two experiments were carried out in which the pressure was varied discontinuously.

(1) A sorption experiment was continued for an hour with an initial pressure of about 600 mm.; by distribution to the evacuated pipette the pressure was then suddenly reduced to 337 mm. and further readings taken.

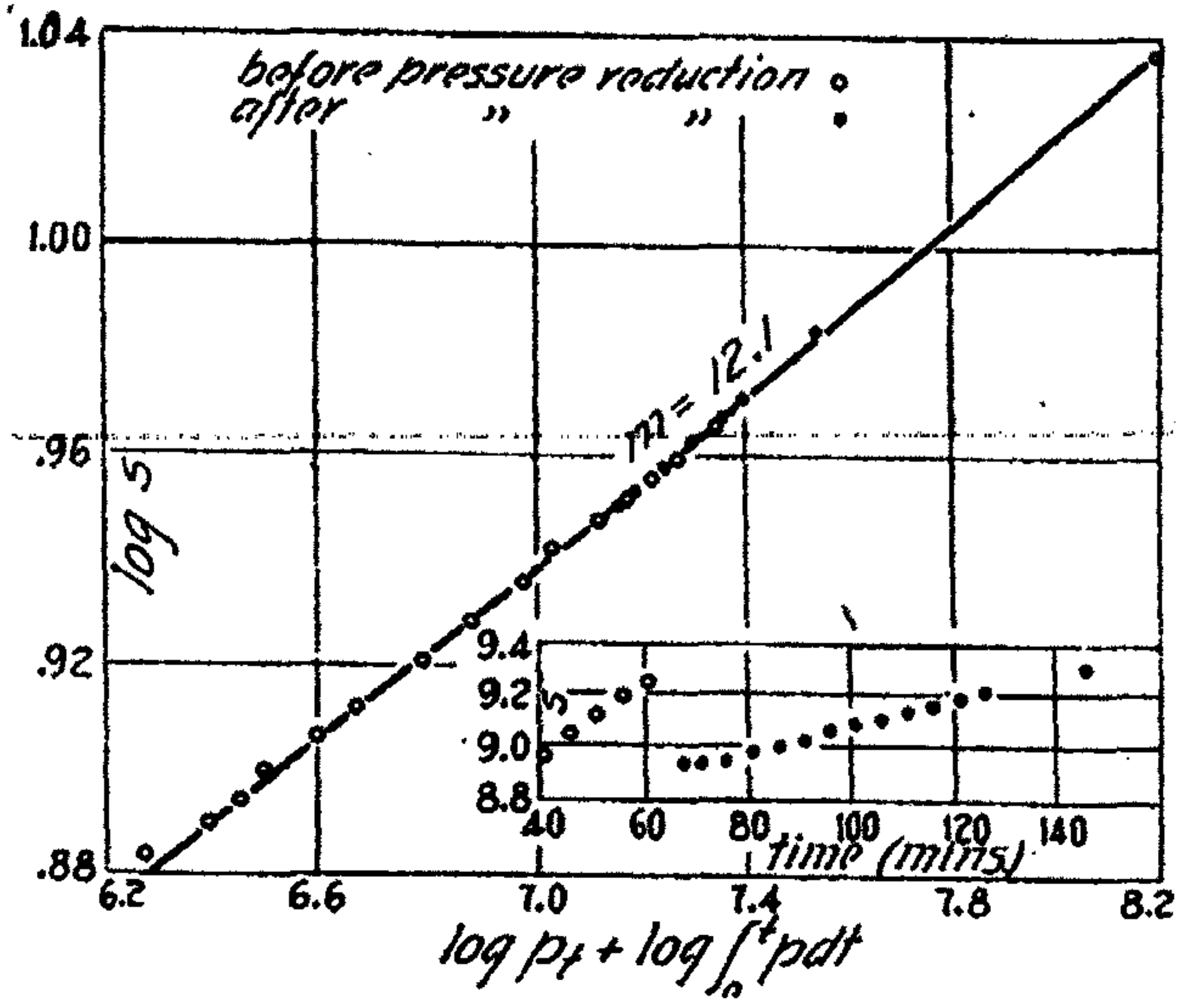

FIG. 5

Fig. 5 shows log s plotted against (log p_t+log $\int_0^t$ p.dt) and brings out clearly the linear relationship. Inset is shown a section of the *s*, *t* graph. It may be observed that disengagement of gas accompanied the reduction of pressure and a minimum value of *s* was reached about 7½ minutes later. The conditions of this experiment find a close parallel in the hydrogen-charcoal experiment of McBain[2], in which a sudden reduction of pressure was accompanied by desorption followed in turn by renewed sorption. Both experiments indicate conclusively that the rate of sorption cannot be expressed in terms of *s* and *p* only, but must involve a further variable. The expression $\frac{s^m}{p_t} = k\int_0^t p.dt$, while sufficiently elastic to provide for the attainment of a minimum value of *s* at the moment the pressure is suddenly lowered, fails to account for the finite time occupied by desorption: thus early points after lowering the pressure fall above the line. The value of *m* deduced from the graph is 12.1.

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[1] If, in place of a linear graph, a curve of very large radius (concave to the abscissa axis) is postulated, slightly better agreement with the experimental results is obtained. Such curvature over the range correct by any individual experiment would be quite undetectable.

[2] Z. physik. Chem. 68, 482 (1910).

(2) A sorption experiment at a very low pressure was continued for about an hour when the pressure was suddenly raised from 5.5 mm. to 346 mm.: after a further 79 minutes the pressure was increased again to 515 mm. and 13 minutes later was suddenly reduced to 82 mm. by immersing a part of the system in liquid air. Frequent observations were taken throughout and extended until the following day. While the large number of operations involved in this experiment made it difficult to attain a high degree of precision, it is clear from the graph (Fig. 6) that here again the values of s throughout correspond closely to the demands of the formula. A straight line drawn through the points has a slope very much the same as that of the lines in Figs. 4 and 5., the value of *m* being 12.1. The same figure shows inset the last portion of the graph considerably magnified so as to indicate more clearly the individual observations taken after the sudden lowering of the pressure. The passage of *s* through its minimum value is much more clearly defined than in the previous experiment and is further illustrated in the following table.

TABLE IV

Time (reckoned from moment of lowering pressure) –	s c.c. @ N.T.P.	log s	log $(Pt \int_0^t p.dt)$ (reckoned from beginning of exp.)
2.83	8.058	0.9062	6.507
5.0	8.015	0.9039	6.509
7.5	7.987	0.9024	6.512
18.5	7.942	0.8999	6.525
42.5	7.943	0.9000	6.546
71.5	7.984	0.9022	6.567
76.5	7.993	0.9027	6.571
150.5	8.082	0.9075	6.620
154.5	8.090	0.9079	6.623
1365	8.825	0.9457	7.022

While the integral term necessarily increases throughout this period, it will be noticed that after the pressure reduction the increase per minute is so small (very much smaller, in fact, than the previous experiment) that the points in this neighbourhood suggest the temporary derangement of a steady state and not the final breakdown of the relationship.

Experiments with Carbon Dioxide

The paper already referred to contained the results of ten sorption experiments carried out at a series of nearly constant pressures ranging from 6 mm. to 655 mm. A desorption experiment with this gas was also described, in which, however, considerably longer and approximately equal times (24 hours) were allowed to elapse between the successive pressure reductions. Under these conditions the quantities of gas remaining fixed at the end of each step were found to be related to the corresponding pressures by the Freundlich equation $s^n = k'p$, n having the value 4.2.

Although, qualitatively, the behavior of this gas suggested close analogy with that of ammonia, two complicating features presented themselves.

(1) A conspicuous variation of the index m. Since this index assumed larger values at higher pressures, the variation could not be attributed to the fall of pressure accompanying sorption, because this fall of pressure, being relatively greater in the low pressure experiments, would have tended to depress the later sorption values in such cases.

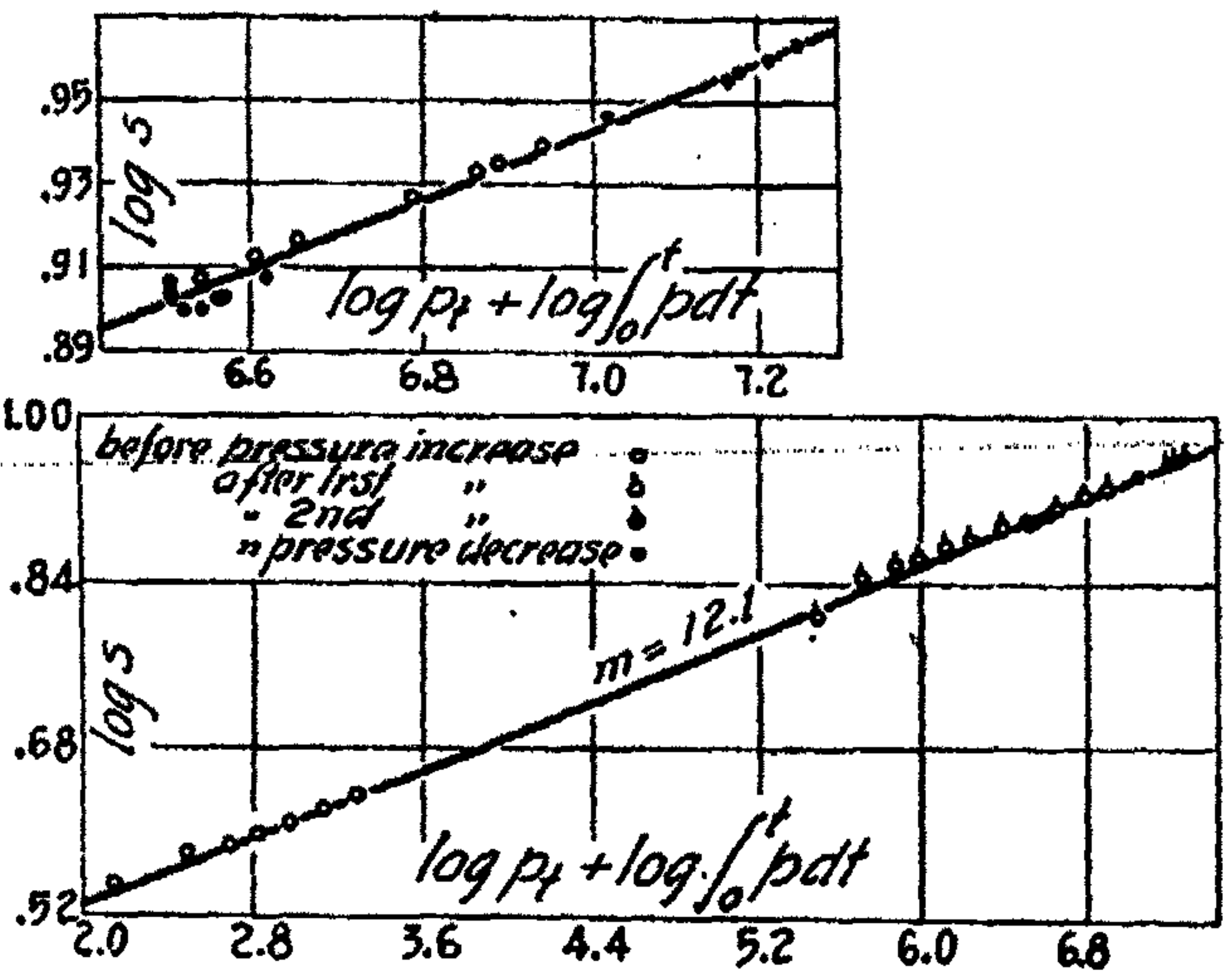

FIG. 6

(2) Values of s for equal times, taken from the ten sorption experiments, were not related, even approximately, to the corresponding pressures by the Freundlich equation.

The graphs obtained by plotting log s against log p_t, (where p_t is the momentary pressure at time t) for $t = 1$ minute and $t = 3000$ minutes, are represented in Fig. 7 by black circles and heavy lines. For purposes of comparison the desorption line obtained after sorbing for 3000 minutes at about ½ atmosphere pressure is also depicted. The marked divergence between this line and the sorption curve for 3000 minutes emphasizes the reluctance of the sorption to assume a value dependent only on the pressure and independent of the past history. Thus after 3000 minutes the rate of sorption is extremely slow, while the rate of desorption is barely detectable 24 hours after the pressure reduction has been made. From the above considerations it will be clear that the pressure-sorption curve for 3000 minutes is subject to systematic error which, though negligible at the high pressure end, is considerable for lower pressures where the pressure-fall is relatively great. A comparison of the straight desorption line with the sorption curve for 3000 minutes clearly indicates that an experiment which starts at a higher and ends at a lower pressure will lead (other things being equal) to larger sorption values than one carried on throughout at the lower pressure.

To make the proper correction for this pressure irregularity would almost certainly demand complete knowledge of the mechanism of the processes involved. Failing this, we have used a method of treating the data which, we believe, leads to results considerably closer to the ideal than the experimental ones.

The method of correction was, briefly, an attempt to reduce the time-sorption measurements to constant pressure, the initial pressure being chosen in each case. The corrections involved were twofold:—

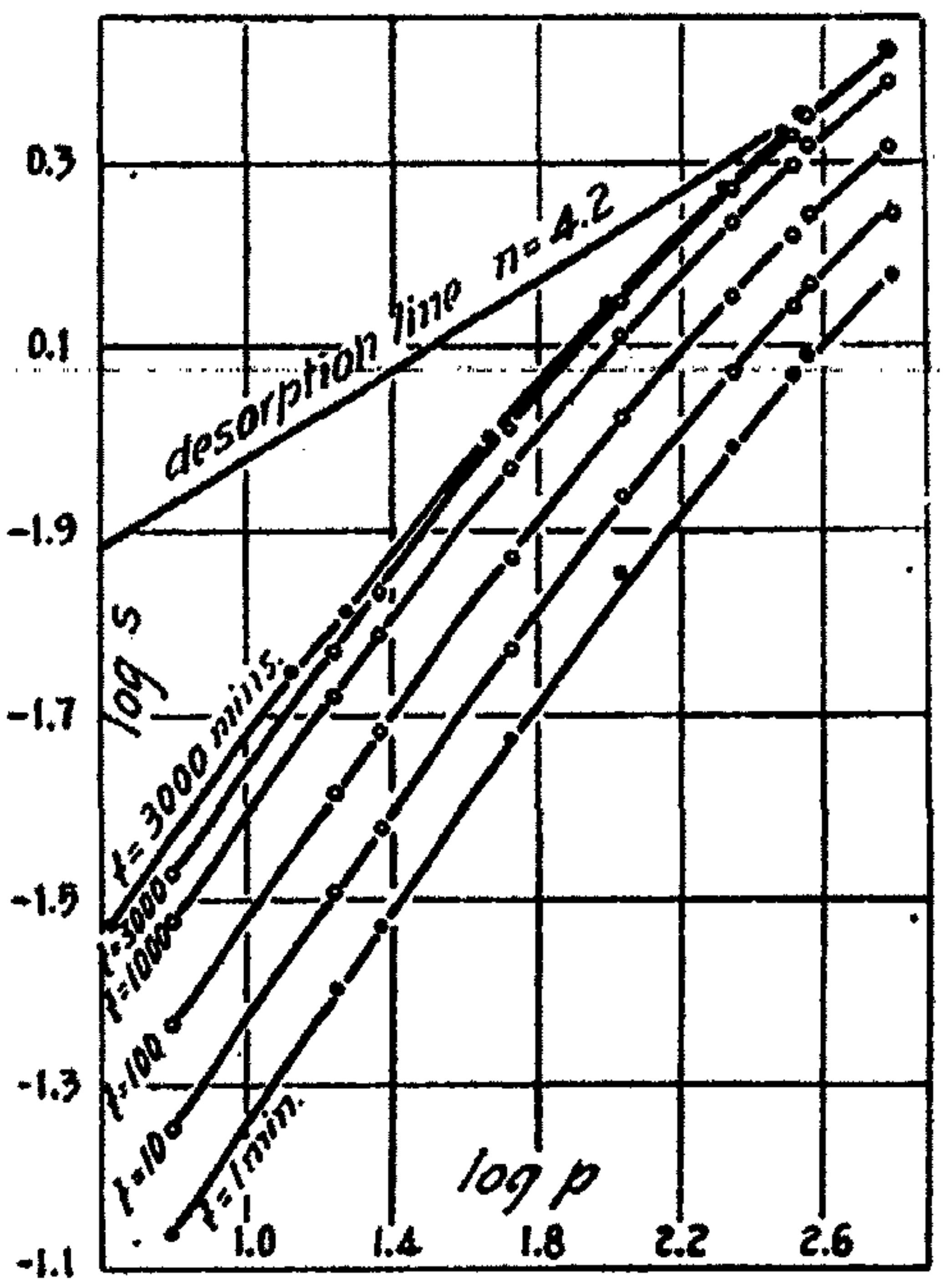

Fig. 7

(1) The sorption value was assumed at any time to adapt itself to the momentary pressure in accordance with the (Freundlich) equation found to hold in the *desorption* experiment: deviation of the "momentary" pressure from the initial value was corrected for on this basis. These corrected sorption values will be given the symbol s_c.

(2) Following the indications of the ammonia experiments that the number of molecular bombardments, rather than the time, was the controlling factor, values of the expression $\log \left(\frac{1}{p_{\text{initial}}} \int_0^t p.dt\right)$ were plotted instead of log t. These corrected times will be given the symbol t_c.

As regards assumption (2) evidence will presently be given that $\int p.dt$ is possibly not without significance in the case of carbon dioxide. In any case the corrections involved here are small. In defense of assumption (1) may be urged the experimental evidence that Freundlich's law is obeyed when the pressure is lowered by successive steps, but it is more difficult to justify the use of the index 4.2, found in the desorption experiment, as a fundamental constant depending only on the nature of the gas and the sorbent. It is possible that this index varies with the previous history of the sorption; that is to say, with the time of contact of the sorbent with the gas, and with the pressure of the latter. It should be remarked, however, that a large variation of this index would affect the corrected results but little.

The effect of these corrections was to make the lower pressure log s, log t graphs somewhat steeper: whatever the pressure, linearity was not visibly affected between $\log t_c = 0$ and $\log t_c = 3$, but it was noticed that for $\log t_c = 3.477$ ($t_c = 3000$ minutes) the points fell a barely perceptible distance below the straight lines drawn.

The values of both the experimental and the corrected reciprocal slopes are given in Table V.

TABLE V

Values of $m = \frac{\partial \log t}{\partial \log s}$

Initial Pressure (mm. of Hg)	$m = \frac{\partial \log t}{\partial \log s}$ from experimental log s, log t graphs	$m = \left(\frac{\partial \log t_c}{\partial \log s_c}\right)_p$ from corrected log s, log t graphs
655	13.9	13.8
384	13.2	13.2
346	13.1	13.0
231.5	12.35	12.2
111.7	11.8	11.5
54.5	10.6	10.1
23.3	10.3	9.5
17.2	10.1	9.4
6.19	10.5	8.9

From the constant pressure graphs (which are not reproduced here) a series of corrected log s, log p values was deduced for $t_c = 10$, 100, 1000 and 3000 minutes respectively: these are indicated by the white circles in Fig. 7. For $t_c = 1$ minute the corrections are negligible and the points therefore coincide with the uncorrected ones. In drawing smoothed curves through the points, licence greater than experimental error was required only in the case of one experiment, namely that in which the initial pressure was 111.7 mm. It is noteworthy that this was the first experiment of the carbon dioxide series, and for that reason may not have been quite comparable with the others.[1]

The corrected log s, log p curves show certain well-marked regularities: not only are the horizontal intercepts between any pair of curves independent of the ordinate value, but they are actually proportional to the difference in value of log t_c for the pair considered. These relations are manifest in Table VI which was compiled from the smoothed curves.

TABLE VI

Carbon dioxide. Data from corrected log s_c, log p curves.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
log s_c	log p					Δ log p (horizontal intercepts between pairs of curves)			
	$t_c = 1$	$t_c = 10$	$t_c = 100$	$t_c = 1000$	$t_c = 3000$	$t_c = 10$ to $t_c = 1$	$t_c = 100$ to $t_c = 10$	$t_c = 1000$ to $t_c = 100$	$t_c = 3000$ to $t_c = 1000$
0.40				2.852	2.747				.105
0.30			2.757	2.551	2.450			.206	.101
0.20		2.677	2.475	2.275	2.172		.202	.200	.103
0.10	2.627	2.426	2.226	2.029	1.930	.201	.200	.197	.099
0.00	2.393	2.200	2.003	1.805	1.708	.193	.197	.198	.097
$\bar{1}.90$	2.185	1.985	1.791	1.590	1.498	.200	.194	.201	.092
$\bar{1}.80$	1.985	1.787	1.591	1.392	1.301	.198	.196	.199	.091
$\bar{1}.70$	1.788	1.593	1.399	1.199	1.108	.195	.194	.200	.091
$\bar{1}.60$	1.603	1.407	1.213	1.015	0.918	.196	.194	.198	.097
$\bar{1}.50$	1.423	1.223	1.032	0.835	0.740	.200	.191	.197	.095
$\bar{1}.40$	1.246	1.050	0.855			.196	.195		
$\bar{1}.30$	1.072	0.875				.197			
$\bar{1}.20$	0.897								
					Mean =	.197	.196	.200	.097
					$\left(\frac{\Delta \log t_c}{\Delta \log p}\right)_{s_c} =$	5.08	5.11	5.00	4.92

For over-all range from t = 1 to t = 3000, $\left(\frac{\Delta \log t_c}{\Delta \log p}\right)_{s_c} = \frac{3.477}{0.690} = 5.04$

Column (1) gives selected ordinate values and columns (2) to (6) the corresponding abscissa values for log $t_c = 0$, 1.0, 2.0, 3.0 and 3.477, while columns (7) to (10) give values of the intercepts (Δlog p) between pairs of adjacent curves: these values therefore correspond to differences in log t_c of 1.00, 1.00, 1.00 and 0.477, respectively. The ratio $\left(\frac{\Delta \log t_c}{\Delta \log p}\right)_{s_c}$, or in the limit, the

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[1] At the end of this experiment the gas expelled from the wool by heating was condensed in a small bulb at liquid air temperature and afterwards measured in the pipette when the original volume was recovered to within about 50 cc. This small discrepancy may have been due to the presence of residual traces of ammonia in the wool, since a minute white deposit (possibly ammonium sulphate) remained in the small bulb after evaporation of the carbon dioxide.

quotient $\left(\frac{\partial \log s_c}{\partial \log p}\right)_t \Big/ \left(\frac{\partial \log s_c}{\partial \log t_c}\right)_p$, is remarkably constant[1] and approximates very closely to the integer 5. These considerations imply that log s, log t graphs for strictly constant-pressure experiments would have the same properties as the log s_c, log p_c graphs in Fig. 7, the curvature being only a question of degree; so that for equal values of *s* the tangents to the curves would be parallel instead of forming greater angles with the abscissa axis as the pressure diminished. It follows that in such a series of experiments the rates of sorption for equal values of *s* should be proportional to $\frac{1}{t}\left(\frac{\partial \log s}{\partial \log t}\right)_p$; that is to $p^{5.0}$, since, at constant *s*, the partial differential coefficient is constant, while $\frac{1}{t}$ varies as $p^{5.0}$.

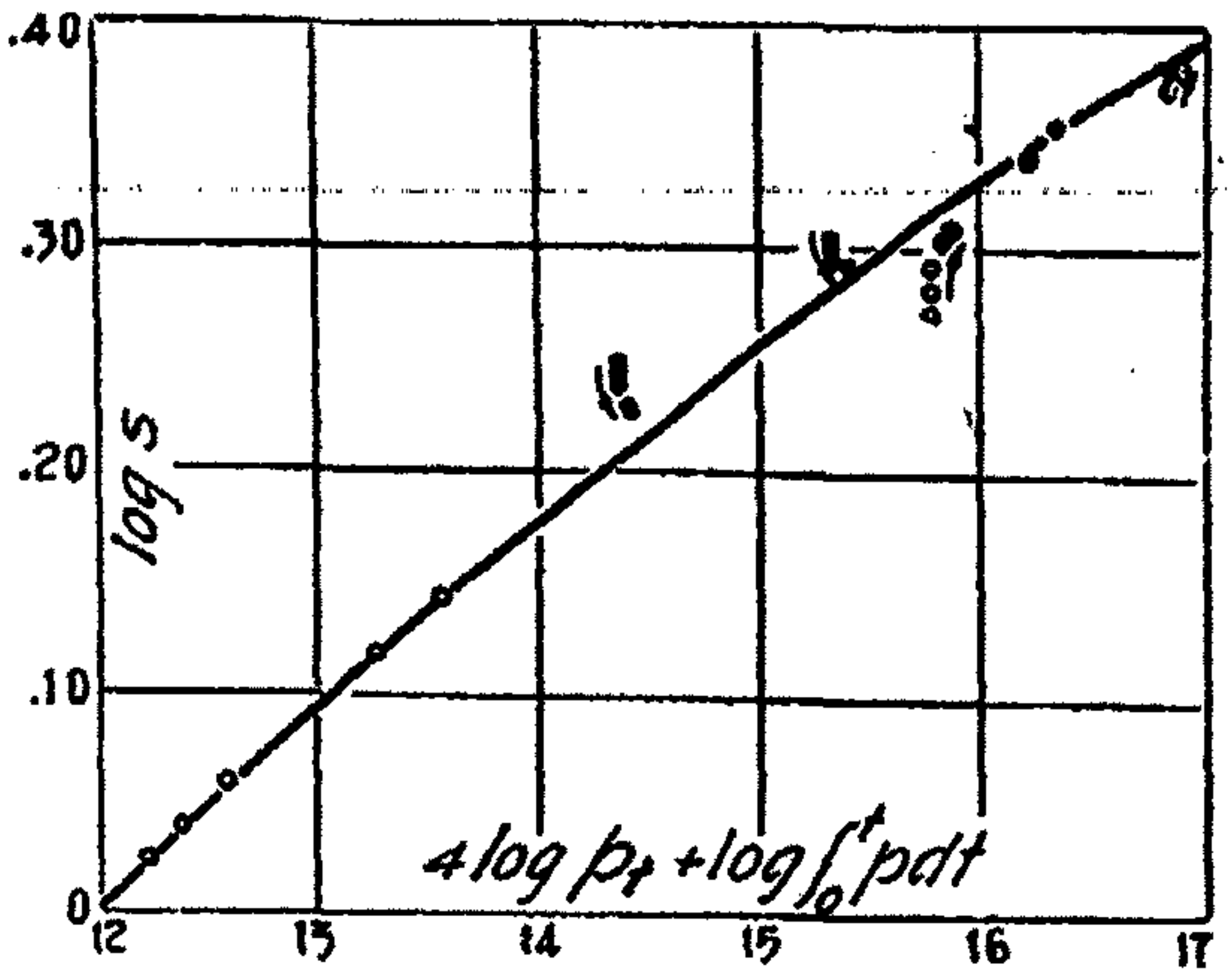

Fig. 8

Since the above relationships lead to the unlikely conclusion that any limiting value of *s* would be independent of the pressure it follows that they can be characteristic only of the initial stages of sorption; those stages, in fact, with which our experiments deal.

Complex Experiments

The above considerations may be summed up in the statement that, as far as constant-pressure experiments are concerned, log s is a single-valued function of the expression (5.0 log p + log t), over the experimental range. Thus log s_c plotted against (5.0 log p_{initial} + log t_c) yields a smooth curve embracing observations at all times and pressures; this complex curve being built up overlapping sections contributed by the various sorption experiments. A

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[1] This relationship recalls at once the behaviour of ammonia since it implies that, in the event of the sorption values (for equal times) obeying Freundlich's equation, the coefficient or index $\left(\frac{\partial \log t}{\partial \log s}\right)_p$ should be independent of the pressure.

section of this curve appears in Fig. 8 and will be referred to later. The curvature is everywhere so slight that a variation in *s* of 2:1 (the order of variation observed in our experiments at nearly constant pressure) is required before it becomes noticeable. The above expression could hardly apply to experiments in which the pressure was varied discontinuously if *p* is taken as representing the momentary pressure at time *t*. The equation $\log s = f(4.0 \log p_t + \log \int_0^t p.dt)$, on the other hand, while yielding a graph identical with the first as far as constant-pressure experiments are concerned, is also sensitive to variations in the past pressure-history: it should hold accurately if such past history is fairly represented by the number of molecular bombardments received by the surface. In order to test the validity of this second equation an experiment was carried out in which the pressure was varied discontinuously. The nature of this complex experiment may be indicated as follows:

From 0 to 2866 minutes pressure = 111.71 falling to 104.44 mm.
" 2866 to 4410 " " = 377.1 " " 373.42 "
" 4410 to 4530 " " = 531.86 " " 531.55 "

$\int p.dt$ was evaluated up to the time of each observation, and the log s values plotted against the expression $(4.0 \log p_t + \log \int_0^t p.dt$. Fig. 8 shows the result of this treatment, the white circles referring to the experiment in question. The full line is the graph of $\log s_c$ against $(5 \log p_{initial} + \log t_c)$, and if the equation $\log s = f(4.0 \log p_t + \log \int_0^t p.dt)$ were strictly valid, all points should lie on this curve. The diagram indicates how, after each pressure-increase, the points, widely divergent at first, approach the curve gradually. The final, isolated point, obtained after the first pressure-increase, is seen to approach the curve very closely. After 1497 minutes at the new pressure the sorption has reached a value which it would have attained only after 578 days at the lower pressure. Following the second pressure-increase the observations were continued for a further 121 minutes only, yet the divergence of the final point from the curve is very small. To reach this value of *s* at the original pressure would have required nearly seven years (assuming the relationship found to be valid throughout). On this evidence one may reasonably regard $\int p.dt$ as a useful measure of past pressure-history when the pressure changes have not been too large or too sudden: it fails immediately after an abrupt pressure change through not being sufficiently sensitive to small time-increments at the higher pressure.

The black circles in Fig. 8 indicate the results of the desorption experiment when plotted in the manner outlined above. The isolated black circle refers to the last observation taken before the first pressure reduction was made. The tendency to approach the line, but this time from the opposite side, is again apparent. The first points, immediately after the first pressure reduction, lie well above the line, while subsequent ones approach it. The last observation of this series was made 24 hours after the first pressure reduction, and immediately before the pressure was reduced for the second time. At each pressure reduction the process repeats itself, the divergence from the curve becoming greater each time. As was the case with ammonia, the equation arrived at on the basis of the sorption experiments fails on reducing the pressure, through its inability to account for the slowness of the desorption process.

It was remarked in the previous paper[1] that the amount of gas disengaged at each desorption step is adequately represented by the equation $r \log \xi = \log t + \text{constant}$ (ξ being the quantity desorbed at time t after the last pressure reduction) as long as t is not too great. For large values of t those of ξ were found greater or less than demanded by the equation, according as gas was being desorbed or sorbed at the moment the pressure reduction was made. It is interesting, therefore, to note that similar regularities apply to the sorption-increment in the experiment in which the pressure was suddenly raised after two days sorption at a steady lower pressure. Thus log (sorption increment) plotted against log (time from moment of increasing pressure) yields a line initially very straight (over the time-range one) to some hundreds of minutes) but thereafter becoming definitely convex to the log t axis.

While this behaviour points to considerable analogy between the process of sorption and that of thermal conduction, or diffusion, attempts to apply the same principles in resolving into simple "waves" the sorption effects following abrupt pressure changes have so far led to disappointing results. It is interesting to note, however, that certain other very simple phenomena display these curious characteristics of the sorption process. Thus the slow stretch of rubber, glass, and of metal wires, under constant load, has been shown to follow a logarithmic instead of an exponential law.[2] Philips[3], who further investigated this subject, makes the following remarks:—"When two loads are put on successively their effects are not exactly superposable, but just after the second load is put on, the effect is as if the last load only were acting, and then it gradually alters till finally the effect is the same as if both loads had been put on simultaneously." If one substitutes "pressure-change" for "load," this statement summarises not inaptly the results of the complex experiments described in this paper.

We are anxious to express our great indebtedness to Mr. W. Sever, not only for the large amount of assistance which he gave us in the experimental work, but also for the many ingenious devices leading to increased accuracy and saving of time which he invented and made.

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[1] Proc. Roy. Soc. 105 A, 487 (1924).

[2] Phil. Mag. 8, 538 (1904).

[3] Phil. Mag. 9, 529 (1905).

We wish also to acknowledge here the receipt of grants from the Royal Society's Committee and from the Brunner Mond Research Fund, which partly defrayed the expenses of this investigation.

Summary

The rate of sorption of ammonia by a glass surface at 0°C. was measured at a number of different and approximately constant pressures. The relationship $s^m = k\ p_t \int_0^t p.dt$, where s is the sorption-value at time t, p_t the momentary pressure and m a (nearly) constant number of about 12, was found to hold for all pressures and times over the experimental range investigated. Except for a temporary derangement, the equation was still found applicable when the pressure was suddenly increased or diminished in the middle of an experiment.

Similar experiments with carbon dioxide yielded analogous results. With this gas, however, the index m was not constant but varied appreciably with the pressure, to which the sorption-value was much more sensitive. While for strictly constant pressure experiments with ammonia it was concluded that log s would be a (nearly) linear function of log (p_t^2), for carbon dioxide, under the same conditions, log s would be a (non-linear) function of log (p_t^5).

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DENSITIES OF CERTAIN AQUEOUS POTASSIUM CHLORIDE SOLUTIONS AS DETERMINED WITH A NEW PYCNOMETER

BY HENRY C. PARKER AND ELIZABETH W. PARKER

Introduction

Density measurements have been variously employed to determine the state of aggregation, the equilibrium existing in mixtures, the ionization in solution, hydrolysis, the distribution of a base between acids and for analytical purposes. Considering their wide application, the ease with which they are made and the high precision attainable, it is surprising that there are available in the literature so few reliable measurements with a high degree of accuracy.

These measurements appear to offer the only purely physical method of determining the state of a substance in solution whose precision may prove sufficient to throw light upon even the most dilute solutions. Their importance would seem to warrant an extended series of accurate measurements.

Work of Previous Investigators. There are four methods of measurement which so far have attained a high degree of accuracy. The displacement method was probably brought to its highest point of perfection by Kohlrausch[1] who claims a precision of two or three parts in ten million. A modified displacement method was used by Lamb and Lee[2] who claim a probable error of less than one in ten million. Piccard and Cherbuliez[3] have described a method of using connecting tubes which was also used by Frivold[4] to an accuracy claimed as one part in ten million. Very accurate measurements with a pycnometer have been made by several investigators. Among these may be mentioned Tammann[5], Dijken,[6] Manley[7], Bousfield,[8] Hartley and Barrett[9], Egerton and Lee[10] and Wade and Merriman[11]. The most accurate of these measurements attain a precision of about one part in a million.

The two principal difficulties met with, in obtaining high accuracy in density measurements, are those of weighing and of temperature control. The displacement method reduces the first of these by removing a considerable part of the load from the balance, but introduces new complications in the form of capillary effects at the point where the supporting wire touches the liquid. The corrections for these effects[12] require a knowledge of the surface

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[1] Ann. Physik. 53, 14 (1894); 56, 184 (1895).
[2] J. Am. Chem. Soc. 35, 1687 (1913).
[3] Arch. sci. phys. nat. 42, 324 (1916).
[4] Physik. Z. 21, 529 (1920).
[5] Z. physik. Chem. 16, 91 (1895).
[6] Z. physik. Chem. 24, 108 (1897).
[7] Proc. Roy. Soc. Edinburgh 24, 356 (1902).
[8] J. Chem. Soc. 93, 679 (1908).
[9] J. Chem. Soc. 99, 1072 (1911).
[10] Proc. Roy. Soc. 103 A, 492 (1923).
[11] J. Chem. Soc. 101, 2430 (1912).
[12] See Klaus: Chem. Ztg. 47, 85 (1922).

tension of the liquid and are uncertain. Although the capillary effects are removed in the modification of Lamb and Lee, the principal difficulty in this method remains, namely that of obtaining temperature equilibrium in the interior of the large mass cf liquid required. Stirring is obviously out of the question and partial stratification of the liquid seems probable. The accuracy of the method of Piccard and Cherubiez can probably only be increased at the cost of producing a cumbersome and unwieldy apparatus. This leaves the pycnometer method which is the easiest and quickest of the three. There has been no systematic investigation as yet to determine to what limits of accuracy this method can be extended.

Temperature control is evidently less difficult with a pycnometer, since it can be made of such shape as to expose a considerable surface to a thermostatic liquid. It is likewise evident that an electromagnetic stirring device may be utilized if necessary. The difficulties met in weighing will be discussed later. A new difficulty enters with a pycnometer, however, in that the volume must be accurately determined either by exact filling or careful calibration of its stem.

In the most common type (Sprengel type) of pycnometer described in the literature, an error is introduced by the necessity of bringing the liquid meniscus to an exact position in two places simultaneously. A modification of this type has two calibrated stems in each of which a reading must be made, introducing a double error both as to calibration and reading. In another type (Gay-Lussac) a single stem is employed but for convenience in filling this must be made large enough to introduce a considerable error[1]. It is believed that this difficulty is removed in a modified Sprengel type of pycnometer which was developed for measuring the densities of potassium chloride solutions, during the course of an investigation[2] on the absolute value of the specific conductance of these solutions.

Apparatus

The pycnometer shown in Fig. 1 can be readily made by an amateur glass blower from materials found in most laboratories. The bulb, *7*, is made of thin soda glass and is large enough to hold about 100 cc. The capillary, *5*, is made from a broken (0°–360°C.) thermometer which has a bore of about 0.3 mm. The capillary *3*, has a bore of about 0.5 mm. The brace, *4*, serves to support the pycnometer on the balance. The enlargement, *1*, serves as an overflow cup when liquids are measured below room temperatures. The calibration mark, *2*, can be made conveniently by turning the capillary in a lathe and making a fine scratch with a sharp steel edge. The caps, *6*, are ground to fit the corresponding tubes, and serve the purpose of preventing evaporation before weighing.

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[1] This type, moreover, cannot be employed without subjecting the liquid to a vacuum which is not desirable in the case of solutions.

[2] J. Am. Chem. Soc. 46, 312 (1924).

If it is desired to make the pycnometer less liable to breakage and easier to wipe dry, the tube, *3*, may be joined by an inner seal at the top of the bulb and be continued to the bottom similar to the corresponding tube in the pycnometer described by Davis and Pratt[1]. Another modification which may be necessary in order to allow the pycnometer to fit in a balance case, is that of having two shorter bulbs connected at the bottom. In this case the tubes, *6*, and *3*, are joined to the tops of the two bulbs, somewhat similar to the pycnometer described by Bousfield[2].

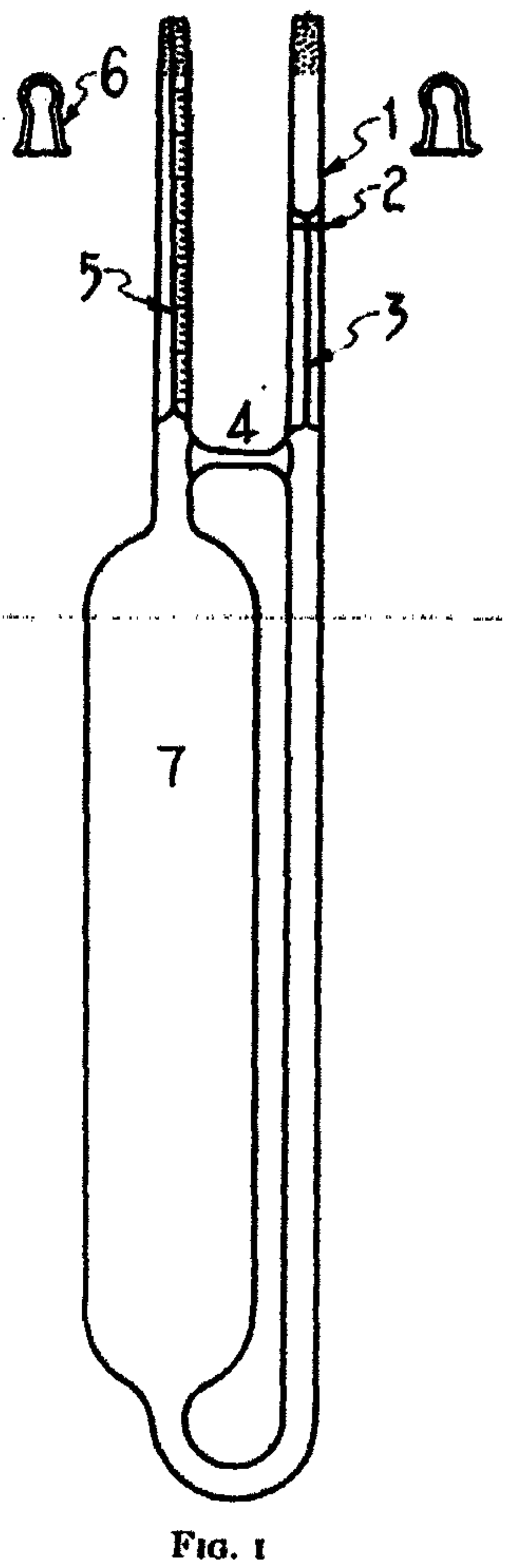

Fig. 1

The new features of this pycnometer are the long calibrated stem, *6*, which is of much smaller diameter than any used formerly, in combination with the stem, *3*, which is larger and bears only a single calibration mark, *2*. The method used for reading the volume is likewise an essential feature.

The manipulation, which was developed for the use of this pycnometer, removes most of the disadvantages which would seem to accrue from the employment of capillary tubing of such small bore.

Experimental Procedure and Results

Manipulation.—The pycnometer was first cleaned with hot cleaning mixture, distilled water and alcohol. It was allowed to age before using and thereafter no heat was applied for either cleaning or drying. The latter was accomplished by rinsing with redistilled alcohol and attaching to an aspirator at *1*. It was found that, if the liquid was always passed through the *larger* capillary and air through the *smaller*, filling or emptying was but slightly delayed by the small bore *6*. Filling was accomplished by attaching a siphon with a four-foot hydrostatic head at *1*, and required but five minutes. This method of transfer can evidently be used with very dilute solutions without danger of contamination. In weighing the pycnometer it was wiped with a clean damp cloth, and 45 minutes were allowed for it to come to equilbrium.

In carrying out a measurement the following prodecure was adopted:—the pycnometer was filled until the overflow cup was half full. It was allowed

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[1] J. Am. Chem. Soc. 37, 1199 (1915).

[2] J. Chem. Soc. 93, 680 (1908).

to stand for 30 minutes in ice water and was then packed into finely shaved ice, in the thermostat described in a recent article[1]. Thirty minutes were allowed before a reading was taken. To take a reading the overflow cup was emptied and carefully dried with cotton wrapped around the end of a small file. A glass stop-cock was fitted to the top of *5* by a short piece of clean rubber tubing. Pressure or suction was then applied at this point through a long rubber tube until the meniscus in *3* coincided exactly with the mark *2*, when the stop-cock was shut off. The reading in *5* could then be conveniently obtained. After several check readings the ice was repacked and 10 minutes allowed before another reading was taken. This procedure was continued until the readings checked to 1 division on the stem. One division represented a temperature difference of only 0°.006 C which speaks well for the temperature control. The water was drained from the thermostat. Otherwise higher readings were obtained which varied with the water level. In order to facilitate a reading in *5* a tiny drop of ink was placed at the top of the liquid in this tube.

Calibrations and *Corrections.*—The set of weights used for weighing the pycnometer had been carefully calibrated against a set with a 1920 Bureau of Standards certificate.

The capillary, *5*, was calibrated and all readings corrected back to an arbitrary mark on the stem. Calibration was made by weighing the redistilled mercury which was sufficient to fill 107 divisions on the stem, and calculating the volume from its density at that temperature. The weight of mercury was 0.05396 g. and its temperature 20°C, making 1 division of the stem equivalent to 0.0372 cu. mm.

In order to obtain the density of the potassium chloride solutions, their relative density in comparison with water at 0° was determined. The value taken for the density of the latter was 0.9998406[2], expressed in grams per centimeter cube. It is evident that the density of a solution will vary with the amount of air dissolved in it. Since the potassium chloride solutions could not be kept air free, the same water was used both for determining the volume of the pycnometer and for making up the solutions. The air was extracted from neither. It was assumed, therefore, that the amount of air dissolved did not change upon making up the solutions and also that this air caused the same decrease in density in the pure water, and in the solutions. For the dilute solutions measured, it is probable that these assumptions hold within the limits of accuracy obtained.

Use was made of "conductivity" water with a specific conductance in the neighborhood of 1×10^{-6}. It was kept in 4 liter bottles of resistance glass and after two liters had been used from a bottle the rest was discarded.

To correct the weights of water to a vacuum, a factor of 1.001055 was used. All the results obtained were corrected to an arbitrary reading (150) on the thermometer stem and to 750 mm. barometric pressure.

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[1] J. Am. Chem. Soc. 46, 316 (1924).

[2] Thiesen, Scheel and Diesselhorst: Wiss. Abh. Phys.-Tech. Reichsanst. 3, 68 (1900). Assuming 1 liter = 1.0000270 cu. dm.

To correct the weighings for change in barometric pressure, the volume of air displaced by the pycnometer was found by adding to its inner volume a volume equal to that of the glass vessel. The latter was found from its weight by assuming the density of glass to be 2.5. The total volume found thus was 141 cc. If the density of air under usual conditions is assumed to be 0.0012, the pycnometer would then displace 0.1695 g. of air. If the effect of temperature and humidity are neglected the density of the air varies directly as the pressure and a change of 1 cm. in the barometric pressure would make a difference in weight of the pycnometer of 0.000226 g. which is a sufficiently close approximation for this correction.

Table I gives the results of five different determinations of the volume of the pycnometer with samples of water from the five different bottles used. It is seen from the data in the second column that the weights of the pycnometer filled with water were even more consistent than the tare weights. Since the densities of the different samples were thus within the experimental error an average volume for the pycnometer was taken in calculating the densities of the solutions. This volume is given in the last column.

TABLE I

Calibration of Pycnometer at 0°C.

	Tare Weights	Weight with H_2O	
	66.5042_2/	180.9178_0	
	66.5042_0/	180.9174_4/	Average weight of water
	66.5036_5/	180.9183_0^a/	in air = 114.4136_0/
	66.5037_8/	180.9174_6/	in vacuum = 114.5343_1/
		180.9175_4/	Volume[b] = 114.5525_7/
Av.	66.5039_6/	180.9175_5/	

[a] Discarded in the average.

[b] Density of water assumed = 0.9998406.

Experimental Results.—The density of three different solutions was determined, namely 0.099271 *D*, 0.1 *D*, and 0.01 *D*. (D or *demal* representing equivalents per cubic decimeter). The measurements on the first concentration were made to perfect the manipulation and to estimate the accuracy of the method. The solutions were all made up by weight methods after the manner recently described[1]. To make up a solution to an exact concentration by this method requires a previous knowledge of its density. A series of approximations was used, therefore, and the density of the first solution was carefully estimated before calculating the required proportions of salt and water. The original density in each case was easily estimated to better than 0.01%. This error in the weight of salt used in making up the

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[1] J. Am. Chem. Soc. 46, 322 (1924).

0.1 *D* solution causes an error of only 5 parts in 10 million in the density as finally determined. Consequently the first approximate solution gave nearly as great accuracy as the final.

To reduce the weights of the 0.099271 *D* and 0.1 *D* solutions to a vacuum, the factor 1.001049 was used. For the 0.01 *D* solution the corresponding factor was 1.001054.

The results obtained for the three solutions are given in Table II.

TABLE II

Density measurements at 0°C.

0.099271 D^a Solution		0.1 D^a Solution	
Wt. KCl to 1000 g H_2O^b	Density^c	Wt. KCl to 1000 g. H_2O^b	Density^c
7.4244$_5$/	1.004838$_8$^{d}	7.4788$_1$/	1.004883$_1$/^{d}
7.4242$_3$/	1.004839$_7$/	7.4787$_6$/	1.004880$_8$/
7.4242$_6$/	1.004840$_3$/	7.4787$_4$/	1.004881$_6$/
Accepted value	1.004840$_0$/	Accepted value	1.004881$_2$/

0.01 D^a Solution

Wt. KCl to 1000 g. H_2O^b	Density^c
0.74624$_6$/	1.000372$_1$/

[a] Expressed as equivalents per cubic decimeter; molecular weight 74.553.

[b] Both weighed in air.

[c] Expressed in grams per centimeter cube.

[d] Discarded in the accepted value.

In the first column are given the weights of potassium chloride to 1000 grams of water (weights in air) used in making up the solutions. The correct weight for the 0.1 *D* solution as calculated from the accepted density is 7.47895 g. The difference between this andt he values actually used would make a difference of but 1 in the last decimal place.

The density estimated for the 0.01 *D* solution was 1.00036 and hence the weight of potassium chloride used in making the solution was far more exact than necessary to obtain an accurate density measurement. The manipulation had been so well perfected at this time that it was thought necessary to make but a single determination of this value.

Discussion

From the results given in Table II, it is evident that a precision of about ±1 part in a million has been obtained. In comparison with other investigators, this appears to be as great a precision as has ever been attained with a pycnometer. When consideration is taken of the fact that other investigators have obtained this precision only when working close to room temperature, it is evident that even greater precision could be obtained in measurements with the new pycnometer when working under these ideal conditions.

In the introduction it was stated that there had been no systematic investigation to see to what limits of accuracy density determinations with a pycnometer could be extended. The numerous investigations which have been made with a *glass* pycnometer have all pointed rather definitely to the limitations of this instrument. A precision of about 1 part in a million seems to be the highest attainable even in spite of the removal of the source of error caused by filling to an exact volume as has been accomplished in the present investigation. The cause for this limitation is not difficult to find.

In Table I it is seen that in determining the tare weight of the pycnometer, an average deviation from the mean of 0.25 mg. is made. In weighing the pycnometer full of water the average deviation is 0.12 mg., providing one determination is discarded[1]. These deviations represent approximately the limits of accuracy obtainable in the weight of such a large glass apparatus, due presumably, to electrostatic effects and the absorption of water vapour. No further proof is necessary that the use of glass must be discarded when an increase in accuracy is desired.

It has been the writer's experience that a quartz vessel can be weighed reproducibly to about 0.02 mg. The measurements of Edgerton and Lee[2] indicate a still greater accuracy.

In order to estimate the highest precision attainable in measurements with a quartz pycnometer we will assume that such an apparatus with a capacity of 500 cc. could be weighed (on a balance especially adapted to that weight) to 0.02 mg. This would be equivalent to 4 parts in 100 million. Such a precision would require a temperature control in the thermostat of ±0.002°C. Several thermostats have been described which have claimed closer regulation.

A series of more or less obvious corrections[3] would have to be applied to the results in order to obtain an accuracy of this order. A correction would have to be made for variations in the density of the air and this latter quantity would have to be determined with some accuracy at each weighing. A difference of 1 cm. in the barometric pressure would cause an error of about 2 parts in a million[4]. Another correction which would become significant is the change in density caused by changes in external pressure. From the compressibility of water it is evident that a change of 1 cm. in the barometric

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[1] Compare the accuracy obtained by Block: Z. angew. Chem. **33**, I, 198 (1920).

[2] Proc. Roy. Soc. **103 A**, 493 (1923).

[3] A discussion of, and equations for most of these corrections are to be found in Refs. 5, 7, 8, and 9, p. 000. See also Saar: Chem. Ztg. **46**, 433 (1922); **48**, 285 (1924); and Bordas and Touplain: Bull. Soc. encour. ind. nat. **133**, 1052 (1921).

[4] The use of a counterpoise would naturally be suggested to obviate the need for this correction. No great success has been attained with the use of a counterpoise in density measurements, however. (See Refs. 5, 7, 8 and 9, p. 130). There is some difficulty in making the counterpoise of sufficiently identical volume to entirely remove the need for corrections. Correction must be made for the volume occupied by the additional weights in any case. On the whole, correcting the weighings without the use of a counterpoise seems preferable.

pressure would cause an error of about seven parts in one hundred million. The changes in pressure on the solution caused by variations of surface tension in the capillary tubes, might also become significant. In the pycnometer described in this article the surface tension of the liquid could be measured while reading the volume of the pycnometer, and hence, this correction could be easily made. A close regulation of the amount of air dissolved in the solution would be necessary and might prove difficult to obtain.

The error introduced by the necessity of filling a pycnometer to an exact volume would obviate the use of any other type of pycnometer but the one described in this article. The readings on this type would evidently have to be made to an accuracy of about 1/2 of one division on the calibrated stem. Such an accuracy could undoubtedly be obtained with the use of a cathetometer.

Although the corrections and precautions which would be necessary to attain a precision of 4 parts in 100 million, seem rather numerous, for the degree of precision involved, there are few physical measurements where they appear so few.

Summary

1. A modified Sprengel type of pycnometer is described which eliminates the difficulty and error introduced by the necessity of filling to an exact volume. The volume can be read accurately to 4 parts in 10 million. The manipulation required in its use is described.

2. Density determinations at 0° have been made on three solutions: 0.099271 *D*, 0.1 *D* and 0.01 *D* (equivalents per cubic decimeter), to an accuracy of about 1 part in a million. The results are 1.004840_0, 1.004881_3 and 1.000372_1 respectively, expressed in grams per cubic centimeter and based on the vale 0.9998406 for water at 0°.

3. A discussion of the errors, incurred in measuring densities with a pycnometer, is included. With the use of a quartz pycnometer of the new type it is predicted that a precision of 4 parts in 100 million could be obtained.

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THE DENSITIES OF SOLUTIONS OF ALUMINIUM CHLORIDE IN LIQUID PHOSGENE

BY ALBERT F. O. GERMANN

In a study undertaken in this laboratory on the conductivity of phosgene solutions of aluminium chloride, it was found necessary to know the densities of these solutions, in order to convert the percentage concentrations given by the method used to molecular concentrations. The literature seems to contain no data on the density of phosgene solutions. The density of liquid phosgene itself has been determined by several investigators. Emmerling and Lengyel[1] give the density at 0° as 1.432; at 18.6°, 1.392. Beckmann[2] gives the value 1.42 at 8.2°. Paternò and Mazzucchelli[3] determined the density of liquid phosgene from $-15.4°$ up to 181.6° in the neighborhood of the critical point; two independent observations in the neighborhood of zero gave values as follows: at 0.07°, 1.4269; at 0.01°, 1.4272; they found that the equation $D_t = 1.4264 - 0.002326\ t$ agreed very well with their observations at other temperatures up to 15°, the maximum deviation amounting to only seven units in the fourth decimal place. Finally, Atkinson, Heycock and Pope[4] have made a series of determinations of the density of liquid phosgene at four temperatures, ranging from $-104°$ to 49.9°; at 0°; two measurements made with the same weight thermometer gave values 1.436 and 1.433 for the density by a method involving absorption of the phosgene by concentrated sodium hydroxide, and titration of the excess of sodium hydroxide.

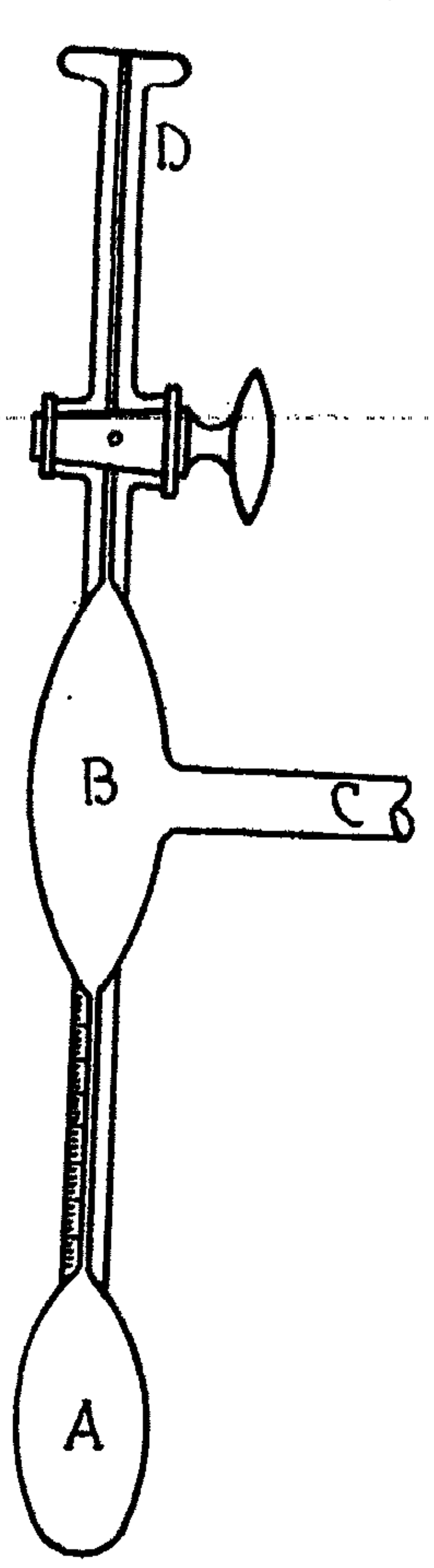

Fig. 1

Method

The form of apparatus used in the present determination is shown in Fig. 1, in which the lower bulb A was calibrated at both 0° and 25° to various points on the stem of the graduated capillary tube; since the preparation of the solutions of aluminium chloride had to take place within the instrument, the graduated capillary tube was surmounted by a

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[1] Ann. Suppl. 7, 106 (1870).

[2] Z. anorg. Chem. 55, 371 (1907).

[3] Gazz. 50, 30 (1920).

[4] J. Chem. Soc. 117, 1410 (1920).

bulb B, of somewhat larger capacity than A, to the top of which was fused a stop-cock and flat joint D, and to the side a filling tube C, large enough to admit a small weighing tube capable of holding about 1 gram of anhydrous aluminium chloride; after introducing a weighed sample of the salt, C was sealed off, and the tube was evacuated and weighed. Pure phosgene was then distilled in, condensing it in B with liquid ammonia applied with a swab, until all of the aluminium chloride was dissolved; condensation was continued in A, until the bulb was perhaps half full; then the solution was boiled off for several minutes, to drive off any foreign gases and more phosgene distilled in until the meniscus stood at some point on the capillary at 0°. To permit the establishment of thermal and pressure equilibrium in the tube, the latter was immersed in a thermostat at the requisite temperature until the position of the meniscus remained constant for at least a half hour; then a reading of the volume was made, and the tube was carefully weighed.

For the density of the solution at the higher temperature the amount of phosgene was adjusted to bring the meniscus on the scale at 25°, and observations made as before.

Two dilatometers were prepared and calibrated for the measurements, the bulb A being constructed with heavy walls, to resist deformation under pressure—the maximum to be withstood being less than one atmosphere excess pressure. Calibration gave the following values for the two tubes, designated dilatometer S (the one shown in the figure) the graduated capillary of which was 4 cm. long, and dilatometer L, the graduated capillary of which was 13 cm. long. Freshly distilled mercury was used for the calibrations. The volumes are given when bulb A was filled up to the indicated graduation mark:

Dilatometer	Meniscus	Volume	Temperature
L	27.14 cm.	7.4630 cc.	25°
L	26.80	7.4739	25
L	15.39	7.8304	25
L	27.74	7.4401	0
L	16.35	7.7950	0
S	5.30	6.2579	25
S	2.00	6.2916	25
S	3.70	6.2745	25
S	4.40	6.2632	0
S	6.10	6.2461	0

The volume of bulb B, with the filling tube C 1.5 cm. long, was 15.7 in dilatometer L, and 14.9 in dilatometer S.

The aluminium chloride used was the same sample used by Germann and McIntyre[1], for the determination of the vapor tensions of these solutions, and the phosgene was purified in the same way.

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[1] J. Phys. Chem. 29, 102 (1925).

Calculation of Results

The total weight of phosgene in the dilatometer during a measurement had to be corrected for the weight of vapor filling bulb B; this could be accurately estimated, since the vapor tension of the solution was known from the work of Germann and McIntyre, and the volume of the vapor was known, proper correction being made for the length of the filling tube C during each measurement. A direct measurement under the conditions of the experiment gave as the weight of saturated phosgene vapor at 25°, 8.18 mg. per cc. and at 0°, 3.65 mg. per cc. These values were used as the basis of the calculations of the vapor correction. The volume of liquid was read from a graph, drawn to large scale, and the percentage concentration and density followed directly from the figures thus obtained.

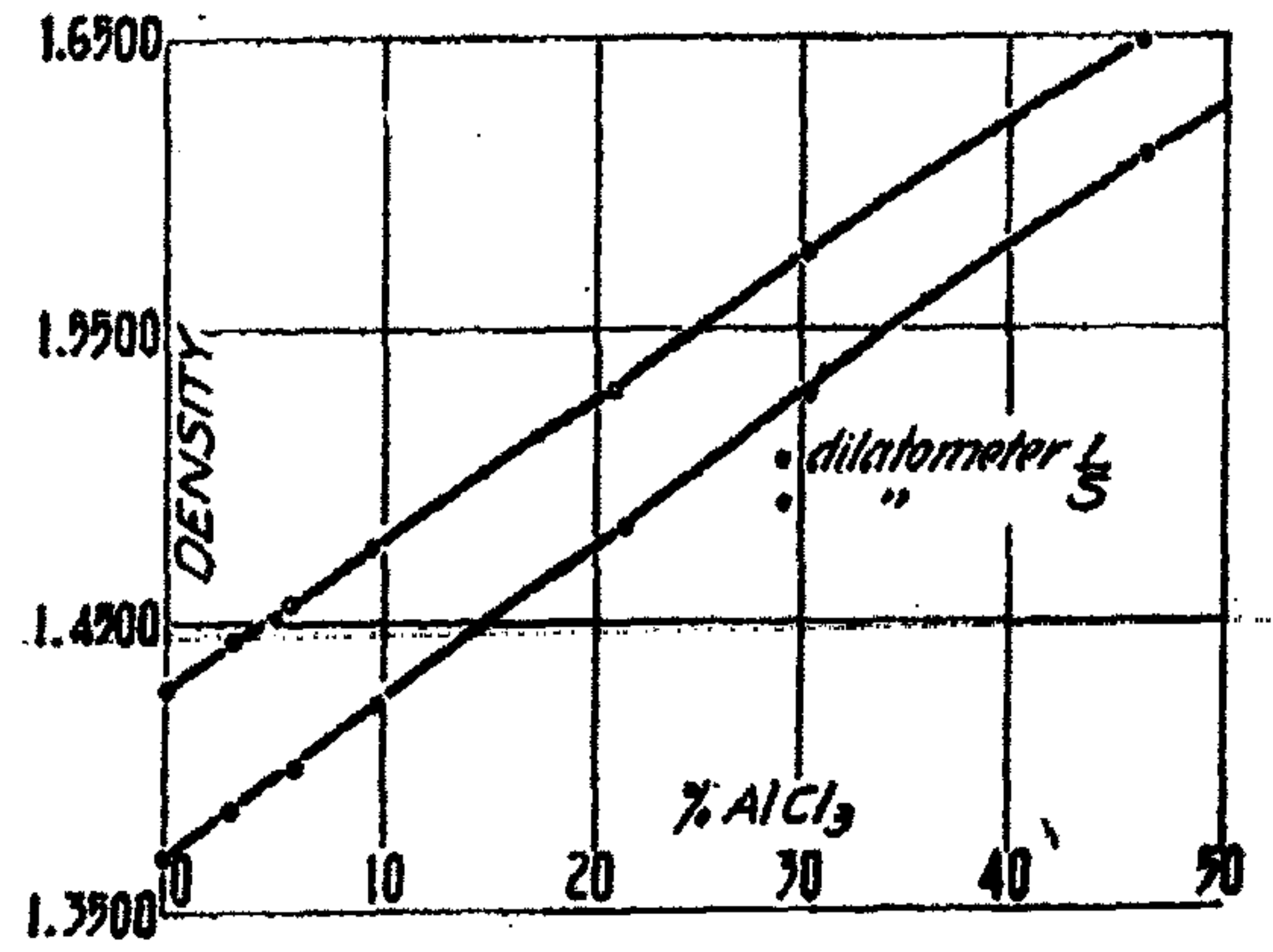

Fig. 2

Results

Table I contains the results obtained for the density of pure phosgene at 0° and at 25°, while Table II contains the results obtained for the solutions:

Table I

Dilatometer	Density at 0°	Density at 25°
L	1.4263	1.3678
L	1.4287	1.3691
S	1.4273	1.3693
S	1.4275	1.3680
L	1.4278	1.3681
Average	1.4275	1.3685

These values check those obtained by Paternò and Mazzucchelli very closely, though with phosgene made by the same method as that used by Atkinson, Heycock and Pope.

The mean coefficient of cubical expansion between 0° and 25° is found to be

$$\frac{1.4275-1.3685}{1.3685\times 25}=0.001725$$

Table II

Dilatometer	% $AlCl_3$	Temperature	Density
L	2.97	0°	1.4422
L	2.99	25°	1.3861
S	5.72	0°	1.4573
S	5.96	25°	1.4009
L	9.70	0°	1.4758
L	9.77	25°	1.4215
S	20.89	0°	1.5303
S	21.55	25°	1.4825
L	30.38	0°	1.5760
L	30.50	25°	1.5283
L	46.33	0°	1.6473
L	46.53	25°	1.6089

Figure 2 contains the density curves as given by plotting the values obtained, and shows the excellent concordance of the results obtained with the two dilatometers. From the curves drawn on a large scale, the densities at intervals of 5% were obtained; these, with the corresponding molar concentrations have been recorded in Table III.

Table III

% $AlCl_3$	Density at 0°	Mol. conc. at 0°	Density at 25°	Mol. conc. at 25°
0%	1.4275	.....	1.3685	.....
5	1.4530	0.545	1.3966	0.523
10	1.4782	1.108	1.4225	1.066
15	1.5027	1.689	1.4483	1.629
20	1.5270	2.289	1.4740	2.210
25	1.5505	2.906	1.5000	2.811
30	1.5741	3.540	1.5257	3.431
35	1.5972	4.191	1.5512	4.070
40	1.6194	4.856	1.5765	4.727
45	1.6416	5.538	1.6018	5.403
50	1.6632	6.234	1.6272	5.099
55	......	.....	1.6526	6.814

Acknowledgment

I wish to express my thanks to the Chemical Warfare Service for supplying the phosgene necessary for this investigation.

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ACTION OF NITRIC ACID ON METALS

BY N. R. DHAR

In three previous papers[1] the action of nitric acid on metals has been studied. In the first paper it has been proved that, contrary to the prevailing views, both ferrous and ferric salts accelerate largely the action of copper on nitric acid and an explanation of this behaviour has also been advanced. In the same paper it was also observed that out of fifty-six substances (electrolytes as well as non-electrolytes) investigated for their catalytic behaviour on the action of copper and nitric acid, twenty-two acted as accelerators and an equal number exerted a negative action in all concentrations, whilst eight of them are slight accelerators in small concentrations and are retarders in concentrated solutions. Only four of these substances have been found to be without effect in small concentrations, whilst in concentrated solution even these four substances are negative catalysts.

In the second paper we have found that other metals like silver, mercury, lead, and an alloy of copper and nickel, brass, and an alloy of iron and nickel, etc., all dissolve more readily in dilute nitric acid in presence of ferrous salts. Moreover with the exception of mercury all the above metals and alloys dissolve more readily in nitric acid in presence of ferric salts as well. It has been also observed in the same paper that there is a periodicity in the action of nitric acid on the alloy of nickel and iron.

In the third paper interesting results have been obtained for the action of mercury and nitric acid. We shall discuss this question further later on.

Recently Prof. Bancroft[2] in an important paper has drawn the attention of chemists to this important problem again. He has thrown out some important suggestions which are worth while investigating. For the last twelve years I have been interested in oxidation and reduction processes, their kinetics, their temperatures coefficients and the influence of catalysts, etc. I have always considered that the action of nitric acid on metals is a complicated oxidation—reduction process. Nitric acid is very rich in oxygen and contains 76% by weight of oxygen and is a very convenient oxidizing agent. Nitric acid is a fairly unstable oxidising agent and it can be converted into all sorts of reduction products and hence it is such a suitable and useful reagent in the chemical laboratory especially because most of the reduction products are more or less soluble in water. We know that substances like starch, sugar, camphor, pentamethylbenzene, chloronitrotoluene, glycerol, metabutyltoluene, etc., can be oxidised conveniently by nitric acid aided by catalysts like vanadium pentoxide and so on. Similarly most common

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[1] Dhar: Proc. Akad. Wet. Amsterdam, 28, 545 (1919); Banerji and Dhar: Z. anorg Chem. 122, 73 (1922); Palit and Dhar: 124, 91 (1924).

[2] J. Phys. Chem. 28, 475 (1924).

metals with the exception of gold and platinum are oxidised readily by nitric acid. Personally, I do not find any fundamental difference in the nature of the oxidation of metals and of other reducing substances like starch, sugar, camphor by nitric acid.

We have made certain experiments on the oxidation of sugar and starch alone and in presence of catalysts like vanadium pentoxide, silver oxide, molybdic acid, manganous sulphate, sodium-nitrate and the following experimental results were obtained: With vanadium pentoxide as catalyst the oxidation of sucrose to oxalic acid takes place at about 70° more rapidly than in the absence of the catalyst. Consequently the yield of oxalic acid from a known weight of sugar is much greater in presence of vanadium pentoxide provided the solution is not boiled. If the solution is boiled for concentrating it, the oxalic acid is further oxidised to carbonic acid and water, and consequently, in all cases when the solutions were boiled no yield of oxalic acid was obtained. Similar results were obtained by Naumann, Moeser, and Lindenbaum[1]. Consequently the partial oxidation of sugar to oxalic acid and the oxidation of oxalic acid to carbon dioxide and water by nitric acid are increased by vandium pentoxide. Similarly manganous salts have been found to be accelerators of both the above reactions and hence the yield of oxalic acid when sugar is oxidised by nitric acid in its presence is much smaller than in its absence when the solutions are concentrated by boiling. The yield of oxalic acid when sodium nitrate is used as a catalyst is a little less than in its absence because nitrous acid is also a feeble accelerator in the oxidation of oxalic acid by nitric acid. On the other hand, with molybdic acid and silver oxide the yield of oxalic acid even when the solutions were boiled for concentration is greater than in the absence of these catalysts. Consequently the rate of oxidation of oxalic acid by nitric acid is decreased in presence of the above catalysts. In a foregoing paper[2] it has been proved that the rate of oxidation of oxalic acid by chromic acid is retarded by molybdic acid. On the other hand, Kempf[3] has shown that the rate of oxidation of oxalates by potassium persulphate is accelerated by silver oxide.

I have already shown that metallic copper, zinc, etc., dissolve copiously in a solution of ammonium nitrite[4]. Instead of ammonium nitrite a solution of any soluble nitrite and an ammonium salt can be used. If copper foil or copper wire is placed in a beaker containing a solution of a nitrite and an ammonium salt, the solution becomes blue in a few minutes. It has also been proved that other unstable nitrite solutions like ethyl ammonium nitrite can also dissolve copper at the ordinary temperatures, whilst solutions of sodium and potassium nitrites which are fairly stable do not dissolve metals like copper. It is likely that the solvent power of nitrite solutions depends on their unstability. Ammonium nitrite will be partially hydrolysed into

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[1] J. prakt. Chem. (2) 275, 143 (1907).

[2] Dhar: J. Chem. Soc. 111, 707 (1917).

[3] Ber. 38, 3975 (1905).

[4] Dhar: Z. anorg. Chem. 119, 174 (1921).

NH_4OH and HNO_2 and both these substances are good solvents of copper. This is probably the reason for the dissolution of copper in ammonium nitrite solutions.

Moreover it is well known that persulphate solutions slowly dissolve metals and the explanation is not far to seek. Persulphate solutions are known to decompose in aqueous solution into acid sulphate and oxygen $K_2S_2O_8+H_2O=2KHSO_4+O$. The oxygen that is set free acts on the metal and forms oxide, and immediately the oxide dissolves in the free sulphuric acid. Thus the persulphate oxidises the metal and the acid dissolves the oxide. In this way, the metals dissolve in persulphates by the joint action of oxygen and acid. No other salt solutions can readily dissolve metals like Cu, Ag, etc. If strips of copper are placed in test tubes and covered with solutions of persulphates, the solutions soon become blue, showing that the metal is attacked. If a fairly concentrated solution is employed the liquid becomes quite warm. There is no evolution of gas if the temperature is low, the two sulphates being the only products ($K_2S_2O_8+Cu=K_2SO_4+Cu\ SO_4$). The interaction of persulphate and metals in other cases, viz: Ag, Au, Mg, Zn, Cd, Hg, Al, Ti, Sn, Pb, As, Sb, Bi, Cr, Se, Te, U, Mn, Fe, Ni, Co, Pd, Pt, etc. has been investigated. All the metals except Au, and Pt, react with persulphate solutions either passing directly into solutions or remaining undissolved in the form of oxides or basic salts. The results show that those metals go into solution as anions which in their general chemical behaviour exhibit a marked non-metallic character e.g., Cr, Mn, Se, As, Mo, etc. Some metals of this type, however, such as Sb, are transformed into insoluble oxides. Elements which are distinctly metallic in character pass into solution as cations, the persulphate being decomposed sometimes with evolution of gas. With Zn, Hg, Cd, Al, Ni, Co, etc., no gas is evolved and as for example in the case of Zn, the reaction may be represented by $Zn+K_2S_2O_8=Zn\ SO_4+K_2SO_4$. When gas is evolved it is found to be hydrogen due to the action of hydrogen ion set free by hydrolysis on metals like Zn, Mg, etc. Oxygen gas may also be given off due the decomposition of persulphates. This action ($K_2S_2O_8+H_2O=2KHSO_4+O$) is accelerated by Au, and Pt, resulting in the decomposition of the persulphate. It is evident therefore that the chemical changes involved in the action of metals on persulphate solutions are closely allied to those happening in the action of nitric acid on metals. Similarly metals like Cu, Ag, etc., can dissolve slowly in oxidising agents like H_2O_2, chromic acid, potassium permanganate, etc., aided by acids like sulphuric acid. Just as nitric acid can oxidise several substances, numerous oxidations of organic substances have been effected by persulphates.

I am inclined to the view that the action of nitric acid on metals is more or less similar to that of metals in persulphate solutions. If you allow nitric acid to come in contact with metals, they will try to reduce the nitric acid to the nitrous state and will be converted into oxide and the oxide thus formed will immediately dissolve in the excess of the nitric acid. In other words, this action is mainly an oxidation of the metals to the oxide state and its consequent solution in the nitric acid. It is needless to mention that there are several side reactions along with the main chemical change. I shall discuss the special function of nitrous acid later on. I do not see any advantage in the electrolytic theory of corrosion. The assumption that all corrosion is electrolytic in nature does not lead to any important fact with regard to the solution of the problem in question. To my mind the hypothesis of Acworth and Armstrong[1] who regard the first change as consisting of the replacement of the hydrogen of the acid by metals and the formation of the metallic nitrate is also not suitable. It is well known that metals like Cu, Ag, Hg, etc., hardly replace hydrogen in acids like HCl, H_2SO_4. On the other hand, the above metals readily dissolve in ordinary dilute nitric acid. Theoretically, we can assume that an infinitely small amount of hydrogen is set free when metals like copper is put in contact with acids. In order to explain the rapid action of metals on nitric acid we have to imagine that the hydrogen set free reacts instantaneously on the unchanged nitric acid; but we know from our experience in chemical dynamics that gases react rather slowly with liquids. Consequently there is considerable difficulty based on kinetics in the hypothesis of Acworth and Armstrong with regard to the action of nitric acid on metals Moreover, on the hypothesis of Acworth and Armstrong the action of metals on nitric acid is put in an entirely different category from that of nitric acid on substances like sugar, starch, camphor, etc., because in the latter cases we cannot make the assumption of the replacement of the hydrogen by the reducing agents. Similarly if we assume that all corrosion is electrolytic in nature we are faced with the same difficulty, because we have to assume that the action of nitric acid on metals is an entirely different type of reaction from that of the action of nitric acid on substances like sugar, starch, oxalic acid, charcoal, sulphur, camphor, etc., on the other hand, if we imagine that the action of nitric acid on metals is essentially the formation of the oxide of the metal and its subsequent solution in the nitric acid or nitrous acid, then this action is immediately brought in line not only with the oxidation of other substances by nitric acid but all oxidation reactions in general. It is well known that when sugar is added to hot concentrated nitric acid, partial oxidation of the sugar molecules into oxalic acid takes place and nitrous fumes are given out, but if manganous sulphate is present complete oxidation takes place and the sugar is converted into carbon dioxide and water by nitric acid simply because the oxidation of oxalic acid by nitric acid is largely accelerated by manganous salts. Harcourt and Esson[2] have shown that the action of potassium permanganate on oxalic acid is accelerated by manganous salts. In a previous paper[3], I have shown that the action of chromic acid and oxalic acid is largely accelerated by managanous salts, similarly the oxidation of the oxalates by persulphates is accelerated by manganous salts. Consequently the oxidation of oxalic acid by nitric acid is more or less allied to its oxidation by other oxidising agents.

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[1] J. Chem. Soc. 32, 56 (1877).

[2] Phil. Trans. 156, 198 (1866).

[3] Dhar: J. Chem. Soc. 111, 707 (1917).

It is well known that manganese can exhibit different valences. Skrabal[1] has assumed the existence of various intermediate stages in the oxidation of oxalic acid by potassium permanganate. Similarly, intermediate stages have been observed in other oxidation-reduction processes. Thus we have proved that in the oxidation of arsenious acid by iodic acid, hypoiodous acid and probably iodous acid are intermediate stages. This is possible because compounds in the intermediate stages can exist in the free state. Thus manganates, manganites, manganic and manganous salts which are lower stages of oxidation than permanganate are known to exist. Different stages of the oxidation of chromium have also been supported by Jablczynski[2]. Similarly nitric acid can readily pass into nitrous acid, hyponitrous acid, etc. Considering these facts I do not find any special reason for assuming either that the action of nitric acid on metals is essentially electrolytic or that it is really a displacement of hydrogen in acids. On the other hand, the simpler assumption that the action of nitric acid on metals is a formation of its oxide and subsequent solution is more satisfactory and brings the action in line along with other oxidation reactions.

More than eighty years ago Millon[3] discovered the marked accelerating effect of nitrous acid on the action of nitric acid on metals like Cu, Ag, Hg, Bi, etc., and suggested that nitrous acid behaved more or less like an inorganic ferment, though this important observation was ridiculed by Gay-Lussac[4]. Following up the idea of Millon, Veley[5] has shown that nitrous acid plays a very important part in the oxidation of metals and that metals like Cu, Ag, Hg, Bi, etc., have no action on cold dilute nitric acid unless a trace of nitrous acid is present. The nitrous acid may be present in the nitric acid as an impurity, or it may be formed by the incipient decomposition of nitric acid when it is warmed. According to Veley, therefore, the dissolving of copper in nitric acid occurs according to the following equations: $Cu+3HNO_3=Cu(NO_3)_2+HNO_2+H_2O$. This reaction is a resultant of a series of consecutive reactions: $Cu+4HNO_2=Cu(NO_2)_2+2H_2O+2NO$, followed by $Cu(NO_2)_2+2HNO_3=Cu(NO_3)_2+2HNO_2$. The small trace of nitrous acid thus acts as a catalytic agent. It is well known that nitrous acid is continuously produced and decomposed according to the equation: $3HNO_2 \rightleftarrows HNO_3+2NO+H_2O$. From my experiments in this line I am also convinced that nitrous acid is an important factor not only in the action of nitric acid on metals but also in its action on substances like sugar, starch, etc. It seems certain that nitric acid is at first reduced to nitrous acid by the action of metals like Bi, Hg, Cu, Ag, etc, and $FeSO_4$, sugar, etc. There is a lot of experimental support of the above view. Thus Rây[6] obtained mercurous nitrite $Hg_2(NO_2)_2$(not mercurous nitrate) in the solid state by the action of

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[1] Z. anorg. Chem. 42, 1 (1904).

[2] Z. anorg. Chem. 60, 38 (1900).

[3] Compt. rend., 14, 104 (1842); Ann. Chim. Phys. (3) 6, 95 (1842).

[4] Ann. Chim. Phys. (3) 6, 385 (1842).

[5] Phil. Trans. 182A, 279 (1891).

[6] Z. anorg. Chem. 12, 365 (1896).

mercury and dilute nitric acid. We have studied the action of mercury and nitric acid in detail and we always find that the first product of the reaction of mercury and dilute nitric acid is yellow crystals of $Hg_2(NO_2)_2$. Strong nitric acid decomposes $Hg_2(NO_2)_2$ and hence with a strong nitric acid we get white crystals of $Hg_2(NO_3)_2$. If we start with dilute nitric acid and mercury at the ordinary temperature we always get yellow crystals of mercurous nitrite after some hours, but if the reaction is allowed to proceed in excess of nitric acid, say for a few days in open air in a beaker, the crystals of mercurous nitrite disappear gradually and white crystals of mercurous nitrate appear, because on evaporation of water, the nitric acid becomes more concentrated and hence can decompose mercurous nitrite. It has been observed that the greater the surface of mercury the smaller is the yield of mercurous nitrite formed by the action of mercury and dilute nitric acid, because the active substance nitrous acid which is formed by the action of mercury on nitric acid is spread over a larger area. It has been observed that by keeping the amount of mercury the same and by changing the amount of nitric acid of definite concentration, the quantity of mercurous nitrite formed is greater at the beginning in the beaker containing smaller quantities of nitric acid, whilst after the reaction has proceeded for twenty-four hours it has been observed that the yield of mercurous nitrite in the beakers containing an excess of acid is much greater. The explanation is not far to seek; in the beakers containing smaller quantities of nitric acid the solution becomes saturated with respect to mercurous nitrite more readily than in beakers containing larger quantities of nitric acid and hence crystals of mercurous nitrite separate out more readily in beakers containing smaller quantities of nitric acid. On the other hand, in beakers containing larger quantities of nitric acid the yield of mercurous nitrite will be greater in the long run because of the larger amount of one of the reacting substances. In order to find out under what conditions the maximum yield of mercurous nitrite is obtained by the action of nitric acid on mercury, we made experiments with nitric acid of different concentrations and at different temperatures with and without catalysts. Acids of concentration 15.1%, 19.1%, 22.8%, 26% and 29.2% were used. It has been established by us that acid of 26% concentration produces the maximum yield of mercurous nitrite at the temperature of about 30°.

Rây[1] observes: "I have sometimes been struck with the remarkable fact that under analogous conditions the yield of mercurous nitrite has been very poor. This abnormal behaviour of nitric acid in isolated cases led me to undertake a close and systematic investigation of the disturbing causes. It was soon discovered that the retarding effect was due to the presence of minute quantities of iron in the acid, for whenever the acid was redistilled in glass retorts no such anomaly was noticed. The residue after distillation was invariably ferric iron." Rây proved that in presence of ferric iron less mercury dissolves in dilute nitric acid than in its absence. The interval of reaction was

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[1] J. Chem. Soc. 99, 1012 (1911).

four hours and in this time no crystals of mercurous nitrite separated. We repeated some of these experiments carefully and we confirmed the experiments of Rây and we also found that when the interval of the reaction is four and a half hours, less mercury dissolves in nitric acid in presence of ferric salts. In other words, ferric nitrate is a retarder in the action of nitric acid and mercury, though we have observed that ferrous sulphate accelerates the action of mercury and nitric acid. We have also observed an interesting fact that though the amount of mercury dissolved by dilute nitric acid in presence of ferric nitrate is less than in its absence, the yield of mercurous nitrite is much greater in the presence of ferric nitrate than in its absence. We have, in all our experiments with nitric acid of 26% concentration, got much larger quantities of mercurous nitrite formed in presence of ferric nitrite than in its absence. This observation contradicts the statement of Rây already quoted. We have also observed that in presence of mercurous nitrate the yield of mercurous nitrite is much greater than in its absence. We have found out that sodium nitrite is a great accelerator in the action of mercury and dilute nitric acid. It is an interesting fact that in presence of sodium nitrite mercury dissolves copiously in nitric acid but there is hardly any yield of mercurous nitrite. This observation can be explained very readily from the following facts:

It is well known that mercuric nitrite, silver nitrite, etc., are much less ionised than ordinary salts in aqueous solutions and these nitrites readily form complex nitrites with alkali or alkaline earth nitrites[1]. From the researches of Rây[2] it is clear that mercurous nitrite decomposes in presence of water according to the following equation:

$$Hg_2(NO_2) \rightleftharpoons Hg+Hg(NO_2)_2$$

If to this mixture sodium nitrite be added the mercuric nitrite will immediately combine with sodium nitrite forming a complex nitrite of the type $Na_2Hg(NO_2)_4$. Hence the equilibrium will be displaced from left to right. In other words, the whole of the mercurous nitrite will be converted into sodium mercurinitrite. Moreover, there is the possibility of the formation of sodium mercuronitrite formed by the interaction of sodium nitrite and mercurous nitrite and this complex nitrite is likely to be more soluble than mercurous nitrite. Consequently the action of nitric acid on mercury in presence of sodium nitrite produces hardly any mercurous nitrite. The greater yield of mercurous nitrite by the action of mercury and dilute nitric acid in presence of mercurous nitrate is due to the decreased solubility of mercurous nitrite due to the presence of a common ion.

It is difficult to explain at this stage the increased yield of mercurous nitrite in presence of ferric nitrite. It has been observed that in presence of urea the action of nitric acid on mercury does not produce any mercurous nitrite because the urea present completely destroys the nitrous acid originally existing in the nitric acid as well as that produced by the reduction of

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[1] Abegg and Pick: Z. anorg. Chem. 51, 1 (1906); Rây and Dhar: J. Chem. Soc. 101, 965 (1912).

[2] J. Chem. Soc. 87, 777 (1905).

nitric acid by mercury or by nitric oxides; hence very little mercury dissolves in nitric acid in presence of urea and so there is practically no yield of mercurous nitrite in this case.

Stansbie[1] has suggested that with copper and silver in the presence of dilute nitric acid, approximately half the nitric acid is reduced to nitrous acid. The experimental results show that with silver the following expresses the reaction:

$$2Ag+2HNO_3 = AgNO_3+AgNO_2+H_2O$$

In the case of copper the reaction is most probably as follows: $3\ Cu+6HNO_3$ $=Cu(NO_3,\ NO_2)+3H_2O$.

Stansbie observes that no gas is given off when dilute nitric acid is used and the amount of reaction taking place is increased by the addition of free nitrous acid. Consequently it is clear that nitrous acid plays a very important part in the action of nitric acid on metals like copper, silver, mercury, bismuth, etc. The formation of nitrous acid by the action of metals on nitric acid can be readily demonstrated in the following way:

If metallic copper is covered with 20% nitric acid at the ordinary temperature, at the beginning there is very little chemical change. After a few minutes, blue colour appears at the bottom of the tube, due to the dissolving of copper and there is hardly any evolution of gas. Now if urea is added to the reacting mixture, copious evolution of nitrogen and carbon dioxide takes place, showing the existence of nitrous acid in the mixture.

Curiously enough the action of nitric acid on lead is not markedly accelerated by nitrous acid which is really produced in this case also as a first step in the reaction[2]. This behaviour can be partly explained from the following facts:

Lead nitrate is a sparingly soluble substance in comparison with silver nitrate, copper nitrate, mercurous nitrate, etc., especially in presence of nitric acid. It is quite likely that when lead is brought in presence of fairly dilute nitric acid there is the possibility of the formation of lead nitrite and lead nitrate just as in the previous cases we always get a mixture of nitrite and nitrate. In the case of lead, it seems certain that lead nitrite is much more soluble than lead nitrate and consequently lead nitrate comes out of the solution very readily and the amount of lead ions from the dissociation of lead nitrite is very small. Moreover the lead nitrite formed in the solution is gradually decomposed by the excess of nitric acid with the formation of sparingly soluble lead nitrate. Consequently the chemical change between lead and nitric acid results mainly in the formation of lead nitrate. Hence the catalytic action of nitrous acid cannot be prominent in this reaction. On the other hand with mercury and silver the case is otherwise, because with those metals, the nitrites are much less soluble than the nitrates and these nitrites tend to come out as precipitates. Hence in the action of nitric acid on mercury, silver, copper, etc., the action of nitrous acid is more prominent

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[1] J. Soc. Chem. Ind. 32, 311 (1913).

[2] Compare Veley: J. Soc. Chem. Ind. 10, 206 (1891).

than in the case of lead. Looking at the problem from another point of view, we can explain the difference in the behaviour of lead and mercury towards nitric acid from the following facts:

It is well known that nitrous acid decomposes according to the following equation: $3HNO_2 \rightleftarrows HNO_3+2NO+H_2O$. With mercury, silver, etc., the nitrites being sparingly soluble come out readily as crystals in their action with nitric acid. Consequently nitrous acid is being continually removed from the solution due to the precipitation of the nitrites. Hence, in order to establish the above equilibrium, more and more nitric acid will be converted into nitrous acid. In other words, in these cases, it is to be expected on theoretical grounds that nitric acid will gradually pass into the nitrous state and hence the action of nitric acid will be far less prominent than that of nitrous acid which really appears to be the chief solvent of these metals and these conclusions are actually corroborated by the experiments of Millon, Veley, Rây, Stansbie and others. On the other hand, with lead the case is different because lead nitrate which is a very sparingly soluble substance comes out as a precipitate more readily than the nitrite. In other words, nitric acid is removed from the sphere of the chemical change due to the separation of lead nitrate. In order to establish the foregoing equilibrium nitrous acid will be converted into nitric acid and in this chemical change the nitric acid will play more prominent part than the nitrous acid.

Now Millon and Veley have pointed out that the presence of ferrous sulphate "which removes the nitrous acid as fast as it might be formed" serves to prevent the chemical change between nitric acid and the metals. But we have found that ferrous sulphate markedly accelerates the action of nitric acid on copper, silver, mercury, nickel, silver coin, nickel-copper alloy (Ni 50%, Cu 50%), brass and iron-nickel alloy (Fe 50%, Ni 50%). Other ferrous salts have also been found to be accelerators. In explaining the accelerating action of ferrous salts, I have advanced the argument "that a part of the ferrous ion reduces the nitric acid to nitric oxide and passes into the ferric state. The nitric oxide dissolves in the ferrous salt solution forming the unstable bivalent ion, $FeNO^{\cdot\cdot}$. The dissolved nitric oxide then reduces a part of the nitric acid according to the following equation: $HNO_3+2NO+H_2O \rightleftarrows 3HNO_2$.

It is quite possible that some nitrous acid is produced by the direct reduction of nitric acid by ferrous ions. The formation of nitrous acid either by the direct reduction of nitric acid by ferrous salts or by the indirect reduction through the intervention of nitric oxide is proved by the following experiment. If nitric acid of 20% strength be taken in a test tube and a crystal of ferrous ammonium sulphate or ferrous sulphate be added to it, almost immediately the crystal is covered with the deep-brown $FeNO^{\cdot\cdot}$ ion and a little nitric oxide also escapes. If urea crystals are now added, they are immediately oxidised with the evolution of carbon dioxide and nitrogen, indicating the presence of nitrous acid. So in the presence of ferrous salts, nitrous acid, which is the active substance in the action of nitric acid on copper, is formed when we have an excess of nitric acid. This explains the accelerating influence of ferrous salts in the complete dissolving of copper in 20% nitric acid.

As a matter of fact, the accelerating influence of ferrous salts is slightly greater than the accelerating effect of sodium nitrite on the dissolution of copper in nitric acid. The greater the concentration of the ferrous salt, the greater is the acceleration.

Ferric sulphate, ferric nitrate and ferric chloride exert a marked accelerating effect though their activity is slightly less than that of sodium nitrite and the accelerating effect is proportional to the concentration of the ferric salt. It would appear that the acid radicle in this case also, plays no part. The explanation of this activation seems to be in the reduction of ferric salts by the nitric oxide which is a product of the chemical change between nitric acid and copper. The ferrous salt, may thus be formed, will reduce a part of the nitric acid to nitrous acid, which activates the action of nitric acid on copper. It seems plausible that a part of the ferric salt would be reduced to the ferrous state by the metallic copper. It is well known that when a solution of a ferric salt is shaken with metallic copper, the ferric salt is partly reduced to the ferrous state and the copper is oxidised to the cupric salt, an equilibrium being set up: $2FeCl_3+Cu \rightleftarrows 2FeCl_2+CuCl_2$.

The ferrous salt thus formed reduces the nitric acid to nitrous acid, which accelerates the action of nitric acid on copper.

In a similar way the accelerating effect of arsenious oxide, strychnine sulphate, phthalic anhydride, etc., may be explained on the basis of the formation of nitrous acid by the action of these reducing agents on the nitric acid[1]."

"In this connection, it is interesting to observe, that several reactions in which nitric acid is the oxidising agent, are autocatalytic. As for example, the action of nitric acid on metals like Cu, Ag, Bi, Hg, etc., on starch, on sugar, on arsenious oxide, on hydrogen iodide[2], on nitric oxide[3], etc., become more pronounced as the chemical changes proceed.

The explanation is not far to seek. The nitrous acid is the active substance and its concentration and hence the reaction velocity increase with the progress of the chemical change. In all these cases I have found that the chemical change becomes more rapid when a nitrite is added at the commencement of the reaction. It has been observed that the chemical change between nitric acid and copper may be practically stopped by agitating vigorously the tube containing copper and nitric acid, because the nitrous acid cannot accumulate round the copper."

Just as the action of nitric acid on metals is accelerated by nitrous acid, I have repeatedly observed that the action of the same substance on starch, sugar, oxalic acid, arsenious oxide, etc., is also accelerated by nitrous acid.

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[1] Dhar: Proc. Akad. Wet. Amsterdam 28, 545 (1919).

[2] Eckstädt: Z. anorg. Chem. 29, 57 (1901).

[3] Lewis and Edgar: J. Am. Chem. Soc. 33, 292 (1911).

Here again we find there is no essential difference in the nature of the action between nitric and the metals on the one hand and nitric acid and reducing agents like sugar, starch, etc., on the other hand, it is interesting to note that the oxidation of iodine to iodic acid by concentrated nitric acid is not accelerated by nitrous acid.

Ostwald has observed that nitric acid in which copper has already been dissolved readily acts on further quantities of copper and he has compared this phenomenon with memory and habit. Apparently, the reason for this peculiarity is that the nitric acid in which copper is already dissolved, contains free nitrous acid, which markedly accelerates the change.

Hence, from the foregoing experimental evidence we find that nitrous acid is likely to be always produced in the first stage. The nitrous acid can be further reduced to hyponitrous acid, or hydroxylamine, or, hydrazine or to ammonia. As I have already said nitrous acid is an unstable substance and it readily decomposes into nitric acid and nitric oxide, $3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O$). Hence the production of nitric oxide by the action of nitric acid on metals like copper, silver, mercury, bismuth, etc., and reducing agents like ferrous sulphate, titanous chloride, sugar, starch, etc., is really due to the decomposition of nitrous acid which is the first product in the reduction of nitric acid. Hence in most reactions of nitric acid and reducing agents we get the evolution of nitric oxide due to the decomposition of nitrous acid.

It seems likely that nitrous oxide which is sometimes a product of the reaction between nitric acid and a reducing agent is mainly due to the decomposition of hyponitrous acid, $H_2N_2O_2 = N_2O + H_2O$. At the same time one cannot ignore the possibility of the formation of H_2O by the action of hydroxylamine and nitrous acid or by the decomposition of ammonium nitrate. But to my mind the formation of nitrous oxide in the action of nitric acid on metals is mainly due to its production by the decomposition of hyponitrous acid.

It is well known that more nitrous oxide is formed by the action of lead on nitric acid than that produced by the action of copper and nitric acid. Lead reacts much more readily than copper producing with equal concentration of nitric acid relatively more nitrous oxide and less of the higher oxides of nitrogen[1]. This is certainly due to the fact that with lead more hyponitrous acid is formed than with copper because lead is a better reducing agent than copper (compare electrode potentials of copper and lead). Consequently the production of nitric oxide of nitrous oxide will depend on the reducing power of the metal in question.

Bancroft has noted that the direct reduction products of nitric acid are nitrous acid, hyponitrous acid, hydroxylamine and ammonia while nitrogen peroxide, nitric oxide, nitrous oxide, and nitrogen are due to secondary reactions. Similarly Stansbie[2] has observed that the liberation of nitrogen

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[1] Compare Freer and Higley: Am. Chem. J. 21, 377 (1899).

[2] J. Soc. Chem. Ind. 32, 311 (1913).

peroxide, which is the result of the interaction of nitrous and nitric acids, takes place as the concentration of the nitric acid increases, thus $HNO_2 + HNO_3 \rightleftharpoons H_2O + 2NO_2$. But it is very difficult to make a definitely hard and fast rule about the direct and indirect products of the reaction between nitric acid and metals, simply because all the reduction products of nitric acid are fairly unstable and are interconvertible one into the other under suitable conditions. Thus Reynolds and Taylor[1] have shown that in presence of light strong nitric acid decomposes according to the following equation: $4HNO_3 \rightleftharpoons 2H_2O + 2N_2O_4 + O_2$. According to this reaction N_2O_4 can be also a direct product of the decomposition of nitric acid. Spiegel[2] has observed that nitrous acid in a good deal of water loses two thirds of its oxygen in presence of H_2SO_3 and is reduced to nitrous oxide when less water is present or when SO_2 is passed into a solution of nitric acid in H_2SO_4, nitric oxide is formed. This is due to the fact that the reduction of nitric acid or nitrous acid to hyponitrous acid is more favourable in dilute solutions than in concentrated ones.

It seems probable that very dilute solutions of nitric acid are more apt to pass into the hyponitrous stage by the action of suitable reducing agents than concentrated solutions of the acid. The hyponitrous acid formed from dilute solutions will decompose into nitrous oxide and water. Commenting on the work of Divers on the formation of hydroxylamine, Bancroft has observed that "the presence of sulphuric acid increases the tendency to form hydroxylamine during the reduction of nitric acid by zinc;" but that no satisfactory explanation of this has yet been offered. I suggest the following explanation of the increased yield of hydroxylamine in presence of sulphuric acid. Ammonium hydroxide is certainly more basic than hydroxylamine hydroxide. Consequently the formation of ammonia is undoubtedly more difficult than the formation of hydroxylamine in strongly acid solutions. Moreover metallic zinc alone is a better reducing agent than zinc and sulphuric acid because by the action of zinc and sulphuric acid hydrogen is set free, which is far less reducing in its properties than metallic zinc. (Compare electrode potentials of hydrogen and zinc). Consequently with the better reducing agent zinc alone, nitric acid can pass into ammonia whilst with zinc sulphuric acid which is not as good a reducing agent as zinc alone we get mainly hydroxylamine. Divers and Shimidzu[3] have observed: "In one experiment 10 cc of a solution of hydroxyammonium chloride containing 0.033 gram of hydroxyamine were made up to 100 cc with water containing a little H_2SO_4. The mixture was poured upon 45 grams of granulated zinc, and thus exposed to a relatively very large surface of zinc. It was left in contact with the zinc for two hours, dilute H_2SO_4 being occasionally added, so as to keep up effervescence. The solution still effervescing was poured off and titrated for hydroxyamine and the whole of this was found unchanged. We then tried the action of zinc

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[1] J. Chem. Soc. 101, 131 (1912).

[2] "Der Stickstoff," 571 (1903).

[3] J. Chem. Soc. 47, 587 (1885).

alone upon a dilute solution of hydroxyammonium chloride. Here there was a marked destruction of the hydroxyamine in two hours, one-eigth to one-fourth disappearing." It appears from the above observations that hydroxylamine is reduced by metallic zinc alone to ammonia and not by zinc and acid. As has been already explained this happens because metallic zinc alone is a better reducing agent than zinc and sulphuric acid. Divers observes that hydroxylamine is destroyed, but I am sure it is converted into ammonium salts.

Divers has divided metals into two classes as regards their behaviour with nitric acid, namely those which yield nitrite and nitrate with water but exert no further action forming neither ammonia nor hydroxylamine. In this class are placed Ag, Hg, Cu, and Bi. Secondly those which form ammonia and generally also hydroxylamine but do not yield nitrite or nitrous acid with free nitric acid. On the other hand they readily form nitrite. To this class belong Zn, Cd, Mg, Al, Pb, Fe, and the alkali metals. I am of the opinion that this division is a sound one. With the metals Ag, Hg, Cu, Bi, and HNO_3 we always get nitrous acid as the first reduction product and this unstable substance decomposes into nitric oxide and nitric acid. So the main gaseous product obtained by the action of dilute nitric acid on Ag, Hg, Cu, Bi, etc., at the ordinary temperature is nitric oxide. Small quantities by hyponitrous acid may also be formed by the reduction of nitric or notrous acid by the above metals. The hyponitrous acid being unstable will mainly decompose into nitrous oxide and water. This is certainly the origin of nitrous oxide obtained under certain conditions in the oxidation of metals like Cu, Hg, Bi, etc., by nitric acid. It is well known that in the action of copper and nitric acid more and more nitrous oxide is set free instead of nitric oxide as the cupric nitrate goes on increasing in the system. It seems likely that in presence of cupric nitrate and in dilute solutions of nitric acid, nitrous acid can be reduced to the hyponitrous state which readily breaks up into nitrous oxide and water.

Traces of nitrogen are sometimes set free by the action of metals like Cu, Ag, Hg, etc., and an explanation is difficult to find. Nitrogen can be formed either by the action of ammonia and nitrous acid or by the action of hydroxylamine and hyponitrous acid. It is not sound to assume the formation of either ammonia or hydroxylamine by the action of nitric acid on metals like Cu, Ag, etc. One has to take recourse to the suggestion of Hantzsch and Kaufmann[1] who state that hyponitrous acid may also break down according to the following equation:

$$3H_2N_2O_2 = 2NH_3 + 2N_2O_3$$

It is likely that ammonia will immediately react with N_2O_3 with the formation of nitrogen and water. This is the possible explanation of the formation of nitrogen in the action of nitric acid on metals like Ag, Cu, etc. Just as nitrous acid is known to decompose according to the equation $3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O$, similarly it is very likely that hyponitrous acid

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[1] Ann. 232, 317 (1896).

will be in equilibrium with nitrous acid according to the equation $3H_2N_2O_2 \rightleftarrows 2HNO_2+2N_2+2H_2O$ and the nitrous acid produced will be in equilibrium with nitric acid. Hence in a solution we should get $HNO_3 \rightleftarrows HNO_2 \rightleftarrows H_2N_2O_2$. Moreover, Berthelot and Ogier[1] and Rây and Ganguli[2], have shown that hyponitrous acid can also decompose according to the following equation:

$$5H_2N_2O_2 = 4H_2O+2HNO_3+4N_2$$

Metals like Zn, Mg, Sn, Fe, etc., which are strong reducing agents and which set free hydrogen by their action on dilute acids can certainly reduce nitric acid to hydroxylamine, hydrazine, and ammonia; sometimes free hydrogen also escapes. It is very likely that the observations of von Dumreicher[3] claiming the possibility of the reduction of nitric oxide to ammonia by acidified stannous chloride are correct. It appears to me that Divers is incorrect in saying that nitric oxide is not reduced to ammonia by acidified stannous chloride and that ammonia is only formed to some extent in presence of nitrogen peroxide. Experiments on these lines are in progress in this laboratory.

When nitric acid is reduced theoretically the following compounds may be produced:

$$H_2N_2O_6 \longrightarrow \overset{(1)}{H_2N_2O_5} \longrightarrow \overset{(2)}{H_2N_2O_4} \longrightarrow \overset{(3)}{H_2N_2O_3} \longrightarrow \overset{(4)}{H_2N_2O_2} \longrightarrow \overset{(5)}{H_2N_2O}$$

$$\longrightarrow \overset{(6)}{NH_2OH} \longrightarrow \overset{(7)}{N_2H_4} \longrightarrow \overset{(8)}{NH_3}.$$

Of these Nos. (1), (3) and (5) are extremely unstable and are of doubtful existence. It is most interesting that in the above chain of compounds, those with an even number of oxygen atoms are much stabler than the ones with an odd number of oxygen atoms. It may be that in compounds with an even number of oxygen atoms the valency of nitrogen is saturated and is possibly five whilst in the compounds with an odd number of oxygen atoms, the valency of nitrogen is unsaturated and the compounds are in a strained condition. It will be very interesting if one could isolate Compounds Nos. (1) and (5).

If we take metals like silver, copper, mercury bismuth, etc., which do not set free hydrogen by their action on dilute acids (HCl, H_2SO_4, etc.), theoretically we should get compounds Nos. (1), (2), (3), (4), (5), but not compounds (6), (7) and (8). The above metals can take up oxygen from nitric acid but as they cannot produce hydrogen by their action on acids or water, they should not hydrogenate nitric acid and form hydroxylamine, hydrazine, or ammonia. So with the above metals the formation of hydroxylamine and hydrazine and ammonia seems practically impossible. They can form compounds (1), (2), (3) (4) directly and by the decomposition of these compounds we can get NO_2, NO, N_2O, and N_2.

With metals like Zn, Mg, Al, Sn, etc., which can readily give off hydrogen from acids, along with nitrates and nitrites we can expect the formation of

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[1] Compt. rend. 96, 30, 84 (1883).

[2] J. Chem. Soc. 91, 1866 (1907).

[3] J. Chem. Soc. 20, 460 (1861).

hydroxylamine, hydrazine and ammonia and the actual hydrogenation of nitric acid is possible because the above metals are very good reducing agents and can actually add hydrogen to nitric acid whilst at the same time they take away oxygen from nitric acid. On the other hand, metals like Cu, Hg, Ag, Bi, etc., can only take away oxygen from nitric acid and cannot add hydrogen to it and that is why with the above metals and nitric acid we get HNO_2, $(HNO)_2$ and their decomposition products and not NH_2OH, N_2H_4 and NH_4OH.

It is well known that hyponitrous acid can be reduced by hydrazine under favourable conditions. Consequently it seems very likely that hydrazine can also be a direct reduction product of nitric acid.

Bancroft has observed: "In the ordinary reduction of nitric acid, nitrogen probably occurs as the result of a reaction between hydroxylamine and hyponitrous acid more often than as the result of a reaction between nitrous acid and ammonia." This statement seems very sound in all cases where reduction of nitric acid is effected by metals like Zn, Mg, Sn, etc., where there is the possibility of the formation of hydroxylamine. As hydroxylamine hydroxide is less basic than ammonium hydroxide, it is natural that the former compound would be formed more readily in an acid solution than the latter. Moreover, ammonia being certainly in a higher state of reduction than hydroxylamine, is formed with greater difficulty in the reduction of nitric acid by reducing agents than hydroxylamine. Hence, on the whole, there is far greater possibility of the formation of hydroxylamine than that of ammonia and the former compound will react on hyponitrous acid forming nitrogen. But in the case of metals like Ag, Cu, Hg, Bi, etc., the formation of hydroxylamine or hydrazine or ammonia is extremely doubtful as has already been emphasised. Consequently, the formation of traces of nitrogen sometimes obtained in the action of metals like Ag, Cu, Hg, etc., on nitric acid cannot be satisfactorily explained by the reaction between hydroxylamine and hyponitrous acid as suggested by Bancroft. As we have already observed, we have to explain the formation of nitrogen in these cases by the decomposition of hyponitrous acid according to following equations:

$$5H_2N_2O_2 = 4H_2O + 2HNO_3 + 4N_2$$
$$3H_2N_2O_2 = 2HNO_2 + 2N_2 + 2H_2O$$

Veley[1] suggested that nitrous acid decomposes according to the following equation:

$$3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O$$

Lewis and Edgar[2] have studied the equilibrium $3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O$, and have shown that the equilibrium constant changes with the concentration of nitric acid. It seems likely that secondary reactions interfere with the main reaction and affect the equilibrium constants of the main reaction.

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[1] Proc. Roy. Soc. **52**, 27 (1893); compare Veley and Manley: **62**, 223 (1897); **68**, 128 (1901).

[2] J. Am. Chem. Soc. **33**, 292 (1911).

Following the analogy of nitrous acid, I suggest that hyponitrous acid will undergo change according to the following equilibrium relation.

$$3H_2N_2O_2 \rightleftarrows 2HNO_2+N_2+H_2O \qquad (1)$$

Although Rây and Ganguli[1] have shown that hyponitrous acid decomposes into nitric acid and not to nitrous acid.

$$5H_2N_2O_2=4H_2O+2HNO_3+4N_2 \qquad (2)$$

I am of the opinion that hyponitrous acid decomposes into nitrous acid which in its turn passes into nitric acid. We are trying to establish equilibrium experimentally.

De Girard and de Saporta[2], Dey and Sen[3] and Sommer[4] have studied the action of nitrous acid on hydrazine.

Solutions of metallic nitrites and hydrazine disulphate react vigorously even at 0°, the gases evolved containing two volumes of nitrous oxide to one volume of nitrogen.

Sommer has shown that hydrazine nitrite $N_2H_4HNO_2$ decomposes according to the equation $N_2H_4HNO_2=NH_3+N_2O+H_2O$ and this decomposition is very greatly accelerated by nitrous acid. The decomposition of ammonium nitrite has also been shown to be accelerated by the presence of nitrous acid[5]. If hydrazine disulphate and barium nitrite react together, the products are ammonium nitrite and nitrous oxide. Consequently under similar conditions hydrazine nitrite is less stable than ammonium nitirite.

From the foregoing facts it is clear that hydraxine is more readily acted upon by nitrous acid and hence the possibility of its existence as a reduction product of nitric acid is much less than that of ammonia. Moreover Tanatar[6], Purgotti and Zanichelli[7] and Gutbier and Neundlinger[8] have shown that hydrazine decomposes into NH_3 and N_2 in presence of platinum. It is quite possible that other catalysts might accelerate the decomposition of hydrazine according to the equation $3N_2H_4=N_2+4NH_3$ and that in the reduction of nitric acid by reducing agents, the hydrazine formed will partly decompose according to the above equation. Consequently we seldom get hydrazine in the reduction of nitric acid by metals like Zn, Al, Fe, Mg, etc.

I am of the opinion that hydrazine can be a direct product in the reduction of nitric acid by metals like Zn, Mg, etc., although hydrazine is not usually found in such reaction and we get ammonia instead, because hydrazine is more readily oxidized by nitrous acid than ammonia.

It has been already stated that the following substances are likely to be produced in the reduction of nitric acid by metals or other reducing agents:

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[1] J. Chem. Soc. 91, 1866 (1907).

[2] Bull. 31 III, 905 (1904).

[3] Z. anorg. Chem. 71, 236 (1911).

[4] Z. anorg. Chem. 83, 119 (1913).

[5] Veley: J. Chem. Soc. 83, 736 (1903); Blanchard: Z. physik. Chem. 41, 681 (1902).

[6] Z. physik. Chem. 40, 475; 41, 37 (1902).

[7] Gazz. 34 I, 57 (1904).

[8] Z. physik. Chem. 84, 203 (1913).

$H_2N_2O_5$, $H_2N_2O_4$, $H_2N_2O_3$, $H_2N_2O_2$, H_2N_2O, NH_2OH, N_2H_4 and NH_3. Now some of these compounds are extremely unstable and decompose readily into NO_2, NO, N_2O and N_2, whilst some others will react on each other also forming more or less the same substances—that is why all the direct reduction products of nitric acid cannot be obtained at the same time.

In this connection it will be interesting to note that according to Sommer, hydrazoic acid is formed as a product of the secondary reaction between hydrazine and nitrous acid and is due to the action of nitrous acid on the ion N_2H_5 derived from the dissociation of $N_2H_5NO_2$ ($N_2H_4HNO_2$).

Summary

1. It appears that there is no fundamental difference in the nature of the oxidation of metals and of other substances like starch, sugar, etc., by nitric acid.

2. The action of nitric acid on metals is similar to that of solutions of persulphates on metals.

3. The hypothesis that the action of nitric acid on metals is electrolytic in nature and that of Acworth and Armstrong who regard that hydrogen of the acid is first replaced by the metals, seem inadequate.

4. The partial oxidation of sugar by nitric acid to oxalic acid is accelerated by vanadium pentoxide and manganous sulphate.

5. The complete oxidation of oxalic acid by nitric acid is accelerated by vanadium pentoxide, manganous sulphate and nitrous acid but retarded by molybdic acid, silver oxide, etc.

6. The oxidations of metals, starch, sugar, oxalic acid, arsenious oxide, etc., by nitric acid are all autocatalytic and are accelerated by nitrous acid.

7. The action of nitric acid on metals like copper, silver, etc., is accelerated by ferrous and ferric salts, because these salts help in the formation of the active substance, nitrous acid.

8. Metallic copper disolves in ammonium nitrite solution (or in a mixture of any ammonium salt and a nitrite) because the products of hydrolysis NH_4OH and HNO_2 derived from ammonium nitrite ($NH_4NO_2+H_2O \rightleftarrows NH_4OH+HNO_2$) exert a marked solvent action on copper.

9. It seems certain that nitric acid is at first reduced to nitrous acid, by the action of metals like Bi, Hg, Cu, Ag, etc., $FeSO_4$, sugar and similar reducing agents. Nitric oxide (NO) is produced in these reactions mainly by the decomposition of nitrous acid.

10. Mercury dissolves copiously in nitric acid to which sodium nitrite is added, but no mercurous nitrite is produced in this way. Nitric acid of 26% concentration by its action on mercury produces the maximum yield of mercurous nitrite.

11. By the action of nitric acid on metals like Cu, Ag, Hg, and Bi, we can get HNO_2 or $H_2N_2O_2$ but not NH_2OH, N_2H_4 and NH_3, which can only be formed by the action of metals like Zn, Mg, Al, Fe, Cd, etc., which can

actually hydrogenate nitric acid, whilst Cu, Ag, Bi, Hg, etc., can only take away oxygen from nitric acid and cannot add hydrogen to it, as these metals do not set free hydrogen from acids or from water.

12. It seems probable that hyponitrous acid will be decomposed according to the following reaction:

$$3H_2N_2O_2 \rightleftarrows 2HNO_3 + N_2 + 2H_2O.$$

Hence in a solution containing hyponitrous acid we get $H_2N_2O_2 \rightleftarrows HNO_2 \rightleftarrows HNO_3$.

13. Hydrazine can be a direct product in the reduction of nitric acid by metals, although we seldom get it in this way because it is much more readily oxidized by nitrous acid than ammonia.

14. The formation of traces of nitrogen obtained in the oxidation of metals like Cu, Ag, etc., by nitric acid is due to the decomposition of hyponitrous acid. The formation of nitrogen in these cases cannot be due to the interaction of hydroxylamine and hyponitrous acid or that of ammonia and nitrous acid, because hydroxylamine and ammonia are not formed by the action of nitric acid on copper, silver, etc.

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Allahabad, India,
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THE ACID PROPERTIES OF AMMONIUM SALTS IN LIQUID AMMONIA

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It is the purpose of the present investigation to show the extent to which solutions of ammonium salts in liquid ammonia possess acid properties. A study has therefore been made of the action of such solutions upon a number of elements.[2]

Franklin[3] found that magnesium is readily acted upon by a solution of ammonium nitrate or iodide to give magnesium nitrate of iodide hexammonates, and that the blue colors of solutions of the alkali and alkaline earth metals in liquid ammonia are discharged by solutions of ammonium salts. The bases of the ammonia system, that is, the metallic amides, imides and nitrides, insofar as investigated, were found to dissolve in or to react with solutions of ammonium salts.[4] Franklin and Kraus[5] found that solutions of ammonium salts change the color of indicators in liquid ammonia. Divers states that potassium sodium, zinc and calcium dissolve in the very concentrated solution of ammonium nitrate in liquid ammonia known as Divers' solution without evolution of gas and with the formation of nitrites. The hydroxides of potassium and sodium and many metallic oxides were found slowly to dissolve. Magnesium dissolves with the evolution of hydrogen and the formation of nitrites. Iron, aluminum, nickel, tin, silver, platinum, lead, bismuth, copper and mercury remain practically unattacked[6]. Davis, Olmstead, and Lundstrom[7] during an investigation of the systems ammonium nitrate-ammonia-water and ammonium thiocyanate-ammonia-water noticed that the concentrated solutions of these salts in liquid ammonia rapidly corroded the steel containers first used in their work. Browne and Houlehan[8] have found that the alkali and alkaline earth metals and magnesium dissolve in ammonium ammononitrate solution[9] with the evolution of approximately the theoretical volume of hydrogen. Tin and aluminum are not attacked to an appreciable extent. Franklin[10] found that zinc and manganese are readily attacked by a dilute solution of ammonium nitrate in liquid ammonia. The

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[1] National Research Fellow.

[2] The hydrogen ion in ammonia, just as in water, is solvated, the complexes formed in the latter case being relatively unstable. For a discussion of the solvation of the hydrogen ion and of the nature of the acidic ion in ammonia, see Kraus: The Properties of Electricity Conducting Systems, 198-210, 313-316, (1922).

[3] J. Am. Chem. Soc., **35**, 1459 (1913); Franklin and Kraus: Am. Chem. J., **23**, 305 (1900); J. Am. Chem. Soc., **27**, 822 (1905).

[4] Cf. Franklin: J. Phys. Chem. **16**, 690 (1912).

[5] Am. Chem. J., **23**, 305 (1900); J. Am. Chem. Soc., **27**, 822 (1905).

[6] Proc. Roy. Soc., **21**, 109; Phil. Trans., **163**, 368 et ff.

[7] J. Am. Chem. Soc., **43**, 1583 (1921).

[8] J. Am. Chem. Soc., **33**, 2742 (1911).

[9] = Ammonium azide or hydrazoate. Cf. Franklin: J. Am. Chem. Soc., **46**, 2142 (1924).

[10] Unpublished Observations.

phenomenon of ammonolysis in liquid ammonia is strictly analogous to hydrolysis in water. The ammonolysis of salts in liquid ammonia may be prevented by the addition of a suitable quantity of the ammonium salt of the anion, just as hydrolysis in aqueous solution may be prevented by addition of the acid containing an anion in common with the solute[1].

It was found in the present work that lanthanum, cerium, manganese, aluminum (amalgamated), cadmium, iron, nickel, and cobalt are all attacked by solutions of ammonium salts at room temperatures with the formation, in a few months in the case of the slowest reaction, of sufficient material for an accurate analysis. The rate of reaction was greatest with lanthanum, cerium, and manganese. Tin, arsenic, molybdenum, chromium, gallium, lead, copper, thallium and selenium all either failed to react or else reacted only to a very slight degree with solutions of ammonium salts.

Experimental Work

In the following, the same experimental procedure has been uniformly followed. Reference will merely be made to articles of Franklin and coworkers containing descriptions of the manipulations used in working with liquid ammonia solutions at laboratory temperatures[2]. When a reaction took some time for completion, it was necessary to seal off the stopcock of the reaction tube to prevent loss of ammonia. In view of the fact that several of the compounds prepared are already known, analyses will be given in many instances without the support of analytical data.

Aluminum

Unamalgamated aluminum is not attacked in the least by a dilute solution of ammonium nitrate. Amalgamated aluminum, however, slowly dissolves with visible evolution of gas with the formation of readily soluble aluminum nitrates and perhaps, in addition, reduction products of the nitrate radical. Solutions of normal or acid aluminum nitrates ammonolyze on sufficient dilution with the formation of a white precipitate. A moderately dilute solution of ammonium thiocyanate dissolves amalgamated aluminum with visible evolution of gas. Since, on continued action, very soluble ammonobasic aluminum thiocyanates are formed, it was not found possible to isolate a compound of definite composition. Soluble ammonobasic aluminum iodides are known[3]

Manganese: $MnBr_2 \cdot 6NH_3$.

Manganese in lump form is very readily attacked by solutions of ammonium nitrate or bromide, the product formed in the latter case being

$MnBr_2 \cdot 6NH_3$. Found Mn 17.5, N 26.6. Calc. Mn 17.3, N 26.6.

Manganese reacts readily with a solution of ammonium cyanide, and more slowly with the slightly soluble ammonium bichromate.

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[1] Franklin and Cady: J. Am. Chem. Soc. 26, 512 (1904); Franklin: 27, 826 (1905).

[2] J. Am. Chem. Soc., 27, 832 (1905); 29, 1694 (1907); 35, 1460 (1913); 46, 1545 (1924); Jour. Phys. Chem., 15, 915 (1911); 16, 694 (1912).

[3] Franklin: J. Am. Chem. Soc., 37, 849 (1915).

Lanthanum: $LaI_3 \cdot xNH_3$.

Lanthanum very readily dissolves in a solution of ammonium iodide in liquid ammonia with the formation of lanthanum triiodide, which is moderately soluble at room temperatures. On concentration of a clear solution of this salt, two liquid phases are formed, the denser phase being relatively rich in lanthanum iodide. The solubility of this phase increases with decreasing temperature, indicating the existence of a lower critical end point, which probably lies above 0°. An abundant crop of small white crystals of an ammonated lanthanum iodide was obtained by cooling a solution of the latter to −40°. One specimen, dried in a vacuum at 140°, was found on analysis to contain 24.8 La, 62.4 I, and 12.2 NH_3, corresponding approximately to the formula $LaI_3 . 4NH_3$. The lanthanum contained small quantities of cerium and other rare earth metals.

Cerium: $CeI_3 \cdot 7\frac{1}{2}$ or 8 NH_3, $CeBr_3 \cdot 7\frac{1}{2}$ or 8 NH_3.

Cerium, like lanthanum, dissolves very readily in a solution of ammonium iodide to form cerium triiodide, which closely resembles in properties the corresponding lanthanum compound, and so need not be further described. The denser cerium iodide rich phase is however noticeably less soluble in ammonia. Both lanthanum and cerium iodide ammonates are slowly decomposed by water and are readily soluble in dilute sulfuric acid.

Cerium iodide was prepared by the action of a solution of ammonium iodide upon a large excess of cerium. The solution of cerium iodide after a few days was separated from the excess cerium by decantation into the other leg of the reaction tube, where, without further purification, it was evaporated to dryness, dried in a vacuum, and submitted to analysis.

Cerium was determined as oxalate and ammonia was estimated by distillation with sodium hydroxide. Iodine in the entire acid solution of the preparation was precipitated as silver iodide.

Preparation 1: Subst. (140°)0.8088[1]. (20°) 0.9065. (2/5) 0.0952 CeO_2. (1/1) 0.9914 AgI. (2/5) 0.03229 NH_3.

Preparation 2: Subst. (140°) 1.0929. (170°, heated only for short time as vapors of iodine were formed) 1.0891. (20°) 1.2356. (1/1) 1.3199 AgI. (3/5) 0.1990 CeO_2. (2/5) 0.04159 NH_3.

20°: No. 1: Ce 21.4, I 59.1, NH_3 19.7; No. 2: Ce 21.9, I 57.8, NH_3 20.3. Calc. for $CeI_3 \cdot 7\ 1/2\ NH_3$: Ce 21.6, I 58.7, NH_3 19.7.

140°: No. 1: Ce 24.0, I 66.3, NH_3 10.0. No. 2: Ce 24.7, I 65.3, NH_3 9.9. Calc. for $CeI_3 \cdot 3\ 1/2\ NH_3$: Ce 24.2, I 65.7, NH_3 10.2.

The higher ammonate may be $CeI_3 \cdot 8NH_3$. Both ammonates are effluoresced white solids.

Cerium readily reacts with a solution of ammonium bromide to form ammonated cerium tribromide, sparingly soluble in liquid ammonia at room

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[1] For the method of reporting analyses see J. Am. Chem. Soc., 46, 1547 (1924).

temperatures. The following specimen was contaminated with small quantities of ferrous bromide hexammonate and bromides of rare earth elements present as impurities in the cerium metal. Subst. (20°) 0.9489. (130°) 0.7645. (1/1) 1.0489 AgBr. (2/5) 0.02147 NH_3. (1/5) 0.1067 $Ce_2(SO_4)_3$. (2/5) 0.1284 CeO_2.
20°: Ce 27.6, NH_3 25.1, Br 47.0. Calc. for $CeBr_3.7\ 1/2\ NH_3$, Ce 27.6, Br 47.2, NH_3 25.1.

Cadmium: $Cd\ (NO_3)_2 \cdot 6NH_3$.

Cadmium foil reacts slowly with a moderately dilute solution of ammonium nitrate to form slightly soluble cadmium nitrate hexammonate, which for the most part forms well defined colorless transparent crystals. Found, Cd 33.8, NH_3 29.9. Calc. for $Cd(NO_3)_2 \cdot 6NH_3$ Cd 33.2 NH_3, 30.2. The specimen perhaps contained a small quantity of metal. The substance was dried in vacuo at −33°, no appreciable loss of ammonia occurring on heating to 20°.

Iron: $Fe\ (NO_3)_2 \cdot 6$ and $\cdot 4NH_3$, $(NH_4)_4\ Fe(CN)_6 \cdot xNH_3$, and $FeBr_2 \cdot 6NH_3$.

Iron wire reacts very slowly with solutions of ammonium nitrate, ammonium cyanide, ammonium bromide and ammonium thiocyanate to give, in the first three instances, the three salts named above. Iron was even found to react with extreme slowness with the almost insoluble salts ammonium sulfate and ammonium oxalate. It is possible that the internal corrosion of refrigerating machines has been due in part to the presence of small quantities of ammonium salts in solution in the liquid ammonia used.

Ferrous Nitrate.

Specimen No. 1 was prepared by the action of a solution of ammonium nitrate upon iron powder containing several percent of oxide. Subsequent attempts to prepare ferrous nitrates by using a 99.2 percent powder for some reason failed. Specimen No. 2 was made by the action of a solution of ammonium nitrate upon the black precipitate prepared by the action of an excess of potassium amide upon ferrous iodide.[1]

The pale green crystals thus obtained were transferred by repeated extractions to the other leg of the reaction tube, washed a few times and prepared for analysis.

Preparation 1: Subst. (25°) 1.4285. (82°) 1.2349. (¼) 0.08437 NH_3. (¼) 0.1023 Fe_2O_3.

Preparation 2: Subst. (−40°) 0.5311. (20°) 0.5268. (¼) 0.04814 NH_3. (¼) 0.0372 Fe_2O_3.
Found (20°) No. 1: Fe 20.1, NH_3 37.2. No. 2: Fe 19.8, NH_3 36.6.
Calc. for $Fe\ (NO_3)_2 \cdot 6NH_3$, Fe 19.8, NH_3 36.2.
Found (82°) No. 1: Fe 23.2, NH_3 27.3. Calc. for $Fe\ (NO_3)_2 . 4NH_3$, Fe 22.5, NH_3 27.5.
It is possible that No. 1 contained some metallic iron.

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[1] Cf.. Am. Chem. Soc., 46, 1558 (1924).

Ferrous Bromide.

A solution containing 1.2 g. ammonium bromide had at the end of four months reacted with an excess of iron wire to form about 0.7 g. ferrous bromide hexammonate. Fe 17.6, N 26.0. Calc. for $FeBr_2 \cdot 6NH_3$, Fe 17.6, N 26.4

Ammonium Ferrocyanide: $(NH_4)_4$ Fe $(CN)_6 \cdot xNH_3$.

A substance whose analyses and properties support the above formula is formed by the action of a solution of ammonium cyanide in liquid ammonia upon iron wire. The reaction, which is very slow, leads to the formation of highly refracting light yellow or green crystals which could not be washed without decomposition. The two following analyses were consequently made of the fine white precipitate prepared by washing the crystals originally deposited. The preparation of this compound was carried out in a two legged reaction tube having a side tube sealed on near the top to facilitate introduction of the hydrocyanic acid. This latter was distilled directly into the reaction tube from which air had previously been displaced by ammonia. The white precipitate produced by decomposition of the crystals dissolved in water with the formation of a colorless solution. Iron and cyanogen were determined by the mercuric oxide method of Rose-Finkener[1].

These analyses are a trifle uncertain because of the application of a relatively large correction for non-volatile matter in the HgO.

Preparation 1: Subst. (20°) 0.3094. (¼) 0.0188 Fe_2O_3.
(¼) 0.02463 NH_3. (¼) 0.1537 Ag, total –CN.

Preparation 2: Subst. (20°) 0.2907. (¼) 0.0190 Fe_2O_3. (¼) 0.02187 NH_3. (¼) 0.1462 Ag, total –CN.
Found: No. 1: Fe 17.0, Ammonia N 26.2, CN 47.9. No. 2: Fe 18.3, Ammonia N 24.8, CN 48.5.
Calc. for $(NH_4)_4Fe\ (CN)_6 \cdot 2NH_3$: Fe 17.6, N 26.4, CN 49.2.
The white precipitate accordingly consists chiefly of an ammonated ammonium ferrocyanide.

Iron and Other Ammonium Salts.

Ammonium oxalate and sulfate had at the end of five months reacted with a few milligrams of iron, indicating that these two salts possess a slight solubility in ammonia.

Cobalt.

A solution of ammonium nitrate was found to react very slowly with sheet cobalt, the resulting product being readily soluble in liquid ammonia with the formation of a pinkish red solution.

Nickel: $Ni(NO_3)_2 \cdot 6NH_3$.

A solution of ammonium nitrate reacts very slowly with a cube of nickel to form well defined blue crystals of nickel nitrate hexammonate, which are slightly soluble in liquid ammonia. Ni 21.1, ammonia N 29.5. Calc. for Ni $(NO_3)_2 \cdot 6NH_3$, Ni 20.6, N 29.5. The specimen probably contained a little free metal.

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[1] Analytical Chem., Treadwell-Hall, II p. 343. Wiley and Sons, New York (1915).

Other Elements:

A 0.7 N solution of ammonium nitrate had no action on a lump of chromium in five weeks. A small slab of impure thallium lost 0.02 g. after five months contact with a 0.7 N solution of ammonium nitrate. Commercial gallium at first was slowly attacked by a solution of ammonium bromide, probably because of the presence of impurities. An 0.8 N solution of ammonium bromide failed to react in the slightest degree with a rod of lead in five months. The surface of the rod had previously been cleaned by the action of a dilute solution of sodium. A strong solution of ammonium chloride had no action upon a piece of selenium in seven weeks. In three months a moderately strong solution of ammonium bromide had dissolved 1 mg. tin. Molybdenum powder and arsenic were attacked to a very slight extent by ammonium nitrate, the action perhaps being due to impurities on the surface of the specimens.

In conclusion, the author wishes to thank Dr. Franklin for his kind and helpful interest in this work.

Summary

(1) This article is intended to call attention to the fact already pointed out by Franklin that ammonium salts behave as acids in liquid ammonia solution. It has been shown, in conjunction with earlier work, that solutions of ammonium salts react with most of the elements above hydrogen in the electropotential series as it is known in water.

(2) The following ammonates have been prepared during the course of this work for the first time: $LaI_3{\cdot}xNH_3$, $CeI_3{\cdot}7\frac{1}{2}$ or 8 NH_3, $CeBr_3{\cdot}7\frac{1}{2}$ or 8 NH_3, $Fe(NO_3)_2{\cdot}6$ and $\cdot 4$ NH_3.

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FURTHER EVIDENCE ON THE CHEMICAL THEORY OF THE PROTECTIVE ACTION OF SUGARS. II

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In a previous paper[1] it has been shown that when sugar solutions are mixed with solutions of arsenic and antimony hydrosulphide, the amount of actual rotation observed in the mixture is always less than the amount expected on Beer's Law, showing that the amount of sugar actually adsorbed by the colloidal particles does not contribute to the optical rotation of the mixture. Further experiments were also described in the paper (loc. cit.) to show that the elements constituting the sugar molecules were actually present in the coagula although on solution the coagula did not exhibit any optical rotation. As the coagula tried were the sulphides of antimony and arsenic, they were dissolved in alkali solutions and it was feared that the muta-rotation of sugars might have been responsible for making the rotation due to the small amount of sugar adsorbed undetectable. This was argued out in the previous paper to be almost an impossibility. In this paper actual experiments have been performed to show that even the lowest rotations due to the smallest amount of sugar adsorbed do not show a null rotation on treatment with alkalis and acids, and that the complete absence of optical activity in the adsorbed sugar is to be traced to some cause other than the muta-rotation produced by the dissolving agents. Also some precipitates like zinc oleate, aluminium palmitate, aluminium stearate soluble in organic solvents and requiring less drastic treatment for dissolving, than the sulphides of antimony and arsenic, have been used in this investigation. In order to obviate the complexities which might arise with some sugars due to the hydrolysis of the sulphide sols, colloidal solution of selenium was also tried. The general trend of the results is in the same direction as in the previous paper.

Experimental

The colloidal solutions used were those of arsenic, antimony and cadmium hydrosulphides, and selenium. The former two sols were prepared as detailed in the last paper. The cadmium sulphide sol was prepared by precipitating the sulphide from an ammoniacal solution of cadmium chloride. The cadmium sulphide precipitate was repeatedly washed with distilled water until it was free from any chloride. Then it was suspended in a sufficient quantity of distilled water and a rapid current of hydrogen sulphide was passed till the whole of the precipitate had been peptised into a transparent sol. Hydrogen sulphide was got rid of by boiling the sol. Great care was taken to see by the lead-acetate reaction that there was no free hydrogen sulphide present in the sols of arsenic, antimony and cadmium hydrosulphides. The selenium sol was prepared by reducing a solution of selenium dioxide in gum arabic by

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[1] J. Phys. Chem. 28, 730 (1924).

means of phenyl hydrazine hydrochloride. After reduction the sol was dialysed till the water in the trough of the dialysing apparatus was completely free from any chloride. All these sols were preserved in glass-stoppered bottles.

Optically active sugars used were sucrose, arabinose, mannose, maltose, laevulose and xylose. These sugars were mostly those supplied by the British Drug House. As they were not quite pure their specific rotations had to be determined separately for the experiments described below and for the wavelengths used. The polarimeter used was Tripartite field, International sugar scale Polarimeter manufactured by Adam Hilger, Ltd. The source of light used was an arc lamp with potassium bichromate filter.

Before doing regular experiments with colloidal solutions a very dilute solution of sucrose was taken and its rotation found out. Afterwards it was diluted by means of an equal volume of a strong NaOH solution and kept for 24 hours to see the change in the rotation. The results of one experiment are given below:—

Original Rotation	Rotation expected on dilution	Rotation observed
0.230	0.115	0.100

The above results clearly show that the effect of alkali is not to nullify the very small rotations due to dilute solutions of sugar. Therefore the null rotation observed in the solution got by dissolving the washed coagula supposed to have adsorbed sugar cannot be due to the muta-rotation brought about by the alkali but must be accounted for on some other basis.

The results of experiments with mixtures of various sols and sugars are given below in Tables I-X.

After the experiments on sols, some bivalent and trivalent soaps were also tried as adsorbents. For this measured quantities of the sugar solutions were put in glass-stoppered bottles. In these were put weighed amounts of the soap powders. After shaking once or twice, the bottles were kept aside for 12 hours. With these bottles another bottle was also put containing the original sugar solution. Afterwards the rotations in the original sugar solution and the solutions got by filtering the contents of other bottles were examined. In order to investigate the state of the adsorbed sugar as regards its activity, some of the precipitates used in the above experiments were washed three or four times with distilled water and dissolved as much as possible in alcohol and the rotation observed in the solution. In each case it was invariably found that the rotation was nil, thus supporting the results described in Part I. Incidentally it may be mentioned here that the adsorption due to the filter paper while filtering is inappreciable as no appreciable difference in the rotations of sugar solutions was observed before and after filtration.

Experiments were also made with magnesium oxide. Results obtained by this on dissolving it in a dilute solution of hydrochloric acid were also similar to those described above.

The results of experiments with aluminium stearate, aluminium palmitate, zinc oleate and magnesium oxide are described in Tables XI-XIII.

TABLE I

Optically active substance used : Arabinose
Specific rotation taken =+91.6
220 mm. tube used
Colloidal substance used: Cadmium sulphide hydrosol containing 7.52 gm. of Cadmium per litre.

Original rotation =+5.71
Quantity of Arabinose present per 100 c.c. of the solution=2.8330 gm.

Equivalent quantity of Cadmium per litre.	Ratio of the original sugar solution to the sol.	Rotation expected	Actual rotation observed	Quantity of the sugar present per 100 c. c. of mixed solution examined.	Quantity of the sugar adsorbed per 100 c. c. of the sugar solution.	Quantity adsorbed by the mixture containing 100 c. c. of the sugar solution and the sol in the corresponding ratio indicated in column (2).
7.52 gms	1 : 1	2.86	2.67	1.3250 gms	0.1830 gms	0.3660 gms
	1 : 2	1.90	1.74	0.8634 ”	.2428 ”	0.7284 ”
	1 : 3	1.43	1.27	0.6302 ”	.3122 ”	1.2488 ”
3.76 gms	1 : 1	2.86	2.75	1.3650 gms	0.1030 gms	0.2060 gms
	1 : 2	1.90	1.81	0.8982 ”	.1384 ”	.4152 ”
	1 : 3	1.43	1.33	0.6601 ”	.1926 ”	.7704 ”
2.507 gms	1 : 1	2.86	2.78	1.3790 gms	0.0750 gms	0.1500 gms
	1 : 2	1.90	1.83	0.9082 ”	.1084 ”	.3252 ”
	1 : 3	1.43	1.36	0.6748 ”	.1338 ”	.5352 ”
1.88 gms	1 : 1	2.86	2.81	1.3940 gms	0.0450 gms	0.0900 gms
	1 : 2	1.90	1.86	0.9230 ”	.0640 ”	.1920 ”
	1 : 3	1.43	1.39	0.6898 ”	.0738 ”	.2952 ”

NOTE. Due to an oversight the headings of columns 6 and 7 in Tables II and VII of Part I of this Series (loc. cit), instead of being what they are written here, were put respectively as "Quantity of — — — — —adsorbed per 100 c. c. of the mixed solution examined" and "Quantity adsorbed per 100 c. c. of the sol". An incomplete erratum was communicated to this effect by D. L. S. In Tables IA and IB, Columns 6 and 7 have been calculated from the results described in the previous paper in order to bring the values of adsorption into closer comparison with the rest of results described in this paper.

TABLE IA

Column 6 Quantity of sugar adsorbed per 100 c. c. of the mixed solution examined	Column 7 Quantity adsorbed per 100 c. c. of the sol.

TABLE II[1]

0.133	0.266
0.138	0.207
0.126	0.168
0.104	0.208
0.109	0.164
0.096	0.128
0.074	0.148
0.079	0.119
0.067	0.089
0.045	0.090
0.048	0.072
0.037	0.049

TABLE III[1]

0.234	0.468
0.194	0.291
0.156	0.208
0.195	0.390
0.155	0.233
0.117	0.156
0.155	0.310
0.078	0.117
0.078	0.104
0.117	0.234
0.155	0.233

TABLE IV[1]

0.045	0.090
0.078	0.113
0.065	0.087
0.036	0.072
0.056	0.084
0.042	0.056
0.036	0.072
0.032	0.048
0.042	0.056
0.032	0.048

TABLE IB

Column 6 Quantity of sugar adsorbed per 100 c. c. of the mixed solution examined	Column 7 Quantity adsorbe per 100 c. c. af the. sol.

TABLE V[1]

0.502	1.004
0.307	0.461
0.221	0.295
0.435	0.870
0.281	0.422
0.201	0.269
0.314	0.628
0.206	0.309
0.133	0.177

TABLE VI[1]

0.199	0.398
0.141	0.212
0.148	0.197
0.181	0.362
0.078	0.104
0.129	0.258
0.097	0.146
0.056	0.075
0.040	0.080
0.035	0.053
0.056	0.075

TABLE VII[1]

0.163	0.326
0.106	0.159
0.160	0.213
0.071	0.142
0.054	0.081
0.117	0.156
0.060	0.120
0.025	0.038
0.044	0.088
0.025	0.038
0.052	0.069

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[1] Number of Tables in the first part of this paper. Cf. J. Phys. Chem. 28, 730 (1924).

TABLE II

Optically active substance used: Sucrose
Specific rotation taken = +67.5
220 mm. tube used.
Colloidal substance used: Cadmium sulphide hydrosol containing 7.52 gms. of cadmium per litre.

Original rotation = +11.83
Quantity of sucrose per 100 c.c. of the solution = 7.968 gms.

Equivalent quantity of cadmium per litre.	Ratio of the original sucrose solution to the sol.	Rotation expected	Actual rotation observed	Quantity of sucrose present per 100 c. c. of the mixed solution examined	Quantity of sucrose adsorbed per 100 c. c. of the mixed solution examined.	Quantity adsorbed per 100 c. c. of the sol.
7.52 gms	1 : 1	5.92	5.39	3.629 gms	0.355 gms	0.710 gms
	1 : 2	3.94	3.83	2.579 "	.077 "	.116 "
	1 : 3	2.96	2.85	1.919 "	.073 "	.097 "
3.76 gms	1 : 1	5.92	5.79	3.899 gms	0.085 gms	0.170 gms
	1 : 2	3.94	3.90	2.626 "	.030 "	.045 "
	1 : 3	2.96	2.95	1.986 "	.006 "	.008 "

TABLE III

Optically active substance used: Arabinose
Specific rotation = +91.6
220 mm. tube used.
Colloidal substance used: Arsenious hydrosulphide sol containing arsenic equivalent to 0.4879 gms. of As_2O_3 per litre.

Original rotation = +4.17
Quantity of arabinose per 100 c.c. of the solution = 2.0690 arsenic

Equivalent quantity of As_2O_3 per litre.	Ratio of the original arabinose solution to the sol.	Rotation expected	Actual rotation observed	Quantity of arabinose present per 100 c. c. of the mixed solution examined.	Quantity of arabinose adsorbed per 100 c. c. of the mixed solution examined.	Quantity adsorbed per 100 c. c. of the sol.
0.4879 gms	1 : 1	2.09	1.93	0.9579 gms	0.0766 gms	0.1532 gms
	1 : 2	1.39	1.23	0.6103 "	0.0794 "	.1191 "
	1 : 3	1.04	0.93	0.4615 "	0.0558 "	.0744 "
0.2439 gms	1 : 1	2.09	2.03	1.0070 gms	0.0275 gms	0.0550 gms
	1 : 2	1.39	1.34	0.6649 "	0.0248 "	.0372 "
	1 : 3	1.04	0.97	0.4814 "	0.0359 "	.0479 "
0.1626 gms	1 : 1	2.09	2.05	1.0170 gms	0.0175 gms	0.0350 gms
	1 : 2	1.39	1.36	0.6748 "	0.0149 "	.0224 "
	1 : 3	1.04	1.00	0.4963 "	0.0210 "	.0280 "
0.1220 gms	1 : 1	2.09	2.06	1.0220 gms	0.0125 gms	0.0250 gms
	1 : 2	1.39	1.36	0.6748 "	0.0149 "	.0224 "
	1 : 3	1.04	1.01	0.5012 "	0.0161 "	.0215 "

TABLE IV

Optically active substance used: Xylose

Specific rotation taken = +18.8

220 mm. tube used.

Original rotation = +.86

Quantity of Xylose present per 100 c.c. of the solution = 2.079 gms.

Colloidal substance used: Arsenious hydrosulphide sol containing arsenic equivalent to 0.4879 gms. of As_2O_3 per litre.

The sol and Xylose solutions were mixed in the ratio of 1:1

Quantity of Xylose per 100 c. c. of the mixture before adsorption.	Rotation expected	Actual rotation observed	Quantity of Xylose present per 100 c. c. of the mixture after adsorption	Quantity of Xylose adsorbed per 100 c. c. of the mixture.	Quantity of Xylose adsorbed per 100 c. c. of the sol.
1.0395 gms	0.43	0.32	0.7736 gms	0.2659 gms	0.5318 gms
0.5198 "	0.22	0.15	0.3626 "	0.1572 "	0.3144 "
0.3465 "	0.14	0.10	0.2417 "	0.1048 "	0.2096 "
0.2599 "	0.11	0.07	0.1692 "	0.0907 "	0.1814 "

TABLE V

Optically active substance used: Arabinose

Specific rotation taken = +91.6

220 mm. tube used

Original rotation = +7.83

Quantity of Arabinose present per 100 c.c. of the solution = 3.8860 gms.

Colloidal substance used: Antimony sulphide hydrosol containing antimony equivalent to 1.770 gms. of Sb_2O_3 per litre.

The sol and the Arabinose solutions were mixed in the ratio of 1 : 1.

Quantity of arabinose per 100 c. c. of the mixture before adsorption.	Rotation expected	Actual rotation observed	Quantity of arabinose present per 100 c. c. of the mixture after adsorption	Quantity of arabinose adsorbed per 100 c. c. of the mixture.	Quantity of arabinose adsorbed per 100 c. c. of the sol.
1.9430 gms	3.92	3.68	1.8260 gms	0.1170 gms	0.2340 gms
0.9715 "	1.96	1.79	0.8884 "	0.0831 "	0.1662 "
0.6477 "	1.31	1.18	0.5856 "	0.0621 "	0.1242 "
0.4858 "	0.98	0.89	0.4417 "	0.0441 "	0.0882 "
0.3886 "	0.78	0.72	0.3573 "	0.0313 "	0.0626 "

TABLE VI

Optically active substance used: Maltose
Specific rotation taken = +123.3
220 mm. tube used

Original rotation = +10.30
Quantity of Maltose present per 100 c.c. of solution = 3.7970 gms.

Colloidal substance used: Antimony sulphide hydrosol containing antimony equivalent to 0.835 gms. of Sb_2O_3 per litre.

The sol and the maltose solution were mixed in the ratio of 1 : 1.

Quantity of maltose present per 100 c. c. of the mixture before adserption	Rotation expected	Actual rotation observed	Quantity of maltose present per 100 c. c. of the mixture after adsorption	Quantity of maltose adsorbed per 100 c. c. of the mixture	Quantity of maltose adsorbed per 100 c. c. of the sol.
1.8985 gms	5.15	4.88	1.7990 gms	.0995 gms	0.1990 gms
0.9493 "	2.57	2.38	0.8776 "	.0717 "	.1434 "
0.6328 "	1.72	1.58	0.5826 "	.0502 "	.1004 "
0.4746 "	1.29	1.21	0.4462 "	.0284 "	.0568 "

TABLE VII

Optically active substance used: Laevulose
Specific rotation taken = −81.27
220 mm. tube used

Original rotation = −7.00
Quantity of Laevulose present per 100 c.c. of the solution = 3.9140 gms.

Colloidal substance used: Antimony sulphide hydrosol containing antimony equivalent to 0.885 gms. of Sb_2O_3 per litre.

The sol and the Laevulose solution were mixed in the ratio of 1 : 1.

Quantity of Laevulose present per 100 c. c. of the mixture before adsorption	Rotation expected	Actual rotation observed	Quantity of Laevulose present per 100 c. c. of the mixture after adsorption	Quantity of Laevulose adsorbed per 100 c. c. of the mixture	Quantity of Laevulose adsorbed per 100 c. c. the sol.
1.9570 gms	3.50	3.19	1.7840 gms	0.1730 gms	0.3460 gms
0.9785 "	1.75	1.57	0.8780 "	0.1005 "	0.2010 "
0.6523 "	1.17	1.02	0.5705 "	0.0818 "	0.1636 "
0.4893 "	0.88	0.80	0.4474 "	0.0419 "	0.0838 "
0.3914 "	0.70	0.64	0.3580 "	0.0334 "	0.0668 "

TABLE VIII

Optically active substance used: Mannose

Specific rotation taken $= +13.1$

220 mm. tube used

Original rotation $= +1.18$

Quantity of Mannose present per 100 c. c. of the solution $= 4.0950$ gms.

Colloidal substance used: Arsenious sulphide hydrosol containing arsenic equivalent to 0.4879 gms of As_2O_3 per litre.

The sol and the Mannose solution were mixed in the ratio of 1 : 1.

Quantity of Mannose present per 100 c. c. of the mixture before adsorption.	Rotation Expected	Actual Rotation Observed	Quantity of Mannose present per 100 c. c. of the mixture after adsorption.	Quantity of Mannose adsorbed per 100 c. c. of the mixture	Quantity of Mannose adsorbed per 100 c. c. of the sol.
2.0475	.590	0.53	1.8400 gms	0.2075 gms	0.4150 gms
1.0238	.295	.25	0.8674 "	.1564 "	.3128 "
0.6825	.197	.16	0.5551 "	.1274 "	.2548 "
0.5119	.148	.12	0.4164 "	.0955 "	.1910 "
0.4095	.118	.10	0.3469 "	.0626 "	.1252 "

TABLE IX

Optically active substance used: Maltose

Specific rotation taken $= +123.3$

220 mm. tube used.

Original rotation — $+5.84$

Quantity present per 100 c. c. of the solution $= 2.1534$ gms.

Colloidal substance used: Selenium sol.

The sol and the maltose solution were mixed in the ratio of 1 : 1.

Quantity of Maltose present per 100 c. c. of the mixture before adsorption	Rotation expected	Actual rotation observed	Quantity of Maltose present per 100 c. c. of the mixture after adsorption.	Quantity of Maltose adsorbed per 100 c. c. of the mixture.	Quantity of Maltose adsorbed per 100 c. c. of the sol.
1.0767 gms	2.92	2.80	1.0320 gms	0.0447 gms	0.0894 gms
0.5384 "	1.46	1.40	0.5162 "	0.0222 "	0.0444 "
0.3589 "	0.97	0.93	0.3430 "	0.0159 "	0.0318 "
0.2692 "	0.73	0.70	0.2581 "	0.0111 "	0.0222 "
0.2153 "	0.58	0.57	0.2102 "	0.0051 "	0.0102 "

TABLE X

Optically active substance used: Laevulose
Specific rotation taken = −81.27
220 mm. tube used
Colloidal substance used: Selenium sol.
Original rotation = −6.97
Quantity present per 100 c.c. of the solution = 3.8987 gms.

The sol and the Laevulose solution were mixed in the ratio of 1 : 1.

Quantity of Laevulose present per 100 c. c. of the mixture before adsorption.	Rotation expected	Actual rotation observed	Quantity of Laevulose present per 100 c. c. of the mixture after adsorption.	Quantity of Laevulose adsorbed per 100 c. c. of the mixture.	Quantity of Leavulose adsorbed per 100 c. c. of the sol.
1.9494 gms	3.49	3.42	1.9130 gms	0.0364 gms	0.0728 gms
0.6498 "	1.16	1.12	0.6263 "	0.0235 "	0.0470 "
0.4873 "	0.87	0.83	0.4641 "	0.0232 "	0.0464 "

TABLE XI

Optically active substance used: Arabinose
Specific rotation taken = +91.6
220 mm. tube used.
Original rotation = +4.14
Quantity of Arabinose per 100 c. c. of the solution = 2.0540 gms.

Adsorbent	Amount of arabinose present per 100 c. c. of the solution added	Rotation expected	Rotation observed	Amount of arabinose present per 100 c. c. adsorption	Amount of arabinose adsorbed.
2 gms. of Aluminium Atearate	2.0540 gms	4.14	4.04	2.0040 gms	0.0500 gms.
"	1.0270 "	2.07	2.02	1.0020 "	.0250 "
"	0.6847 "	1.38	1.34	0.6649 "	.0198 "
2 gms. of Zinc Oleate	2.0540 "	3.14	4.07	2.0190 gms	0.0350 gms
"	1.0270 "	2.07	2.03	1.0070 "	.0200 "
"	0.6847 "	1.38	1.36	0.6748 "	.0099 "

TABLE XII

Optically active substance used: Maltose
Specific rotation = +123.3
220 mm. tube used

Original rotation = +7.23.
Quantity of Maltose present per 100 c. c. of the solution = 2.66 gms.

Adsorbent	Quantity of maltose present per 100 c. c. of the solution added.	Rotation expected	Rotation observed	Quantity of Maltose present per 100 c. c. of the solution after adsorption	Quantity of Maltose adsorbed.
2 gms. of Zinc Oleate	2.6660 gms	7.23	7.15	2.6360 gms	0.0300 gms
"	1.3330 "	3.62	3.58	1.3200 "	.0130 "
"	0.8887 "	2.41	2.38	0.8776 "	.0111 "
2 gms. of Aluminium Palmitate	1.3330 gms	3.62	3.56	1.3120 gms	0.0210 gms
"	0.8887 "	2.41	2.37	0.8738 "	.0149 "

TABLE XIII

Optically active substance used: Mannose
Specific rotation = +13.1
220 mm. tube used

Original rotation = +.97
Quantity of mannose per 100 c. c. of the solution — = 3.3660 gms.

Adsorbent	Quantity of mannose present per 100 c. c. of the solution added	Rotation expected	Rotation observed	Quantity of Mannose present per 100 c. c. of the solution after adsorption.	Quantity of Mannose adsorbed.
2 gms. of Magnesium Oxide	3.3660 gms	.97	.84	2.9150 gms	0.4510 gms
"	1.6830 "	.49	.42	1.4570 "	0.2260 "
"	1.1220 "	.32	.30	1.0410 "	0.0810 "

Conclusions

It is evident from the results obtained on the colloidal solutions of cadmium antimony, arsenic sulphide and selenium shown in Tables I-X that the adsorbed sugars do not contribute to the rotation observed in a mixture of sugar and colloidal solution. Investigations on adsorption by precipitates such as aluminium stearate, aluminium palmitate, zinc oleate and magnesium oxide also lead to similar results. In the previous paper (loc. cit) the effect was shown to be due to the chemical nature of adsorption. The adsorbed sugar gets attached to the colloidal particles chemically probably destroying the asymmetry of carbon atoms of the sugar molecule and making the adsorbed amount of sugar optically inactive.

In an investigation undertaken in the Laboratories of the Benares Hindu University and shortly to appear in the Journal of the Faraday Society, Bhatnagar, Joshi and Ganguli have shown from a study of the adsorption—spectra that there is strong evidence in favour of compound formation when the protective agent is added to a colloidal solution. The shifts are characteristic of a chemical action in case of such protective colloids as sodium oleate and gelatine. It is intended to extend that work to sugars in order to find whether adsorption spectra measurements also would justify the view developed here.

The results show in a very striking and novel fashion that adsorption and protective action cannot be rationally interpreted on a purely Physical Theory, and the chemical forces therein active may produce such marked and anomalous results as described in the first two papers of this series.

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ON THE CONDITIONS OF PRECIPITATION, BY ELECTROLYTES, OF SELENIUM HYDROSOL AND OTHER HYDROSOLS

BY JAMES J. DOOLAN

While there is difference of opinion as to the manner in which colloid particles receive an electric charge, the statement of Jevons[1], and of Hardy[2], that such a charge exists, and is the chief factor in preventing coagulation is now generally accepted.

Schulze[3], and somewhat later, Linder and Picton[4], working with arsenious sulphide hydrosol, shewed that trivalent cations exert a greater precipitating effect than divalent ones, and that monovalent cations were least effective.

Whetham[5], pointed out that the figures of Linder and Picton for the ratios of the precipitating powers of equimolecular solutions of monovalent, divalent and trivalent cations may be represented by the formula $1 : x :: x^2$, x being a constant of 30 to 40.

Many exceptions to this Schulze-Picton-Linder "Law" have since been observed. Some of the most striking deviations from the "Law" are found in the results obtained by Odén[6] in his investigation of the precipitating effect of electrolytes on sulphur hydrosols.

An attempt is here made to determine whether similar discrepancies occur with hydrosols of the allied elements, selenium and tellurium.

On Selenium Hydrosol. The existing literature contains various methods for preparing this sol. The method used by Schulze[7], using sulphurous acid, was used throughout this work.

Preparation and Purification of Selenium Dioxide. It was found impossible to purify selenium dioxide by sublimation when prepared by the methods ordinarily described; some decomposition to the element caused a pink discolouration. Accordingly recourse was made to sublimation in a current of air. Even now a faint rose pink persisted. Hereupon, at the suggestion of Professor Partington the idea was employed of passing over this sublimed product a stream of ozonised oxygen at steam heat. This proved effective in bleaching the sublimate.

Although selenium trioxide was then unknown, tests were made with barium chloride in case any of the higher oxide had appeared. No precipitate was formed, although the solubility of barium selenate is only 82.5 gms. per litre[8].

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[1] Trans. Manchester Phil. Soc. 1870, p. 78.
[2] J. Physiol. **24**, 288 (1899).
[3] J. prakt. Chem. **25**, 431 (1882).
[4] J. Chem. Soc. **67**, 63-74 (1895).
[5] Phil. Mag. (5) **48**, 474 (1899).
[6] Z. physik. Chem. **78**, 682-707 (1912).
[7] J. prakt. Chem. (2) **32**, 390 (1885).
[8] Meyers and Friedrich: Z. physik. Chem. **102**, 369.

Further, selenium trioxide has since been isolated by the action of ozone on selenium, but its discoverers[1] found it necessary to dissolve the element in selenium oxychloride.

The pure colourless selenium dioxide eventually obtained as above was sublimed without any trace of decomposition, but was so hygroscopic that it was necessary to keep it in a desiccator over phosphorus pentoxide to prevent its passing to selenious acid.

Preparation of Selenium Sol. A uniform concentration of nominally, 0.5 gm. of selenium dioxide to the litre, was employed. The best procedure was found to be that of dissolving the compound in a small quantity of water at about 20°C and then passing gaseous sulphur dioxide until 0.58 gm. had been added. (Gutbier's optimum for precipitation.)

The whole was then made up to a litre with conductivity water, when the red precipitate first formed redissolved completely to a ruby sol.

Dialysis of Selenium Sol. References in the literature of the subject are mainly to the undialysed sol, or to sols which had been stablised, say by sodium lysalbinate or sodium protalbate.

In this work however it did not appear justifiable to assume that a stabilsed Selenium hydro sol possesses the characteristics of one in which selenium and water were alone concerned.

Zsigmondy[2] states, for example, that these three phase complexes take on many of the characteristics of the emulsoid. Further, results obtained by Billiter on the effect of electrolyte on the mobility of the particles of protected gold sol were not confirmed by Whitney and Blake[3], using the same sol unprotected. They attribute the discrepancy to the gelatine used as a stabiliser.

It was therefore decided to attempt purification by dialysis, of unprotected sols. As might be expected, considerable difficulty was here encountered. Parchment paper "sausage skin dialysers" were first employed. Although these were well washed to remove any sulphates, so easily did the sol precipitate in them that they were abandoned, as being too destructive on material, in favour of collodionised Soxhlet thimbles. Green's 30 m.m. x 100 m.m. thimbles were selected as being of suitable capacity.

Even now precipitation occurred at first, leaving a very dilute sol. On the second attempt with the same thimble, however, no precipitation occurred. Hence by using a battery of these "seasoned" thimbles dialysis proceded successfully. On starting new thimbles at any stage in subsequent working the phenomenon was again encountered. In the absence of any coagulating electrolyte it may have been due to membrane adsorption.

The sign of the particles was determined by cataphoresis with the ordinary Lodge apparatus and found to be negative.

During the research, all colloid 'solutions' had to be kept in the darkroom, and dialysis was also carried out there. This was due to the fact that light causes the rapid precipitation of the sol, apart from electrolyte action.

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[1] R. R. Le G. Worsley and H. B. Baker: J. Chem. Soc. **123**, 2870 (1923).

[2] "Kolloidchemie" Eng. Trans. p. 86, (1917).

[3] J. Am. Chem. Soc. **26**, 1339 (1904).

The hydrosols were not dialysed entirely free from electrolyte. Attempts to do so always resulted in the deposition of the selenium as a more or less coherent layer on the walls of the thimble. G. Rossi[1] found the same occurs with sulphur hydrosol containing sulphur compounds.

Consequently a method was employed in which dialysis was carried on until a content of electrolyte was reached which was the minimum consistent with stability of the sol.

The attainment of this concentration was indicated by the use of a dipping electrode, which was thoroughly cleaned and placed in the sol at intervals; the resistance being determined each time by means of Kohlrausch's apparatus, until a certain known value was obtained.

Dialysis was usually complete in about a week, with changes of conductivity water twice in the twenty four hours. The known value to which the resistance was taken was 9000 ohms, as against 60,000 ohms with conductivity water in the same apparatus and about 1000 with ordinary water. This represents a sol of specific conductivity 2.4×10^{-5} mho.

In this manner the sol could be reproduced exactly whenever a fresh batch was required.

The dialysed sol, when placed in containers of resistance glass which had been steam blown after the usual chemical cleaning, were quite stable for a month or six weeks in the dark room. One batch which had been left for a year was found to have thrown down a slight sediment, but the supernatant sol was clear.

Addition of Electrolyte to the Dialysed Hydrosol. Various standard solutions were made up from materials pure for quantitative analysis, and small quantities of the hydrosol were titrated by them until perceptible coagulation occurred. This method does not take account of the time factor, and that the concentration of the sol varies with different amounts of the coagulating solution.

For exact determinations the method selected was one due to Hatschek[2]; the titration expts. being, however, useful in affording a rough idea of the concentrations required, and thus indicating the strengths of precipitating solutions to be employed.

A set of resistance-glass coagulation tubes were obtained, each tube fitted with a glass stopper and graduated at 18 c.c. and at 20 c.c. Eighteen cubic centimetres of the dialysed sol were placed in a tube and two cubic centimetres of the coagulating solution added.

Thus the coagulating solution was diluted to one tenth of its original concentration and the concentration of the hydrosol was always the same. The sol and solution were mixed in each case by a uniform procedure and allowed to stand for two hours before examining.

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[1] Kolloid-Z. 30, 228-230 (1922).

[2] "Laboratory Manual of Colloid Chemistry," p. 91."

Reagent	Millimols per litre
NaCl	1000
AmCl	1000
$MgSO_4$	30
$ZnSO_4$	40
$BaCl_2$	15
$Al_2(SO_4)_3$	2

More dilute solutions of known strength were prepared by mixing in test-tubes, 8 c.c. of solution with 2 c.c. of water; 6 c.c. of solution with 4 c.c. of water; 4 c.c. of solution with 6 c.c. of water; and 2 c.c. of solution with 8 c.c. of water; these being labelled 0.8; 0.6, 0.4, and 0.2; their respective concentrations referred to the stock solution.

In cases, where, say, solution 0.6 failed to precipitate the sol after two hours, and that marked 0.8 completely precipitated it; a third solution of strength intermediate to these was tried, and in this way the exact precipitating concentration was obtained.

The limiting concentrations so found are set out in the following table:—

Reagent	Precipitating Sol.	Limit Concentration
NaCl	.4	40.00 millimols per litre.
NH_4Cl	.4	40.00 ” ” ”
$ZnSO_4$	.6	2.40 ” ” ”
$MgSO_4$	Stock (1.0)	3.00 ” ” ”
$BaCl_2$	.9	1.35 ” ” ”
$Al_2(SO_4)_2$	.5	0.10 ” ” ”

It can at once be seen that the order of importance is trivalent, divalent and monovalent for the ions, no monovalent ion being as powerful a precipitant as a divalent one, and aluminium being the most powerful. The lines of demarcation are clearly marked, also, as between monovalent ions and divalent ions, and between the latter and trivalent ions.

This shows the behaviour of selenium hydrosol to be materially different from that of Odén's sulphur, for which barium acts with more than twice the precipitating power of aluminium and potassium with three times that of zinc.

A feature common to both hydrosols is that the limiting concentrations of salts with cations of the same valency differ among themselves; potassium chloride being four times as powerful a precipitant for selenium as sodium chloride and barium nearly two and a half times as effective as magnesium. These differences are however much less accentuated than with Odén's sulphur.

Effect of the Halides of Potassium. It was considered of interest at this stage to investigate the possible effect of the second ion in electrolyte precipitation as a possible explanation of these differences.

Normal solutions of potassium fluoride, chloride, bromide and iodide were made up, and coagulation experiments made in the usual manner. The results are appended:—

Reagent	Precipitating Solution	Limit Concentration
KCl.	.10	10.00
KBr.	.25	25.00
KF	.60	60.00
KI.	.80	80.00

A remarkable lack of uniformity is apparent, the most notable feature being the very feeble coagulating action of potassium iodide.

Electrolyte Precipitation of Unprotected Tellurium Hydrosol

The fact that the behaviour, toward electrolytes, of selenium hydrosol was considerably less abnormal than that of sulphur sol naturally suggested examination of the case of tellurium sols, in case that in this group of elements rise in atomic weight and increasing metallic character had any lessening effect on observed discrepancies.

Preparation of Tellurium Hydrosol. Protected hydrosols of either element may be prepared with the greatest ease, and of extreme stability. The copious literature on this preparative work deals mainly with such protected sols. The exact converse, however, holds with the unprotected hydrosols. Certain of the given methods do yield a sol, but if of a reasonable concentration the sols have little or no stability and cannot stand dialysis.

It was originally intended to work from tellurium dioxide, reducing with SO_2, so as to attain complete analogy to selenium. The very slight water solubility of this oxide, however, and the fact that sulphurous acid precipitates it from alkaline solution, made this method unsatisfactory.

At this stage it was decided to prepare the more soluble compound of tellurium, viz., telluric acid, and to use this as a starting point. The method of Staudenmaier[1] was found tedious. So trial was made of a new method due to Meyer and Moldenhauer[2]. This method proved eminently satisfactory, giving a good yield of white crystal aggregates, easily soluble in water.

Preparation of the hydrosol from this was attempted according to a recipe given by Gutbier[3], in which ⅔ grms. of the purest crystalline telluric acid are dissolved in a litre of pure water at 40-50 degrees and treated with 1:2000 hydrazine hydrate solution; when colouration is supposed to be seen with the first few drops. In actual practice, drastic modifications of this method were required. In no case did any colour appear before several cubic centimetres of the reducing solution had been added.

Further the sol so made was not sufficiently stable.

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[1] Z. anorg. Chem. 10, 189 (1895).
[2] Z. anorg. Chem. 119, 132, (1921).
[3] Z. anorg. Chem. 32, 52, (1902).

The finally modified procedure was to dissolve the telluric acid in a small quantity of boiling water and then to add the hydrazine hydrate drop by drop until turbidity almost occurred.

Just at this point a large quantity of cold water was added, apparently peptising the "nascent" coagulum, so that, instead of a bluish sol, a quite stable, rich brown one resulted.

To secure perfect uniformity, in order that the sol so obtained could at any time be reproduced exactly, the weight of telluric acid used each time was 0.5 grms. in 50c.c. boiling conductivity water, and made up to 250 c.c. with cold water reduction being carried with that volume of the hydrazine solution which just fell short of complete reduction.

Cataphoresis shewed the charge on the particles to be negative, as with selenium. On the other hand, the stability of this tellurium sol does not appear to be affected by light. Old sols occasionally displayed a milkiness, as though the particles of tellurium had undergone superficial oxidation.

The "working conductivity" of the sol of tellurium was such that the resistance in the cell of the Kohlrausch apparatus was ten thousand ohms, representing a specific conductivity of 2.2×10^{-5} mho. This compares favorably with nine thousand for selenium, but the sulphur compounds which are formed in the first case make dialysis very tedious with selenium, and a certain amount is probably absorbed so to be unremovable by dialysis.

The Precipitation of the Sol by Electrolyte. This was carried out exactly as has been already described in detail under selenium, and with standard solutions of the same strengths.

The results are tabulated below.

Reagent	Millimols per litre	2 cc. of stock or more dilute solution ppt. 18 cc. of sol.	Hence ppting. concns. millimols per litre
$NaCl$	1000	0.40	40.00
NH_4Cl	1000	0.80	80.00
$MgSO_4$	30	0.9	2.7
$ZnSO_4$	40	0.20	0.80
$BaCl_2$	15	0.20	0.30
$Al_2(SO_4)_3$	2	0.20	0.04
KCl	1000	0.35	35.00
KBr	1000	9.35	35.00
KF	1000	0.50	50.00
KI	1000	0.60	60.00

It will be noticed that the precipitating effect of Al is again very pronounced, —even more than was the case with selenium.

Also the effect of barium is second to that of aluminium, as it was with selenium, although Odén found the reverse to be true with sulphur.

In connection with the very low efficiency of AmCl, it may be remarked that Svedberg[1] mentions that this salt exerts a particularly powerful influence. On the other hand, the value here given is similar to that found by Odén for sulphur.

The effect of potassium iodide appears to be slight, as with selenium, but the accuracy of the results with this salt could not be relied upon because chemical action of some kind was evident between it and the sol; apparently the potassium iodide reacts with the tellurium, or perhaps with traces of telluric acid, liberating iodine.

Examination of Results

The relationships of the sols of selenium and tellurium to the Schulze-Picton-Linder "law" may be conveniently illustrated by setting down the coagulative powers of the various electrolytes towards the sols and those of Odén. The coagulative powers are the reciprocals of the minimal concentrations. They were multiplied by a factor in order to make them readily comparable with Odén's figures.

In the first column of the table are set down the coagulating powers for a "typical" negative sol. The figures are of course not strictly comparable since the concentrations and methods of coagulation etc. differ.

Electrolyte	Coagulating Powers for sols of:			
	As_2S_3	Se	Te	S (Odén)
NaCl	2.5	2.5	2.5	6.1
NH_4Cl	*1.0*	2.5	1.25	2.3
KCl	2.5	10.0	3.8	47.5
KBr	——	4.0	3.8	——
KF	——	1.66	2.0	——
KI	1.0	1.25	1.66	——
$ZnSO_4$	60.0	41.4	125.0	13.2
$MgSO_4$	*29.0*	33.3	32.0	107.5
$BaCl_2$	*52.0*	74.0	333.0	475.0
$Al_2(SO_4)_3$	957.0	1000.0	2500.0	227 ($AlCl_3$)

Values in italics for As_2S_3 are from Linder and Picton: J. Chem. Soc. 67, 63 (1895); others for As_2S_3 are Freundlich.

In the case of Odén's sulphur alone is there an upsetting of the order of increasing precipitating power with rise of valency. A point common to selenium and Odén's sulphur is the considerable effect of potassium chloride, but while in Odén's case its effect exceeds that of zinc, this is not so with selenium. With this exception sols of selenium and tellurium behave similarly. It is curious that with potassium chloride there is a notable increase of coagulating power from tellurium to sulphur, while the reverse is true for aluminium. In no case have different divalent ions the same power and for all three sols barium is the most effective, but the differences are more exaggerated in the

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[1] "Die Herstellung Kolloider Lösungen anorganischer Stoffe", p. 110.

case of sulphur. It appeared noteworthy that the figures for selenium and tellurium bore much more resemblance to those of a "typical" negative sol than to those of Odén, particularly with regard to the effect of zinc and of aluminium. Freundlich[1] has shown that a sulphur sol prepared[2] by pouring an alcoholic solution of sulphur into water behaves less anomalously than Odén's sulphur. Freundlich and Scholtz[3] consider that the cause of the discrepancies in Odén's case may be due to adsorbed pentathionic acid and to Odén's sulphur being hydrophile. They suggest that addition of anything tending to destroy the pentathionic acid decreases the water content of the sol particles and thereby the stability derived from it. This would explain the sensitiveness of Odén's sulphur to alkalies. On the other hand Raffo's[4] sulphur which also contains pentathionic acid requires very little aluminium for coagulation.

Still, if one considers the figures for selenium it is obvious that no such law as that of Schulze is obeyed; the value of aluminium being smaller than the theory requires.

In the case of tellurium, if the figures for sodium chloride, zinc sulphate and aluminium sulphate be selected, the ratio 1:50:1000 results. This is not the ratio $1:x:x^2$ even though the most suitable figures have been arbitrarily selected. Such a result is not surprising in the present stage of colloid chemistry. It is commonly accepted that, even though a sol consist of particles of a single substance in a pure medium, other factors affect electrolyte precipitation than those taken into account in Whetham's calculation.

It was stated by Prost[5] that with a sol of cadmium sulphide, the concentration of the sol had no effect on the minimum of electrolyte required for precipitation. Since then much work has been done in which various electrolytes were added to sols in such a manner that the concentrations were haphazard.

Of late however the concentration has been shown to be an important factor. Some workers are of opinion that not only does a more dilute sol require more electrolyte but that altering concentration may alter the precipitating order of the electrolytes[6]. Burton and Bishop[7] report that the effect of divalent ions is independent of concentration. Odén[8] has also shown that the size of the particle has influence on the amount of electrolyte required. Recently, too, it has been recognised that if the charge on the colloid particle is to be neutralised as a preliminary to coagulation, a definite charge must be brought actually to the particle, and that adsorption of ions by the particle is a powerful factor, if not the most powerful factor in the precipitating power

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[1] "Kapillarchemie" p. 849 (1922).
[2] v. Weimarn and Malyschew: Kolloid-Z. 8, 216 (1911).
[3] Kolloidchem. Beihefte, 16, 234 (1922).
[4] "Kapillarchemie", p. 849 (1922).
[5] Bull. Acad. roy. Sci. de. Belg. (3) 14, 312 (1887).
[6] Kruyt and Duin: Kolloidchem. Beihefte, 5, 269 (1916).
[7] J. Phys. Chem. 24, 701 (1920).
[8] Z. physik. Chem. 78, 682 (1912).

of electrolytes[1]. It had long been known that one ion of the precipitating electrolyte was carried down in the coagulum. Linder and Picton[2] showed that Ba was carried down by arsenious sulphide sol and was not removable by boiling water.

Freundlich noted that salts of heavy metals and those with organic radicles were abnormally adsorbed, hence his conclusion that adsorption is a specific property of the particle and of the ions.

This readily explained the fact that ions of the same valency had not necessarily the same precipitating power.

Starting from the work of Linder and Picton on adsorption Duclaux[3] has propounded a theory that no sol is composed of particles of a pure substance but that foreign ions are always entertained in the micelle. The colloid particle is thus comparable to a molecule with one ion very large. Duclaux considers that the free ions of the micelle may be replaced by others of the same sign, and shows that if the replacing ions be pelyvalent a sharp fall in osmotic pressure occurs and so a tendency to precipitation results.

Neither of these theories takes the second ion into account. Duclaux, in fact, states definitely that it has no effect. Burton shares this view. In the preceding work however, the action of the halides of potassium does not appear capable of explanation if the second ion plays no part. The peculiar effect of potassium iodide has been noted before.

Partington[4] shewed that the opalescence of negative cholesterol sol is cleared up by addition of potassium iodide.

Briggs[5] too showed that addition of potassium iodide to gelatin prevented setting, while dialysis, by removing the salt, allowed setting again.

In order then to be in a position to determine whether Schulze's Law applies to a given hydrosol, one should fix the concentration and the size of the particles. The temperature, too, should be invariable, for it has been shewn that rise in temperature may either increase the peptising effect of the solvent and promote stability, or favour instability by reducing the adsorbing power of the particles.[6] Even now, however, in view of the principle of selective adsorption, and taking into account the considerable probability of the second ion exerting a peptising effect, it is difficult to imagine a simple law of the type of Schulze covering all the factors of coagulation.

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[1] Ostwald: Kolloid-Z. 26, 28 (1919); Freundlich: Z. physik. Chem. 85, 641 (1913); Bancroft: Trans. Am. Electrochem. Soc. 27, 175 (1915).

[2] J. Chem. Soc. 67, 63 (1885).

[3] "Les Colloides", 79 (1922).

[4] J. Chem. Soc. 82, 587 (1918).

[5] J. Phys. Chem. 24, 74 (1920).

[6] Linder and Picton: J. Chem. Soc. 87, 1906 (1905).

I desire to express my gratitude to Professor Partington for his continued interest in the work and for frequent and very helpful suggestions.

I wish also to thank the Department of Scientific and Industrial Research for a maintenance grant during a large portion of the time of this research, and the Council of the Chemical Society for a grant for apparatus and material of a specialised nature.

My thanks are also due to the American National Council for Research on the Uses of Selenium and Tellurium; who very kindly placed at my disposal a supply of tellurium and tellurium dioxide.

ON ADHESIVES AND ADHESIVE ACTION[1]

BY J. W. McBAIN AND D. G. HOPKINS

No systematic study of the action of adhesives appears to have been published, although various isolated suggestions have been put forward from time to time. In the endeavour to find a rational approach to the study of these phenomena and the general factors upon which they are dependent we have carried out many hundreds of qualitative and quantitative tests with the most diverse materials and adhesives.

It is our experience that joints are of two kinds; namely, mechanical and specific. Mechanical joints are possible only with porous materials, whereas specific adhesion occurs with smooth non-porous surfaces whether these are vitreous, polished or true crystal planes.

We find that a joint results between porous materials whenever any liquid material solidifies *in situ* to form a solid film embedded in the pores. The most important and rather surprising example of a purely mechanical joint is wood joined with gelatin or glue, where apparently even adsorption does not occur. An excellent model of a mechanical joint is obtained by spot welding silver gauze to silver plates so that a porous surface is formed in which embedding can occur. Such surfaces are strongly joined by gelatin whereas smooth silver surfaces are joined but feebly. In mechanical joints the zone of the bedding is often the chief source of weakness.

In the specific type of joint some species of interaction is involved between the smooth non-porous surface and the adhesive. It may be chemical or adsorption or mere wetting. A liquid which wets a surface and is then solidified possibly always makes a joint. The strength of many joints will of course be the resultant of both factors, mechanical and specific. The chief problem is to relate this specific factor to the general properties of the materials involved, and a suggestion in this direction will be made. A further factor into which enquiry is necessary is the nature and strength of the adhesive film itself, which has to transmit and withstand the stress. Another that was soon shown to be of importance is the effect of the solid materials in the formation of a coherent adhesive film.

Finally, it is impossible to overemphasize that the method of employing an adhesive is very frequently as important as the properties of the adhesive itself. Unsuitable procedure with a really good adhesive easily results in the production of unsatisfactory joints.

Qualitative Experiments

A qualitative study of a great variety of glued and cemented joints was made with the object of accumulating sufficient data to enable a satisfactory

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[1] The present investigation was undertaken for the Adhesives Research Committee of the Department of Scientific and Industrial Research and the authors are indebted to the Department for permission to publish the results. A more detailed account will be published by that Committee in their forthcoming Second Report.

explanation of adhesive action to be put forward. These tests were made simply by hand. The surfaces of the various materials were in most cases roughly plane but were thoroughly clean. In many instances the time allowed for the drying of the adhesive was insufficient. In addition, cemented areas varied considerably from material to material so that it was difficult to make an appropriate allowance. Notwithstanding these limitations the results undoubtedly convey some idea of the strength of a joint made under ordinary conditions.

The following adhesives and materials were used in this series of qualitative tests.

Adhesives. Canada balsam, casein and borax cement, commercial glue B, fish glue, a high grade commercial gelatin, commercial starch paste, glycerine cement, gum arabic, commercial nitrocellulose cement A, nitrocotton (alcohol-ether sol), shellac (ordinary and wax free), silicates of soda, starch.

Materials. Aluminum, calcite, charcoal, copper, ebonite, gas carbon, glass, lead, mica, nickel, porcelain (unglazed), pumice, rubber, silica (fused), steel, tin, wood.

The first result was to show that the weakness of many joints is due to the inability of the adhesive to dry between two non-porous surfaces. Subsequent quantitative experiments have shown that gelatin and many other adhesives between closely fitting discs of metal 0.75″ in diameter require as much as three weeks for thorough drying and even then there is the possibility that the maximum strength had not been attained. Drying was effected in numerous instances by the device of employing a "mixed" joint of the type material-adhesive-wood. As a rule the adhesive-wood linkage does not yield first so that the strength of the "mixed" joint depends on the degree of adhesion between the material and the adhesive, assuming of course that the adhesive film is sufficiently strong in itself to withstand the applied stress.

Observations on the Experimental Results

Porous bodies such as wood, unglazed porcelain, pumice, charcoal, etc., yield strong joints with the majority of recognized adhesives. It is obvious that a good joint must result whenever a strong continuous film of partially embedded adhesive is formed *in situ*. Formation of such joints would appear in many cases to be independent of adhesive action, and should then be a function of the mechanical strength of the embedded film. The failure of a few adhesives such as starch paste to unite certain porous materials was seen to be due to the complete soaking away of the adhesive or to the formation of excessively thin films incapable of filling the gap between the surfaces. Investigations into the thickness and strength of adhesive films showed that the thickness of a dried coating of starch paste was less than one thousandth of an inch (cf. footnote to Table III).

Further corroboration of the mechanical explanation of glued wooden joints was found when comparing stained and unstained wood joined with gelatin. Three successive coatings of Stephens' Ebony Stain were applied. With the soft wood (deal) neither the stained nor the unstained joints could be broken by hand but with hard wood (mahogany) the stained joints easily parted.

Calcite with gelatin is an illustration of a strong joint with a true crystal surface, and may serve as a model of true specific action.

Under favorable conditions of drying most adhesives form strong joints with polished glass and fused silica. This is probably not unconnected with the fact that we are here dealing with surfaces which are very nearly plane. These joints with vitreous surfaces cannot possible be due to the purely mechanical action operative in the case of porous bodies. There must be specific interaction between the adhesive and the material whether mere wetting, adsorption or chemical combination.

The results with metals were of interest in that they showed that good adhesives may be rendered ineffective unless appropriate conditions are ensured. If the films incompletely bridge the gap between the surfaces or if the adhesive dries imperfectly then no strong joint is possible. It will be shown later that extremely strong metal-adhesive joints are obtainable under suitable conditions.

In order to explain the action of lubricants W. B. Hardy assumes that the unsaturated molecules of the lubricant unite physico-chemically with the metallic surfaces to form a composite interface of oil and metal, or that the lubricant is adsorbed by the metal. Hence the interaction is truly specific. If, therefore, the fluid film of lubricant can be rendered tenacious by subsequently treating the joint with suitable refrigerants or by other methods a satisfactory joint should result.

Experiments carried out with (i) vaseline between steel and fused silica surfaces (ii) oleic acid between steel surfaces, showed that strong joints were obtained if the lubricants were cooled *in situ* with solid carbon dioxide.

It was also found possible to produce strong joints with water (frozen) and sulphur (molten and subsequently cooled) between fused silica and glass plates.

The above results are of special interest in that whilst they support Hardy's theory of specific interaction they furnish examples of adhesives of definite chemical composition.

Quantitative Tests of Various Joints

The quantitative tests comprise four series; namely:—

(a) Shear tests with walnut surfaces.

(b) Shear tests with various smooth metal surfaces.

(c) Tension tests with various metal surfaces.

(d) Tension tests with various materials mounted on metal pieces.

The chief sources of uncertainty to be guarded against are incomplete drying, incomplete (discontinuous) films, varying thickness of adhesive layer, and bubbles. The latter must be excluded as far as possible by sliding or rubbing the coated surfaces together under pressure. Certain adhesives never dried except with porous bodies and many took weeks to dry.

a) Shear Tests with Walnut Surfaces.

Very carefully prepared walnut test pieces (2½″ × 2″ × ¾″) were supplied by the Royal Aircraft Establishment, Farnborough. They were of a type used and recommended by Professor Andrew Robertson[1], to whom our thanks are due for his constant advice and the invaluable facilities afforded us in the preparation of test pieces and the testing of joints. The walnut test pieces had vertical faces parallel to the grain as found by splitting, and whole series were made from a single plank. The top and bottom surfaces (2″ × ¾″) are accurately at right angles to the other faces. With these test pieces, joints of the type indicated in Fig. 1 were set up. The adhesive was applied in every instance to the vertical 2″ × 2½″ surface Each of the opposing surfaces was coated with a film of the adhesive applied with the finger, and the surfaces were then brought together under hand pressure. (In certain few cases the instructions given by the manufacturers necessitated a slightly different mode of application of the adhesive). The resulting joint was placed in a pressure device the total pressure applied to each joint being 28 lbs., or about 7 lbs. per sq. in. The joints were kept under this pressure until thoroughly dry.

The end surfaces of the joint to be tested rest on a plane steel plate. The load on the projecting end surface is gradually increased until the joint gives way. The break usually takes place on one side only. The strength of the joint is obtained by dividing the load applied, by the total area of contact between the surfaces.

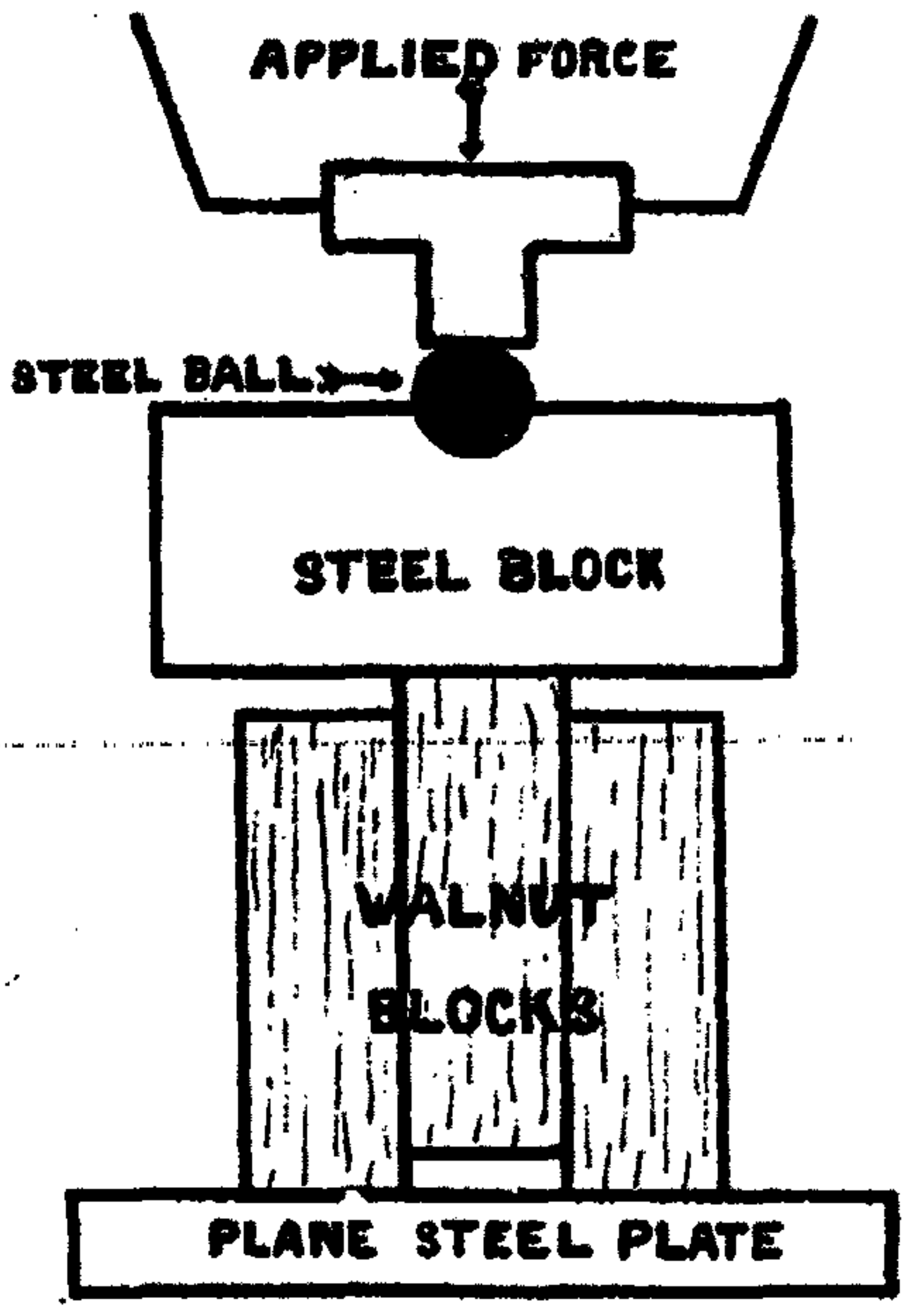

Fig. 1
Form of Test Piece for Shear Tests Between Wooden Surfaces.

Several instructive test pieces have been found where occasionally a joint has not broken under a pressure of 4 or 5 tons but where instead the upper part of the middle wooden piece has flowed in such a manner as to show that the breaking of the joint with such a strong adhesive as glue is not due to shear but to the local stresses set up by the bulging of the central piece. Nevertheless, this appears to be the best form of test piece for all weaker adhesives.

b) Shear tests—Adhesive between Metal Surfaces.

The metal pieces employed in these tests are cylindrical in form, being 2⅛″ in length and ¾″ in diameter. The plane surfaces are accurately at right angles to the length of the test-pieces. When the joint has been set up and has dried thoroughly it is inserted (very tight fit) in a specially constructed device which is then screwed into the axial loading grips. By a proper adjustment of the joint, a shearing force can be applied across the adhering surfaces in a plane perpendicular to the common axis of the test pieces forming the joint.

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[1] "Report on Materials of Construction used in Aircraft and Aircraft Engines", p. 135 (1920). By Lt. Col. C. F. Jenkin.

c) *Tension Tests with Various Metal Surfaces.*

The metal test pieces used in these tests are of the form indicated in Fig. 2. The tin and lead test pieces differ from the others, the diameter of the plane surface being 0.750", giving a superficial area of 0.442 sq. in., whereas in all the other test pieces the diameter is 0.846" with an area of 0.562" sq. in.

The plane surface is perpendicular to the axis of the screw. All the test pieces were prepared in the same way. After being turned in the lathe the remaining slight irregularities were removed on the facing stone. All traces of grease and grit were subsequently got rid of by washing the surfaces successively with methylated spirits, and freshly redistilled mixture of alcohol and ether.

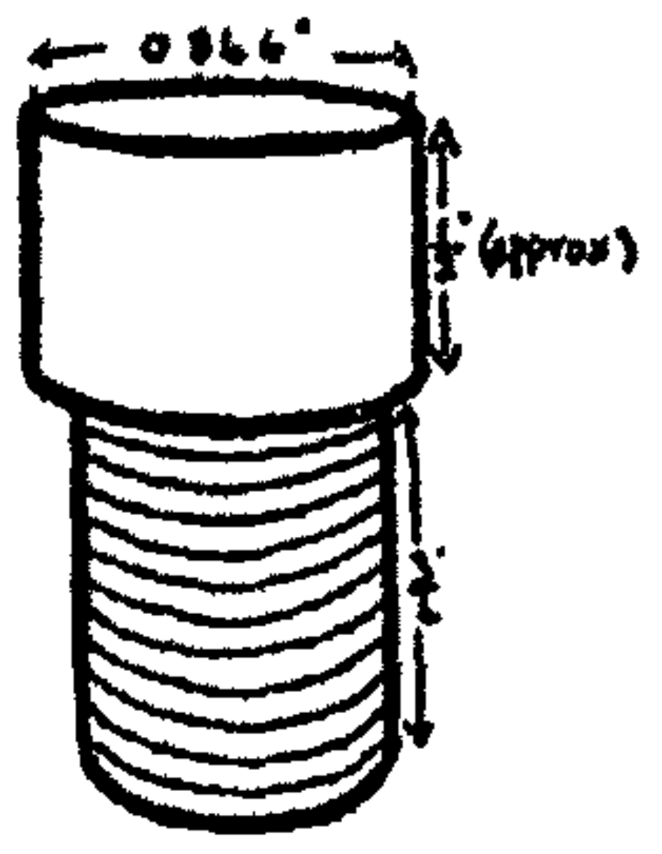

FIG. 2
Form of Metallic Test Piece for Tension Tests.

d) *Tension Tests with Various Materials mounted on Metal Pieces.*

In the preliminary experiments, compound joints were set up by sandwiching a strip of walnut with parallel faces between the two metal test pieces with the object of accelerating drying. It was assumed that the joint would yield first at the metal-adhesive junction but the walnut-adhesive linkage was often the weakest of the system. In subsequent experiments on metal joints the walnut strip was therefore omitted and the metal surfaces were joined directly. The adhesive was applied to each of the surfaces and the two test pieces were pressed together with a slight sliding motion in order to squeeze out the surplus cement and air bubbles. With certain cements, the surfaces were coated and allowed to dry before joining with further adhesive. All joints were made only under hand pressure. The adhesive was allowed to dry or set thoroughly before testing. The joints were tested in a specially adapted Denison Testing Machine; axial loading grips being employed. A gradually increasing load was applied at approximately the same rate with all the joints; viz, 30 lbs. per sq. in. per sec.

Quantitative adhesion tests with metals necessarily precede all other tests because the metal test pieces can readily be adapted to enable us to determine the strength of various other joints, e.g. glass-adhesive, if suitable adhesives for metals are known. In order to find the strength of a material-adhesive joint two types of joints may be set up, viz.,

1) *Metal-Adhesive-Material-Adhesive-Metal,* i.e., a piece of material such as glass, ebonite, etc., with parallel surfaces is cemented to the metal surfaces with the adhesive to be tested.

2) *Metal-Cement-Material-Adhesive-Material-Cement-Metal,* i.e., a piece of material is cemented to each of two metal surfaces with a suitable stronger adhesive for metal and material and the adhesive to be tested is then applied in the usual way to each of the material surfaces.

It is obvious that this method can only succeed with those adhesives which form a linkage with the glass or other intermediate material weaker than the linkages of the system. As the result of a few preliminary experiments, the second type of joint was found to be more satisfactory.

In nearly all cases joints were made at least in quadruplicate and in the summarised data the "representative value" is usually the mean of the two or three highest values rounded off to the nearest hundred pounds per sq. in.[1] This gives a measure of the strength obtainable under favourable conditions.

The materials used in making joints were chemically pure tin, lead, nickel, best commercial copper and aluminum, brass, cast iron and mild steel, oxidised and amalgamated copper, walnut, ebonite, crystals of calcite, mica, fused silica and glass, etc.

The adhesives used were (a) gelatin, highly purified by Professor Schryver and also a high grade commercial gelatine, also a high grade commercial glue A (b) fish glue (c) commercial glue B (d) a liquid commercial glue C (e) gum arabic (f) casein and borax cement (g) casein and silicate cement (h) sodium silicates of different molecular ratios (i) commercial nitrocellulose cement A (j) starch paste (k) shellac (ordinary and wax-free, molten and alcoholic) (l) an American commercial cement B (of shellac basis) in three grades (m) various shellac creosote cements (n) a commercial wax (used for high vacuum work) (o) commercial cement C (a metallic jointing compound,(p) a marine glue.

In the shear and tension tests with the metals or with various materials mounted on the metal surfaces the method of "double coating" with the adhesive was allowed to dry for about 24 hours before applying a second coating when bringing the opposite surfaces together. This procedure yields a much stronger joint.

TABLE I

Tension and Shear Tests
Shellac Creosote Cements of Various Composition*
between Metal Surfaces.
Representative values are given in lbs./sq. in.—Period of Setting 1 to 4 days.
The compositions are given in parts by weight.

Cement	I	II	III	IV	V	VI
Shellac, brown	50	-	-	-	-	-
Shellac, orange	-	50	50	50	50	50
Creosote	5	5	5	5	5	5
Ammonia (0.880)	-	0.5	0.5	-	-	1
Turpentine	-	2	-	-	-	-
Terpineol	-	-	-	-	2	2
Formanilide	-	-	-	5	-	-
TENSION	4400	4900	4000	3300	4000	4400
SHEAR	3400	4800	4600	2500	4300	3400

*Beechwood creosote was used in compounding each cement. In cements V and VI terpineol was employed instead of turpentine as it is a solvent for shellac whereas the turpentine used in II is not. The adhesive was applied in exactly the same way as molten shellac.

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[1] To convert these to kilos per sq. cm. divide by 14.22.

TABLE II.

Tension and Shear Tests—Adhesive between Metal Surfaces. (Representative values are given in lbs./sq.in.)

Adhesive	Test	Time of drying or setting (days)	Nickel	Mild steel	Cast iron	Copper	Amalgamated copper	Platinised copper	Brass	Aluminium	Tin	Lead
A high grade commercial gelatin	Tension	17	900	1000	1100	1200			700	(300)	800	800
	Shear	20		1000	700	800			1100		500	
Silicate of Soda	Tension	20	500	700*	700		800		1000	700	500	300
Commercial nitrocellulose cement A	Tension	14 - 21	1600	1600	1400	2000	400	1100	1500	1700	1000	500
	Shear	21		700	800	500			500	800	600	400
Molten shellac (purified)	Tension	1 - 5	3500	3200	3000	3300			2500	2800	1100	600
	Shear	1 - 3		3400	3000	3300			3300	2200		
American commercial cement B ("Hard")	Tension	1 - 2	4200	4800	4400	4000			2900	2300	1500	500
	Shear	1 - 3		4200	4100	4100			3800	3100	1100	600
American commercial cement B("Medium")	Tension	1				4400				2400		
	Shear	1		3700	3200	3400			3500	2100		
A commercial wax	Tension	1 - 2	1200	1000	1400	1000			1100	1000	800	500
	Shear	1	500			500			600	600	600	500
Fish glue	Tension	16	1200	800	1200	1400			700	1000		
	Shear	16	500	1400	1200	1100			1400	(200)		
Liquid commercial glue C	Tension	18				300		400		400	400	
	Shear	18		500	400	500			300	300		
Rubber solution	Tension	16			300							
Marine glue	Tension	4 - 5	1100	1700	900				1500	1400	800	
	Shear	4 - 5	600	1200	800	600				900	900	
Commercial glue B	Tension	77	1300	1900	1600	1600			2000	1000	1100	
	Shear	77	1300	1600	1500	1500			1200	1300		
Gum arabic	Tension	77	1200	900	1100	1600			1600	700	800	
	Shear	77	(1400)	1300	1000	(1600)			800	1500	800	
Commercial cement C	Tension	15 min (at 230°)		300								

*When roughened = 300, oxidised = 500.

TABLE III

Shear Tests—Adhesive between Walnut Surfaces
Representative values given in lbs./sq. in.

Adhesive.	Period of drying. (days)	Strength of joint. (Lbs./sq. in.)
Fish glue	7	1400
Liquid commercial glue C	7	1200
A high grade commercial gelatin	6	1200*
Gelatin, highly purified by Schryver	6	1100
Fish glue, with added bone gelatin	7	700
Casein and borax cement	6	600
Gum arabic	6	400
Commercial glue B	12	400
French Adhesive (silicate basis)	8	400
Casein and silicate cement	8	300
Commercial nitrocellulose cement A	30**	300
Starch	9***	300
Silicates of soda		
Grade D molar ratio 2.0	28	300
Grade K molar ratio 2.45	28	400
Grade C " " 2.9	28	500
Grade J " " 3.0	28	700
Grade A " " 3.3	28	400
Experimental I molar ratio 4.08	15	0
Experimental II " " 4.2	15	0

*This value is reduced to about one third if the joints be heated to 100° for four days when securely clamped to prevent distortion.

**This adhesive dries very slowly between walnut surfaces. It is a matter of some difficulty to set up wood joints with it on account of its quick setting capacity when exposed to the atmosphere.

***Three coatings instead of one raises the strength of joint to 1600 although the film is still incomplete. S. M. Neale, "Shirley Institute Memoirs" 3, 207, (1924), has shown that the tensile strength of a dried starch film may reach 9000 lbs. per sq. in. of cross section.

TABLE IV

Tension Tests—Adhesive between Glass Surfaces

Representative values are given except where otherwise stated. Maximum values are recorded where the results have been so discordant that a representative value could not be fixed.

Adhesive		Period of drying (days)	Single coating of adhesive. lbs./sq. in.	2 coatings of adhesive lbs./sq. in.
Commercial nitrocellulose cement A		19		1000
A high grade commercial gelatin		19	250 i max.	
Fish glue		22	500	
Fish glue, with added bone gelatin		22	499 max.	
Alcoholic shellac (wax free)		21	m 1100 max.	
Silicates of Soda				
Grade D Molar ratio	2.0	19 - 30	m *	*
Grade K " "	2.45	"	300	200
Grade C " "	2.9	"	1000	500
Grade J " "	3.0	"	600	800
Grade A " "	3.3	"	600	800
Experimental sample molar ratio	4.08	"	567 (max.)	600
"Hard" American commercial cement B		½	3700	

i—film incomplete.
m—film moist.
*—no tests possible as the joints were too weak to withstand ordinary handling.

TABLE V

Miscellaneous Tension Tests

	Joint	Adhesive	Time of drying. (days)	Representative value. lbs./sq. in.
(1)	Glass cover slip between two metal test pieces.	A commercial nitrocellulose cement	18	1000
		French Adhesive	22	1100
(2)	Ebonite plate between two metal test pieces.	A commercial nitrocellulose cement	18	800
		Gum arabic	63	400
		Commercial glue B	63	1000
		Liquid commercial glue C	63	800
(3)	Calcite crystal between metal test pieces	A commercial nitrocellulose cement	20	200*

*One test only.

Discussion of the Results of the Quantitative Tests

The results of the preceding tests suffice to give a reasonably clear notion of the strength of a great variety of joints in both tension and shear. An examination of the individual results from which the representative values of the summarised data are computed demonstrates that a number of factors were not sufficiently controlled and that improved manipulative procedure in certain might result in the production of even stronger joints.

Perhaps that most striking result is the remarkable strength of some of the joints set up with shellac cements between smooth metal surfaces. A few such joints have attained a strength of 2¼ tons per sq. in. both in tension and shear whereas the best glued wood joints rarely exceed 1200 lbs. per sq. in.

In many instances the strength of the joints was limited by the flow of the adhesive, as for example, the commercial wax and the commerical nitrocellulose cement A between metal surfaces. In other cases, such as tin, lead, and mica, failure occurred far below the strength of the adhesive or its attachment on account of the yielding of the metals themselves.

A few preliminary experiments have proved that film thickness is a most important factor in adhesion phenomena. Crow[1], in a systematic study of soft soldered joints, has shown that by making the film of solder very thin the strength of the resulting joints may be as great as 11 tons per sq. in., the tensile strength of the solder being exceeded several fold. However, such joints were apparently not strengthened very appreciably when the thickness was diminished from 0.2 mm. to the thinnest attainable. We have had occasion to note the importance of this factor and a precise investigation is now in progress. That thin films are very much stronger than an adhesive en masse is established by Crow's result for soft solder and our much more striking instance of wax-free shellac. Joints made with this shellac, which is quite soft and pliable, actually withstood a pull of nearly 4000 lbs. per sq. in. when a thin film was used between nickel surfaces.

It may be summarized that the thinnest films yield the strongest joints provided, of course, that complete contact is maintained with the surfaces. Using a shellac-creosote cement between surfaces of mild steel and taking no precautions to secure very thin films the maximum strength of joint attainable was just over 3000 lbs. per sq. in. in tension. When care was taken to ensure that the adhesive films were as thin as possible the joints could withstand a pull of 5000 lbs. per sq. in., the difference of 2000 lbs. per sq. in. being apparently due to decreased thickness of the film, although the precautions taken in obtaining excessively thin films result in a more rigorous exclusion of air bubbles and consequently in a greater completeness of film.

Reference may conveniently be made at this point to the opinion expressed by Crow that in soldered joints it is essential that diffusion (alloying) should take place. The whole weight of the evidence brought forward in the present inquiry runs contrary to this conception for there would appear to be no valid

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[1] J. Soc. Chem. Ind. 43, 65, (1924).

reason for assuming any fundamental difference between soldered and glued or cemented joints.

Shear test, carried out with a large number of adhesives between walnut surfaces, show that gelatin preparations are far in advance of other adhesives and a high grade gelatin is best of all. It is very interesting to note that highly purified ash-free gelatin is little, if at all, inferior to a first grade commercial gelatin or glue. In those wood joints we regard the adhesive film as embedded in the pores and surface irregularities. It is somewhat significant, however, that their strength is only a small fraction — a quarter of a sixth, possibly — of the tensile strength of the adhesive itself. Experiments to be described later show the tensile strength of a high grade commercial gelatin may greatly exceed 7000 lbs. per sq. in. Of course, with glued joints failure almost invariably takes place in the wood itself, or in the layer where the glue film is weakened by the embedding in the wood. With less tenacious adhesives such as gum arabic, silicate of soda, etc., where the failure occurs in the adhesive, the strengths of wood joints ought to run parallel with the tensile strengths of the adhesives; and determinations of these are in progress.

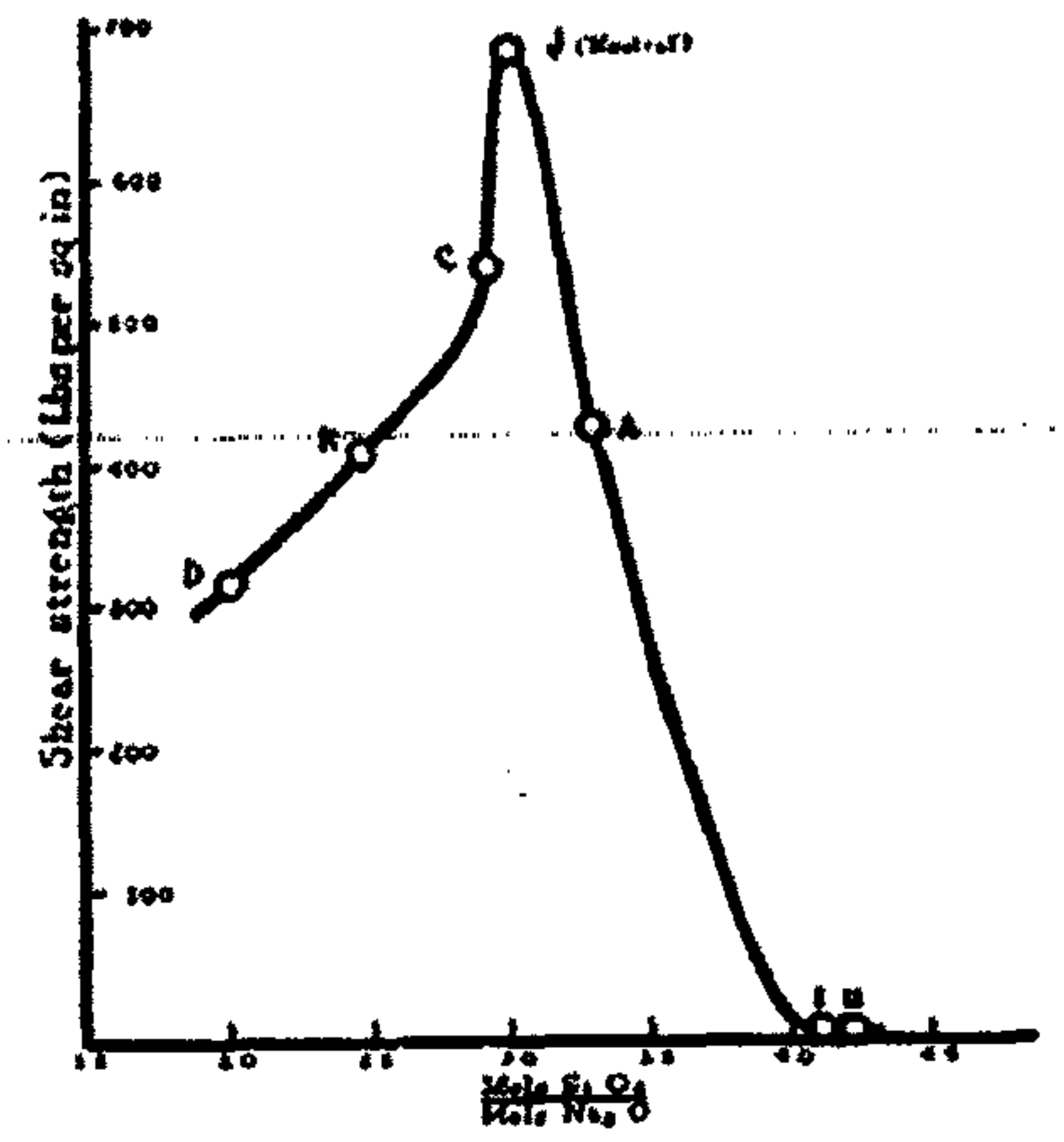

FIG. 3

Shear Tests. Silicate of Soda of Various Compositions between Walnut Surfaces (Maximum Values Plotted)

The results obtained with silicates of soda of different molecular ratios (mols SiO_2/mols Na_2O) between walnut surfaces are noteworthy. Table III and Fig. 3 show that the so-called "neutral" silicate of composition $Na_2O \cdot 3SiO_2$ exhibits maximum tenacity, that a higher proportion of SiO_2 rapidly diminishes this whereas the addition of alkali causes a less marked reduction. A similar maximum is observed with the silicates between glass surfaces although not nearly so pronounced since more acid and more alkaline silicates still yield strong joints. The most alkaline silicates dry only with difficulty.

When the joints between metal surfaces are set up with gelatin, commercial nitrocellulose cement A, etc., merely by bringing together the surfaces with a single coating of adhesive the results almost invariably fluctuate considerably. If, however, the first thin coating of adhesive is allowed to dry thoroughly before applying the second coating just previous to bringing the surfaces together the results are generally higher and more concordant than those obtained in the simple mode of application of the adhesive. The probable explanation is that the method of "double coating" gives rise to more complete adhesive films. It is probable that better results would be obtained with all adhesives if this modified procedure were adopted.

Experiments carried out with the object of comparing the strength of joints made between pairs of surfaces of different roughness prove conclusively that the degree of roughness exerts little influence on the strength of joints, provided that the roughing process has been carried out without pitting the surface appreciably If, however, the metal surfaces are rather deeply furrowed in the process of employing a round nosed roughing tool, then the joints are decidedly weaker than those obtained with smooth surfaces, the lower results presumably being attributable to (i) an increase in the average thickness of the adhesive film (ii) the presence of insufficient adhesive completely to bridge the gap between the two surfaces.

Relation of Strength of Joints to Materials

The qualitative tests show with certainty that the strength of a joint with any one adhesive depends upon the nature of the solid materials joined, even in the entire asbence of chemical action. It is very desirable to identify the properties of the solid materials which are parallel with the strength of joint although we can as yet do this only in a very tentative manner. For the present purpose it is necessary to omit from consideration any adhesives which react chemically with the surfaces or which induce corrosion, so that only a few isolated data remain besides the series tests with molten shellac and commercial cement B. With these cements the adhesive films generally broke away cleanly from the metal showing that true adhesion was being measured. In these cases there is recognisable a manifest parallelism between the strength of joint and the atomic volume, compressibility, tensile strength, elastic limit, elasticity and even the hardness of the metals concerned. Table VI, giving data mostly from Landolt-Börnstein Tabellen, furnishes a comparison between those related properties and the strength of joints. The results with very many adhesives such as fish-glue, gelatin, liquid commercial glue C, gum arabic, etc., are omitted because of the corrosion that occurred. The same parallelism does not occur with these adhesives but this does not necessarily deprive the generalisation of its validity. The higher the values of the atomic volume and compressibility the weaker the joint, and the higher the tensile strength, elastic limit and elasticity (or even hardness), the stronger the joint.

These results show that joints with nickel, iron and copper are of practically the same strength, those with aluminum weaker, tin and lead joints being much weaker still. With tin and lead quite appreciable distortion of the metal occurred in the shear tests. Nickel, tin and ebonite joints made with commercial nitrocellulose cement A and glass with American commercial cement B (3700 lbs. per sq. in.) give results which might have been anticipated from our generalization. It is also in line with this hypothesis that mica forms very weak joints parallel to its cleavage plane and other favourable evidence may also be found in the tests we have made.

If the strength of a joint with a given adhesive depends on the tensile strength of the metal it may be that the strength of a joint with a given metal similarly depends on the tensile strength of the adhesive film itself and the necessary data are now being sought.

TABLE VI

Parallelism between Properties of Metals and the Strength of Joints made therefrom

Metal.	AV	C	TS	EL	Elasticity	H	Shellac T	Shellac S	KH T	KH S	KM T	KM S
Nickel	6.7	0.6			22000		3500		4200			
Steel	7.1	0.6	70	22-40	22000	5-8.5	3200	3400	4800	4100		3700
Iron	7.1	0.3-0.6	23-61	12-32	18-21000	4 5	3000	3000	4400	4100		3200
Copper	7.1	0.8	40	12	12000	2.5-3	3300	3300	4000	4100	4400	3400
Aluminum	0.1	1.4			7000	2	2800	2200	2300	2100	2400	2100
Tin	16.2	1.9	2.5		5000	1.5	1100		1500	1100		
Lead	18.2	2.5	2.1	0.25	1600	1.5	600		500	600		

AV = Atomic volume.
C = Compressibility.
TS = Tensile strength.
EL = Elastic limit.
H = Hardness.
KH = Cement B ("hard")
KM = Cement B ("medium")
T = Strength of joint in tension.
S = Strength of joint in shear.

TABLE VIII

Effect of Heat on the Adhesive Power of Solutions of Glue and Gelatin

Adhesive	Temp. °C	Type of joint.	Time (days). 0	1	2	3	4	5	6	12	21	32
Gelatin (16%)	60	A I D	1097	*			1184*		1199			
Glue A (40%)	60	A I D	947	1018*			1021*		1092	1172	1032	1218
Glue A (25%)	80	D C P	2777	2733		2486		2599				
Glue A (25%)	100	D C P	2777	2979	1971	1904						
Glue A (25%)	130	D C P	After one day the solution had lost nearly all its adhesive power.									

A I D = Aircraft Inspection Dept. Type (Usual). D C P = Double Cover Plate Type.

* Joints unbroken—only the wood yielding under stress.

TABLE VII

Sorption Experiments with Solutions of Adhesives in contact with Porous Materials and with Fibres of Fused Silica.

Materials.	m.	Concentration gms./cc.	Contact (hours)	Change of Concn. (gms./cc.)	Water adsorbed. *x/m	Adhesive adsorbed **x/m	Water vapour-x/m
Filter paper and gelatine.	1.00	0.0050	48	+0.000089	0.18	———	0.1
	1.00	0.0300	3	+0.00039	0.13	———	
	1.00	0.400	3	+0.00054	0.13	———	
Filter paper and gelatine.	2.20	0.0300	3	+0.000616	0.18	———	0.1
	2.10	0.0300	3	+0.000562	0.18	———	
Viscose and gelatine.	1.00	0.0200	18	+0.000656	0.64	———	0.2
	1.00	0.0200	18	+0.000437	0.43	———	
Wood-meal and gelatine.	1.00	0.0333	1.5	+0.000370	0.22	———	(0.1?)
	0.80	0.0300	3	+0.000472	0.39	———	
	1.00	0.0300	20	+0.000364	0.24	———	
Filter paper and silicate	1.21	0.355	18	+0.00244	0.113	———	0.1
	1.21	0.355	18	+0.00245	0.113	———	
Fused silica and gelatine.	1.64	0.0100	24	−0.0000778	——	0.000474	0.002
	1.57	0.0100	0.5	−0.0000462		0.000294	
Fused silica and gum arabic	1.33	0.0300	24	+0.0000490	(0.012)	———	0.002
	1.33	0.0300	24	+0.0000306	(0.008)	———	

*Assuming no simultaneous adsorption of adhesive.
**Assuming no simultaneous adsorption of water.

The tensile strength of films of a number of adhesives, such as gelatin and glue is found to be many times greater than that of the strongest wooden joints made from them.

Adsorption and Adhesion

According to the preceding inquiry both smooth and porous materials yield strong joints. In the former case Bancroft would postulate adsorption, whereas in the latter neither adsorption nor chemical interaction is requisite if the joint is due solely to the mechanical embedding of the film. The adsorption experiments about to be described were carried out both with porous and with smooth impervious materials.

Change in the concentration of an adhesive solution when an insoluble and unreactive material is introduced into it would be ascribed to the adsorption of solvent and adhesive in relative quantities differing from those in which they are present in the original solution. If the adhesive only is adsorbed from the solution then the residual solution is less concentrated than the original. If, on the other hand, both the solvent and the adhesive are adsorbed, then there might be an increase or decrease in concentration according to the relative quantities adsorbed. Thence, in order to ascertain whether the adhesive is adsorbed two distinct determinations have in general to be made, viz.,

(a) The amount of solvent the material is capable of adsorbing.

(b) The change of concentration of the adhesive solution brought about by the adsorptive action of the material of the same quality and in the same physical condition as used in (a).

The method adopted to determine the amount of water adsorbed by the various materials (filter paper, fused silica fibres, etc.) was a modification of that developed in this laboratory by Bakr and King[1], (since superseded by the sorption balance of McBain and Bakr[2]). The effect of bringing various materials into contact with the adhesive solution was determined in the most straight forward case by placing a known weight of material (thoroughly washed and dried) in a known volume of the adhesive solution where it was allowed to remain until equilibrium was established. The change of concentration was determined by means of a Zeiss Interferometer, measuring the refractive index of the solution to eight significant figures. A blank experiment is carried out with the solvent in place of the adhesive sol in order to determine the effect of possible traces of soluble impurities in the material upon the apparent concentration of the solution. Allowance is made in all calculations for this very small source of error, although in most cases it is quite negligible. In the experiments with filter paper the presence of very small amounts of peptised paper would cause an increase in the refractive index of the adhesive solution and this would be sufficient to render the results valueless, for the observed changes of concentration are exceedingly small. In order to eliminate this source of error the filter paper is taken in the form of extraction thimbles, so that, after remaining in contact with the adhesive solution it is possible to filter the residual solution

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[1] J. Chem. Soc., 119, 454 (1921).

[2] J. Am. Chem. Soc., 46, 2781 (1924).

through it. When dealing with wood-meal and certain other materials such as viscose such a direct procedure is not possible. In these instances an additional extraction thimble is employed and allowed for.

The results of the experiments are summarized in Table VII. Note that there is no evidence of adsorption of the various adhesives by the porous materials employed. Positive although slight adsorption of gelatin by fused silica fibres is shown to occur in accordance with expectation for smooth surfaces exhibiting adhesion, but with gum arabic the indications were within the limits of experimental error.

Effect of Heat on the Adhesive Power of Glue and Gelatin Solutions

There seems to be a general impression based upon observations of viscosity and jelly strength that the heating of glue or gelatin even for periods of a few hours brings about a marked decrease in the adhesive powers. To test the truth of this popular idea aqueous solutions of a high grade commercial gelatin (16%) and a high grade commercial glue A (25% and 40%) were maintained at various temperatures (60°, 80°, 100°, 130°C) in a thermostat, evaporation being prevented by using carefully ground glass stoppered bottles at 60°C and sealed tubes at the higher temperatures. At various intervals three joints were set up with portions of the adhesive. Two forms of walnut joint were employed the usual type already described and another form of joint known as the double cover plate type.

The maximum values obtained for each set are given in Table VIII in lbs. per sq. in. except for the double cover plate joints where the total load is given.

The results prove quite conclusively that whatever change or degradation takes place at 60° or 80°C does not effect the strength of the wood joints as measured by the present methods even after heating has proceeded for a month at the lower, and five days at the higher temperature.

Summary

Qualitative and quantitative examination of a large variety of adhesives and materials have led to general conclusions expressed in the opening paragraphs of this communication. Further specific points are as follows:

(a) Although gelatin and glue adhesives including highly purified ash-free gelatine are by far the strongest for wooden joints, there is no evidence of any specific interaction such as adsorption with wood, filter paper or viscose. Heating to 60° for a month does not diminish the adhesive power of glue although on heating to 130° for one day its adhesive power is almost completely lost.

Gelatin is adsorbed by fused silica and unites smooth silica surfaces. Other sorption experiments have been carried out with sodium silicate and gum arabic.

(b) Silicate of soda used between walnut surfaces exhibits a sharp maximum strength at the composition $Na_2O.3SiO_2$. This maximum is by no means so pronounced with glass surfaces but occurs at approximately the same composition.

(c) Most adhesives join smooth metallic surfaces, and even soft pliable shellac yields joints withstanding two tons to the square inch. There would appear to be a certain parallelism between the strength of joints between metals and the mechanical properties (such as tensile strength, compressibility, atomic volume, etc.) of the metals themselves.

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November, 1924.

OVERVOLTAGE AS A FUNCTION OF CURRENT DENSITY AND THE EFFECTS OF TIME, TEMPERATURE, STIRRING, PRESSURE, NATURE OF SURFACE, AND OF A SUPERIMPOSED ALTERNATING CURRENT*

BY WILLIAM D. HARKINS AND H. S. ADAMS[1]

1. Introduction

In 1905 Tafel[2] showed that overvoltage is in some cases nearly a linear function of the logarithm of the current density, which indicates a probable relation to a concentration effect. One year later Lewis and Jackson[3] proved that when the cathodic material is mercury, the overvoltage is represented as a straight line over a limited range, when it is plotted against the logarithm of the current density. The present paper shows that at 20°C. this is true over a very much more extensive range, between 3 billionths and a thousandth of an ampere per square centimeter, when the cathode consists of carefully prepolarized mercury.[4] Figure 1 presents these relations in a graphic form. In this particular instance the current and not the current density, is

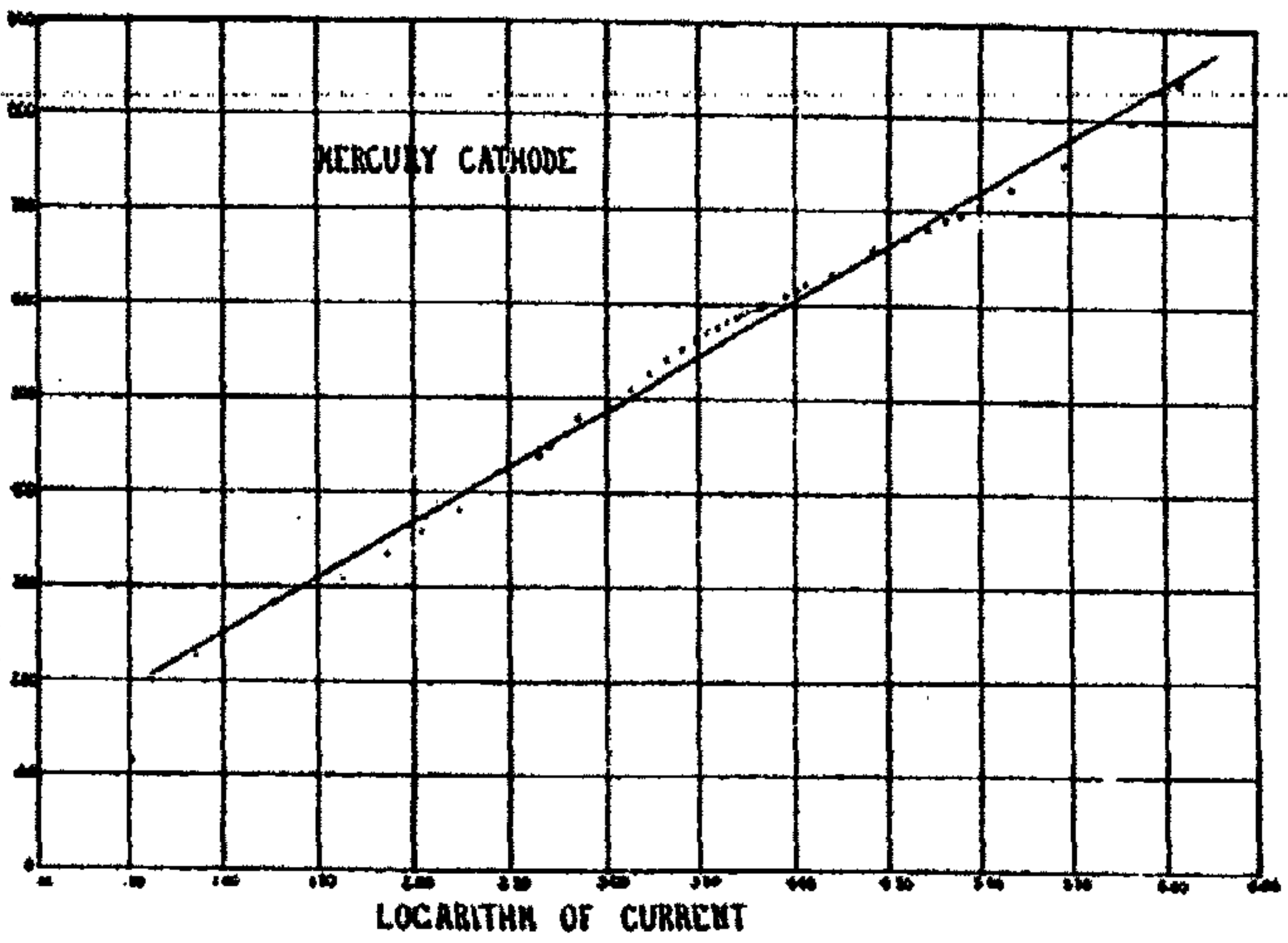

Fig. 1

Effect of Current Density on Overvoltage (Current in Billionths of an Ampere for an Area of 84 sq. mm.).

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*Contribution from the Kent Chemical Laboratory of the University of Chicago.

[1] Presented in the year 1914 to the University of Chicago by H. S. Adams, in partial fulfillment of the requirements of the Ph.D. degree. Practically the only changes made in the thesis as presented are due to the inclusion of references to work done since it was written and to a considerable abbreviation.

[2] Tafel: Z. physik, Chem. 50, 641 (1905).

[3] Lewis and Jackson: Ibid., 56, 193 (1906).

[4] Between current densities of 0.08 and 12 milliamperes per sq. cm. the overvoltage of tantalum is represented by a remarkably straight line, when plotted against the logarithm of the current density.

given, for a cathode which consisted of a mercury meniscus in a circular tube of 0.526 cm. internal diameter.

2. Apparatus for determining Overvoltage under Pressure

The apparatus used for the determination of the effect of pressure upon overvoltage was designed for work below 1 atmosphere and up to 3 atmospheres. It consisted of a 700 cc. bottle of heavy glass,—fitted with a rubber stopper supported by a metal case which surrounded the bottle,—half filled by electrolyte, into which the two electrodes dipped. The anode was a sheet of fine platinum gauze 10x50 cm., made in the form of a spiral, over which hydrogen passed continuously, and which also served as the hydrogen elctrode. The hydrogen was made from zinc amalgam according to the method of Cooke and Richards. The flow of hydrogen was regulated to any desired speed by putting the requisite resistance or potential into the circuit of the hydrogen generator. The acid, 20% hydrochloric, was boiled and cooled in an atmosphere of hydrogen before it was used. No rubber connections were used in any of the work described in this paper.

The electrolyte used in the overvoltage cell and in all of the later work was N/10 sulfuric acid which had been redistilled in a concentrated form and was later diluted by conductivity water. The mercury was purified by the method used at the Bureau of Standards.

The potential measurements were made by a sensitive potentiometer, and the apparatus was in all cases protected by an equipotential shield, such as that described by White.

3. The Effect of Pressure upon the Overvoltage of a Mercury Cathode

When this work was begun, the intention was to determine the effect of pressure upon the overvoltage of cathodes with both high and low voltages, but the work was interrupted after the measurements on a single metal, mercury, had been made. Through the apparatus set up as described above, and filled with pure hydrogen, a current of low current density was passed for four days. The current was then regulated to the desired current density and kept at this density until a steady overvoltage was obtained. Then the pressure was raised in steps to 3 atmospheres, lowered in steps to 1/36 atmosphere, and finally raised again to one atmosphere. Each run of this nature was completed in a period of about 14 hours, and *although the effect was investigated at widely varying current densities, no appreciable variation due to pressure was found*[1].

It must not be lost sight of that what is being measured here is not the change of potential on the cathode with the change of pressure, but the

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[1] Since the completion of this work, some related results have been published by Newbery: J. Chem. Soc., **105**, 2419 (1914), who found no appreciable effect to be produced upon the overvoltage of oxygen upon platinum by pressures as high as 100 atmospheres. Recent work by Bircher and Harkins: J. Am. Chem. Soc., **45**, 2890-98 (1923); is practically in agreement with that of the present paper, but shows that there is an extremely small rise of overvoltage at low pressures when mercury, lead, or nickel is used. It gives definite evidence that the extremely rapid rise with lowering pressure sometimes found is fictitious.

difference between this change and that produced on the hydrogen electrode, where the reaction is assumed to be reversible. For this reason, the experiments of Tammann and Nernst[1] on the liberation of hydrogen by metals under pressure, cited by Lewis and Jackson in this connection, seem not to be strictly pertinent.

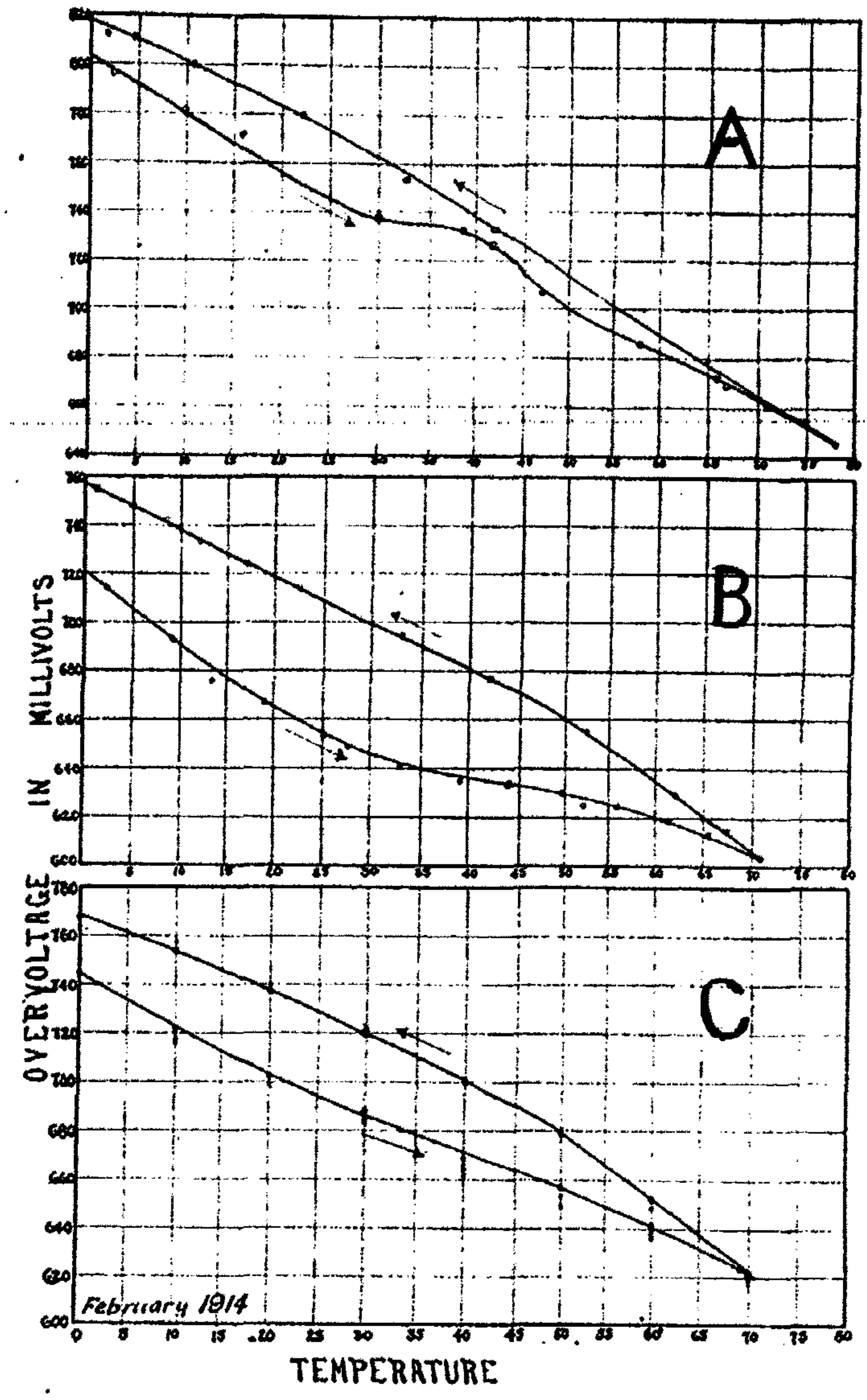

FIG. 2

Effect of Temperature on the Overvoltage of a Mercury Cathode. Temperature changed (A) rapidly and continuously, (B) slowly and continuously (C) ten degrees in ½ hour and then kept constant ½ hour. Current (A) 6 x 10^{-3} milliamperes. (B and C) 3.5 x 10^{-3} milliamperes per sq. cm.

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[1] Z. physik. Chem., 56, 193 (1906).

4. The Effect of Temperature upon Overvoltage

At the time this work was begun, there was a general impression that overvoltage decreases with rise of temperature, though some investigators expressed the opinion that temperature has little effect. Thus this was the conclusion of Lewis and Jackson[1] who found that at the higher temperatures there is even a tendency for the current to decrease, which implies an increase in overvoltage. After the completion of the present work, Rideal[2] found that the overvoltage of a number of metals remains constant as the temperature is changed[3].

The apparatus used by us in investigating the temperature effect was the same as that used in the work on the effect of pressure. It was kept in a thermostat whose temperature could be varied rapidly, and then kept constant to 0.01°. The temperature was determined by the use of a thermometer kept in the overvoltage cell.

The overvoltage of the mercury cathode was lowered about 2 *millivolts per degree* of increase of temperature between 0 and 80 degrees (Fig. 2) whether the temperature was varied rapidly and continuously (A) with a current of 6×10^{-3} milamperes; slowly and continuously (B) with a current of 3.5×10^{-3} milamperes; or changed 10 degrees in 1/2 hour and then kept constant 1/2 hour (C) with the same current. All of the curves exhibit considerable hysterisis. In Fig. 2 C the values obtained during the half hour at which the temperature was kept constant are represented by crosses, while the final values at the end of each period are shown by circles. It may be noted that during each constant temperature period the overvoltage increases on the descending branch, and decreases on the ascending branch of the curve. This tendency of the overvoltage to "recover" after it has been disturbed is a somewhat general phenomenon.

5. Apparatus for the Determination of Overvoltage

In order to extend the work to an investigation of overvoltage phenomena on various metals a second apparatus was constructed, the planning of which was directed by the following considerations. The anode and cathode were to be separated in such a way that the possibility of contaminating the cathode with the anode material or with electrolyte from the anode compartment should be reduced to a minimum. The hydrogen electrode against which the cathode potential was to be measured was to be so constructed as to make it possible to change the cathode without disturbing the hydrogen electrode or admitting air to it. A device for rotating the cathode was to be provided, to which different cathodes might be fitted interchangeably. The manner in which these details were worked out is shown in the accompanying diagram, Fig. 3.

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[1] Rideal: J. Am. Chem. Soc., 42, 94 (1920).

[2] Z. physik. Chem., 9, 1 (1892).

[3] Recent work by Bircher and Harkins indicates that there are two types of overvoltage: (1) The ordinary type such as is investigated in the present paper, which is lowered by a rise of temperature, and (2) overvoltage which is determined largely by the single potential of the metal. Overvoltage of this type increases as the temperature rises.

The anode compartment is represented by (A). The anode (a) was a hydrogen electrode of platinized platinum, made up in the form of a spiral and mounted in a glass tube which passed out through the rubber stopper of the cell. Through a second glass tube (b) hydrogen passed into the cell, and a third tube (c) connected with a small wash bottle provided for its escape. A tube (d) sealed into the side of the cell made possible the withdrawal of electrolyte. A large glass tube (e) bent in the manner indicated and provided with a stopcock, connected the anode compartment with the cathode compartment (C).

The cathode compartment was fitted with a rubber stopper in the center of which was a piece of glass tubing (f) of 12 mm. internal diameter. This opening provided for the introduction and removal of the various cathodes under observation without disturbing any part of the apparatus. The rubber stopper carried also a glass tube (g) through which hydrogen passed from the hydrogen electrode compartment (H) into the cathode compartment, and a second tube (h) provided for the escape of the gas through a wash bottle. The third tube (i) drawn out into a Luggin capillary formed one arm of the bridge which made electrical connection with the hydrogen electrode. This bridge was fitted with two stopcocks, and between them was sealed in a tube (k) through which fresh electrolyte might be syphoned from a reservoir.

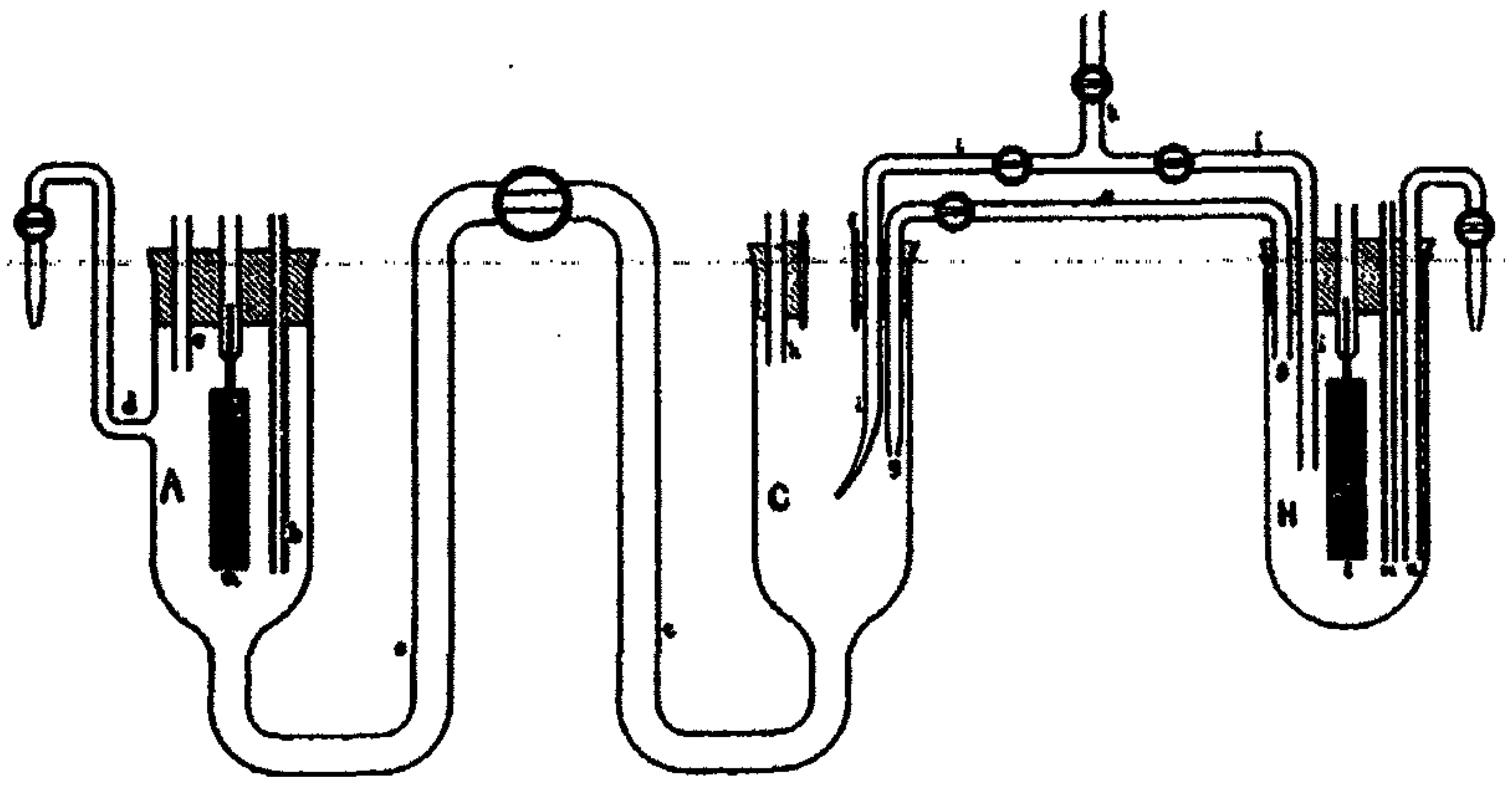

Fig. 3

Apparatus for the Determination of Overvoltage.

The hydrogen electrode compartment (H) was fitted also with a rubber stopper, carrying in the center a glass tube in which was mounted the hydrogen electrode (1), a rectangular piece of platinized platinum gauze. Through the stopper passed also one arm of the bridge (i), a tube through which hydrogen passed into the cell (m), and another (g) through which the gas passed out and over to the cathode cell. Still another tube (n) made it possible to withdraw electrolyte from this compartment. The apparatus was immersed in a thermostat kept at 25.0°C.

Hydrogen for the hydrogen electrode and the cathode, was furnished by the electrolysis of 10% sodium hydroxide. The electrodes were of monel metal, and the cathode enclosed in a porous cup. The gas was passed over palladium asbestos heated to 175°C. in an electric tube furnace, and washed subsequently through N/10 sulfuric acid. No rubber connections were used, the entire train being of glass. A small electrolytic generator, of the U-tube type and electrodes of pure, previously unused, scrap platinum, furnished hydrogen for the anode.

The electrolyte was N/10 sulfuric acid, made as described previously. It was stored in a five-liter bottle under hydrogen, and a syphon of glass tubing provided for its withdrawal through the bridge either into the hydrogen electrode or cathode compartments. After the experiments on a metal had been completed and the cathode removed, the electrolyte from the cathode compartment was drawn into the anode compartment and thence out of the apparatus. The two compartments were then washed out by running in fresh electrolyte through the bridge and withdrawing it as before, and finally the apparatus was filled with fresh electrolyte. A cathode of another metal could now be introduced and measurements commenced.

The source of current consisted of a battery of five storage cells and twenty dry cells, with a device for adding or cutting out the cells one or more at a time, and a decade box in series with the circuit for more closely regulating the current. In series also could be placed resistances of 100000, 10000, or 1000 ohms, from the drop of potential across which the current was calculated. The fall of potential between the hydrogen electrode and the cathode represented the overvoltage. Measurements were made, as described above, with a Leeds and Northrup Type K Potentiometer.

Fig. 4 gives the details of the rotating device. The bearings (b,b) were made by drilling a brass rod, brazing it to the frame (f), and subsequently cutting the opening to receive the pulley (p). In this way perfect alignment was secured. The steel rod by which the bearings were drilled was used as the shaft (s) of the stirrer. All vibration was thus reduced to a minimum, and an air-tight bearing secured. The lower end of the shaft was threaded to receive the various cathodes. The upper end was drilled to form a cup in which mercury was placed and electrical connection thus secured. The pulley was of hard rubber and was slotted to allow the passage downward of oil. The lower bearing carried a rubber stopper (x) which made an air-tight joint with the glass tube in the stopper of the cathode cell. The frame was bolted to the edge of the thermostat, from which it was insulated by a plate and bushings of hard rubber, the details of which are not shown in the diagram. The stirrer was driven by an electric motor, and a speed of 5,600 revolutions per minute was obtained with complete smoothness of operation and freedom from vibration.

Fig. 4, (B) represents one of the interchangeable cathodes. It consisted of a brass cylinder (c) tapped at one end to receive the shaft of the rotating device, and at the other to receive the cathode. Fitted tightly around it was a glass tube (t, t) which served to protect it from the splashing of the electrolyte and formed a cup to catch any oil which might work down from the bearings. The electrode (e) was threaded to fit the brass holder, except in the case of some of the softer metals, where connection was made by soldering. A glass tube (t′, t′) surrounded the electrode for part of its length. Joints between this tube and the electrode, as well as the holder, were made by the use of de Khotinsky cement. The electrolyte in the cathode cell was adjusted to such a height that it covered the exposed part of the electrode and part of the glass tube surrounding it. The area of the electrode accordingly underwent no change during rotation. In general the cathodes were approximately 20 mm. in diameter and 300 mm. in length, and were made by turning or by drawing the metal. The final polishing was made with rouge paper and oil, after which the cathode was washed with benzene, ether, alcohol and distilled water.

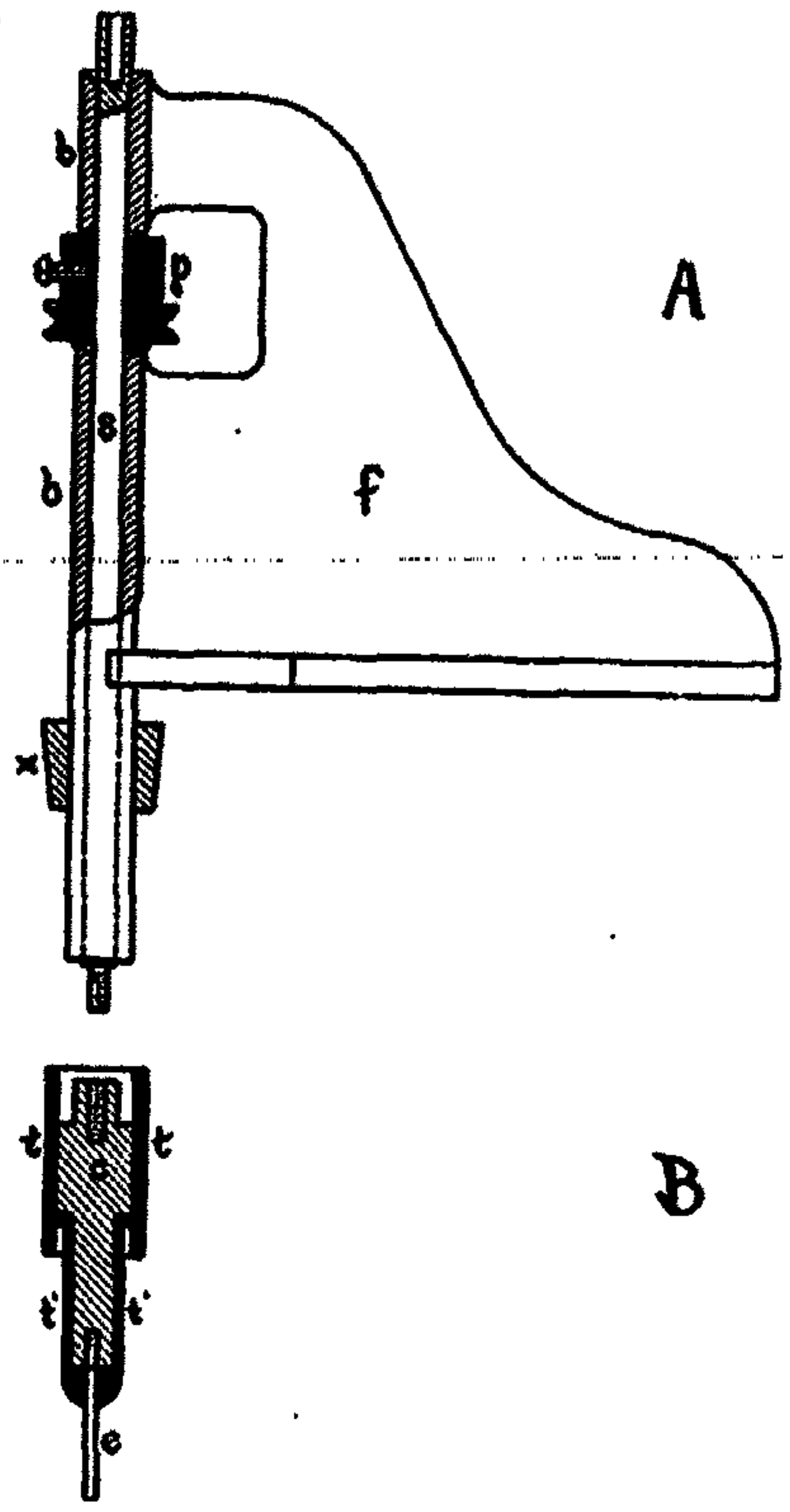

FIG. 4
Rotating Cathode.

6. Effect of Rotating the Cathode

In so far as overvoltage is due to a concentration effect which may be influenced by a diffusion of the hydrogen into the solution it may be expected to fall when the cathode is rotated. Experiments with some nine different metals, under supposedly identical conditions, show that in general this is what occurs.

Figures 5 to 8 show the effect upon the overvoltage of stirring the electrolyte by means of a stirrer (Fig. 5), of rotating the cathode at a speed of 5600 revolutions per minute, or of bubbling hydrogen gas over the cathode. In general any of these procedures gave a considerable lowering of the overvoltage. In the case of a mercury or a tin cathode, the lowering was much greater at the lower current densities then at the higher. With a cathode of polished tin at a current density of 50×10^{-3} milamperes, stirring by means of hydrogen gas lowered the overvoltage from 660 to 140 millivolts and additional rotation of the cathode at high speed did not affect the minimum value (Fig. 7). Rotation of the cathode lowered the overvoltage, but much less, when cathodes of polished gold, or polished or rough platinum were used (Fig. 6). Obviously stirring the electrolyte has a marked effect in lowering the overvoltage. Thus in the case of tin cited above, at the lowest current densities as much as 80%, but at the highest, only 15% of the overvoltage disappears when the cathode is rotated. Rotation of the cathode removes many of the gas bubbles and it also brings near to the surface of the electrode a layer of liquid which is not supersaturated with hydrogen.

7. The Time Effect

Data already presented in the paper illustrate the fact that the overvoltage on a cathode increases in general with the time when the current density is kept constant. Figure 9 shows that the overvoltage of a monel metal cathode was increased 20 millivolts at a current density of 13×10^{-6} amperes, and 40 millivolts at 11.810×10^{-6} amperes, in a period of 24 hours.

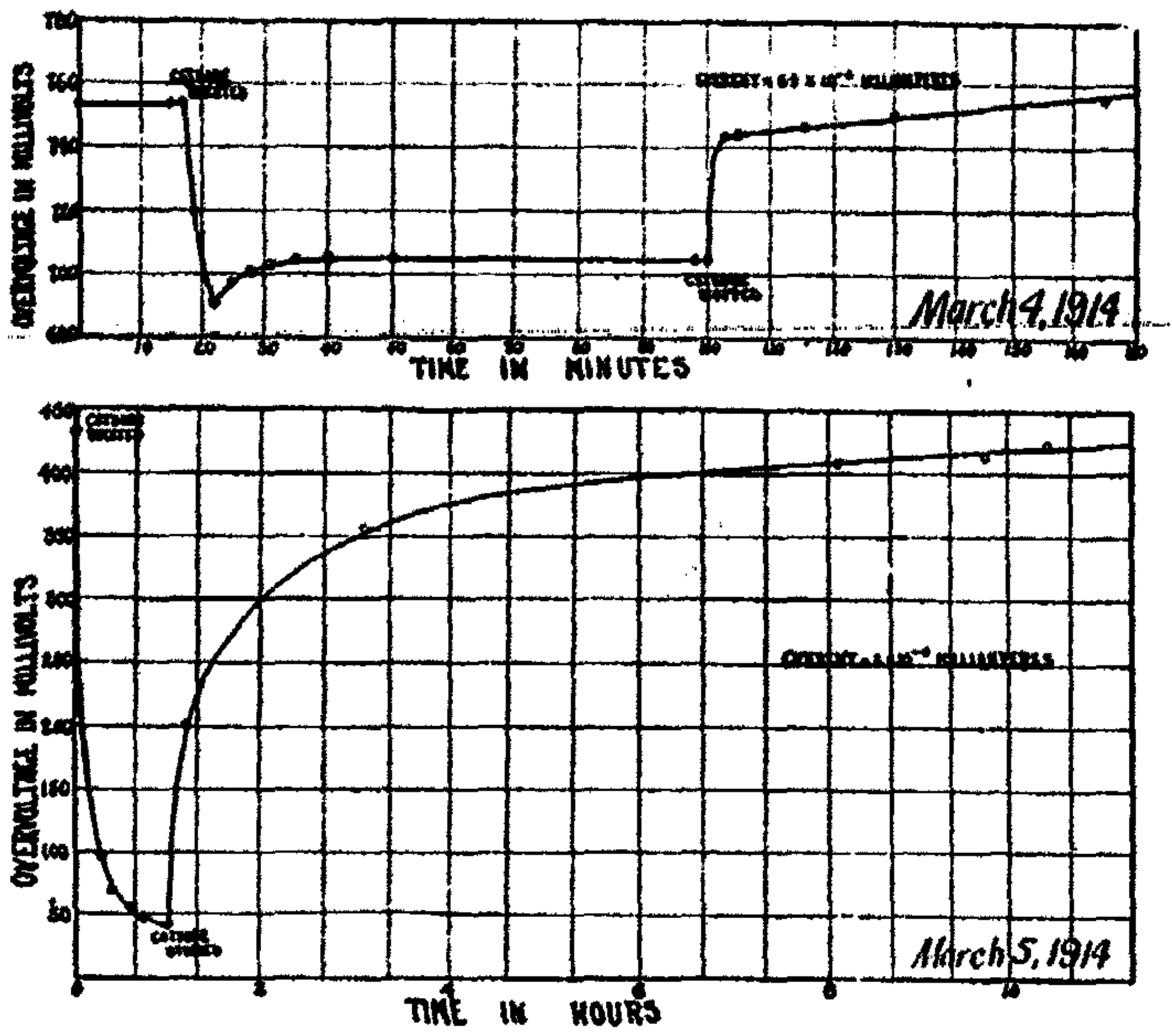

FIG. 5

Effect of stirring the Electrolyte on the Overvoltage of a Mercury Cathode at Higher and Lower Current Density.

8. The Effect of a Superimposed Alternating Current

Experiments on tin, cadmium, and platinum (Figs. 8, 10, 11), and on tungsten, and molybdenum, show that the general effect of superimposing an alternating current upon an electrode which is a cathode for a direct current is to lower the overvoltage. It was found that with platinum, tungsten, and molybdenum, metals of low overvoltage, the alternating current changes the overvoltage to an undervoltage except at the higher current densities for the direct current. While this effect may be due in part in some cases to an asymmetry of the alternating current, this is not the underlying cause of the effect, since it persists when the alternating current is reversed. The effectiveness of the alternating current in lowering the overvoltage seems to decrease as its frequency increases.

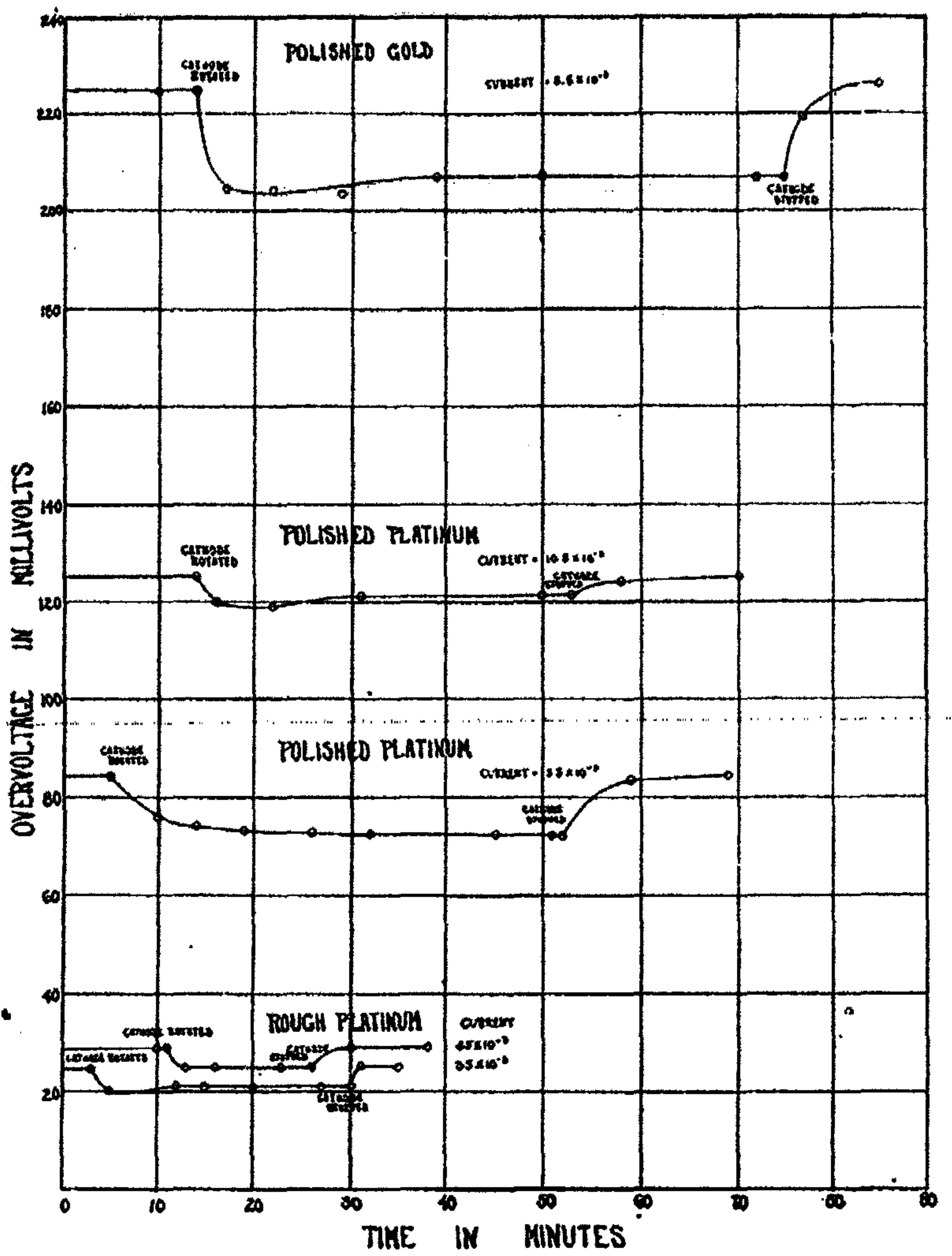

FIG. 6
Effect of Rotating Cathodes of Gold and Platinum on Overvoltage. (Current in Milliamperes).

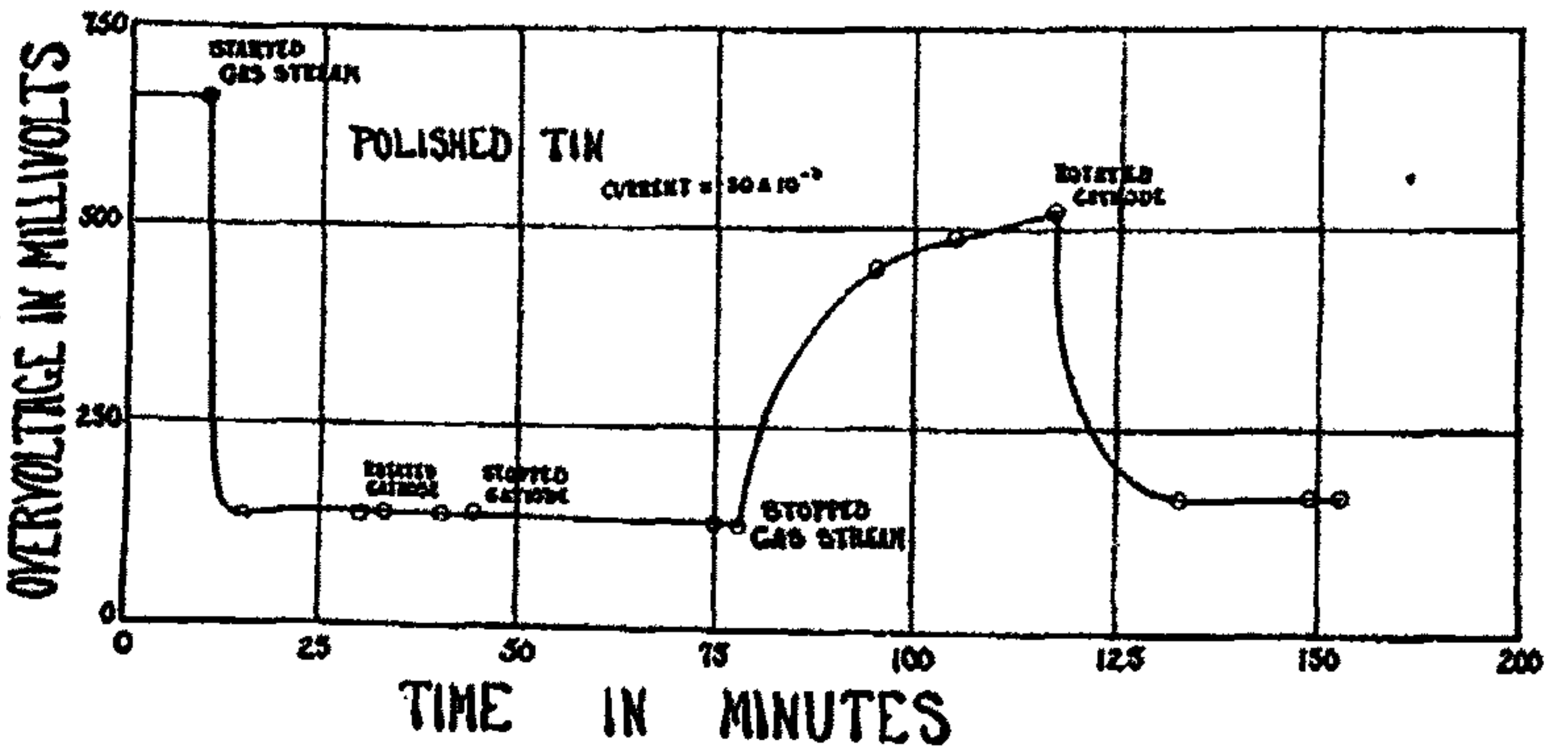

FIG. 7
Effect of Rotating Cathode on Overvoltage. (Current in Milliamperes per 84 sq. mm.).

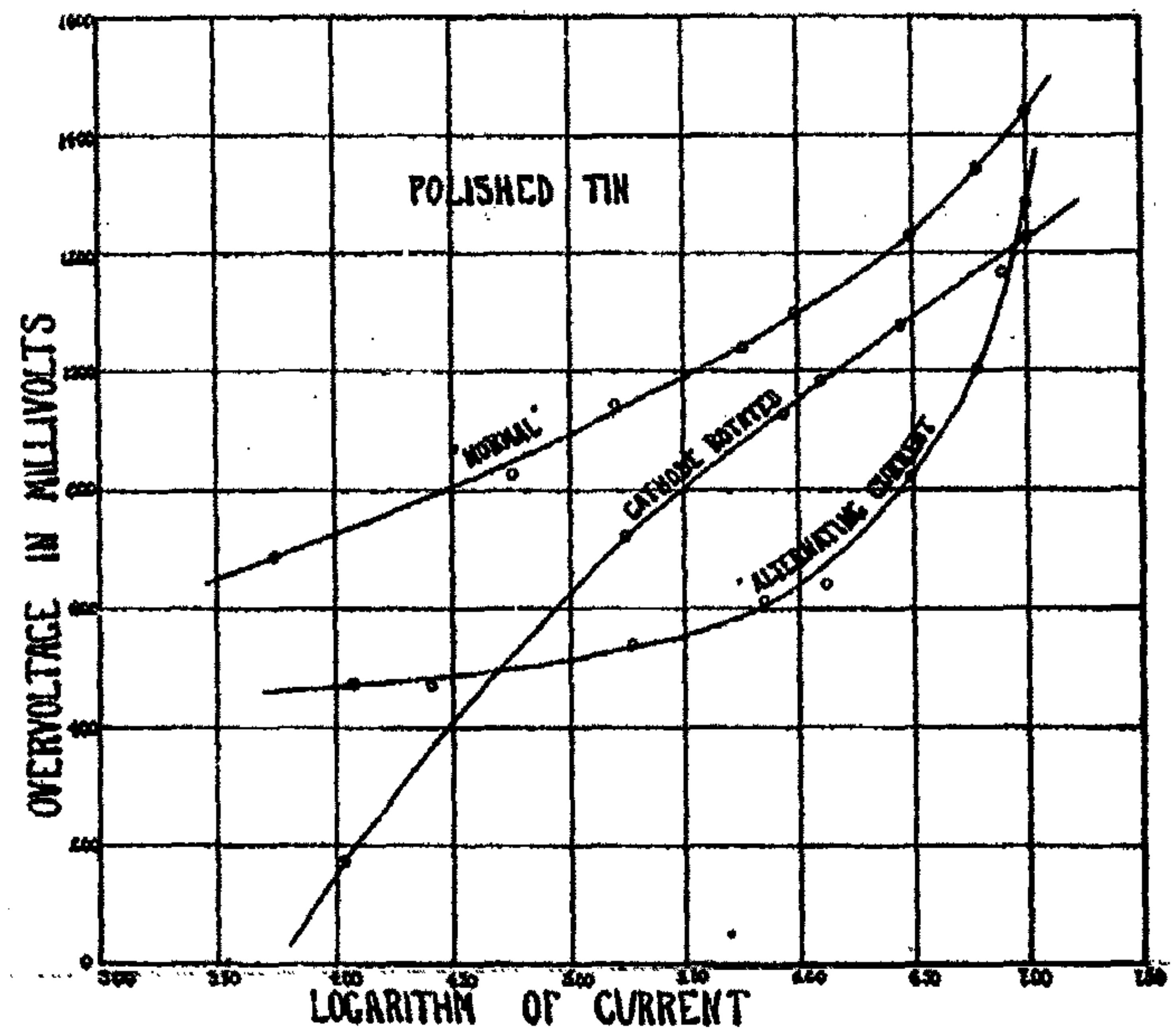

FIG. 8

Effect of a Rotating Cathode and of a Superimposed Alternating Current on Overvoltage (Current in 10^{-9} Amperes).

It may be assumed that the negative phase of the alternating current raises, and the positive phase lowers the overvoltage, since it has a strong depolarizing action and probably oxidizes the hydrogen atom before they forms molecular hydrogen. It is of interest to note that the lowering produced is the greatest on platinum, a metal of extremely high oxygen overvoltage.

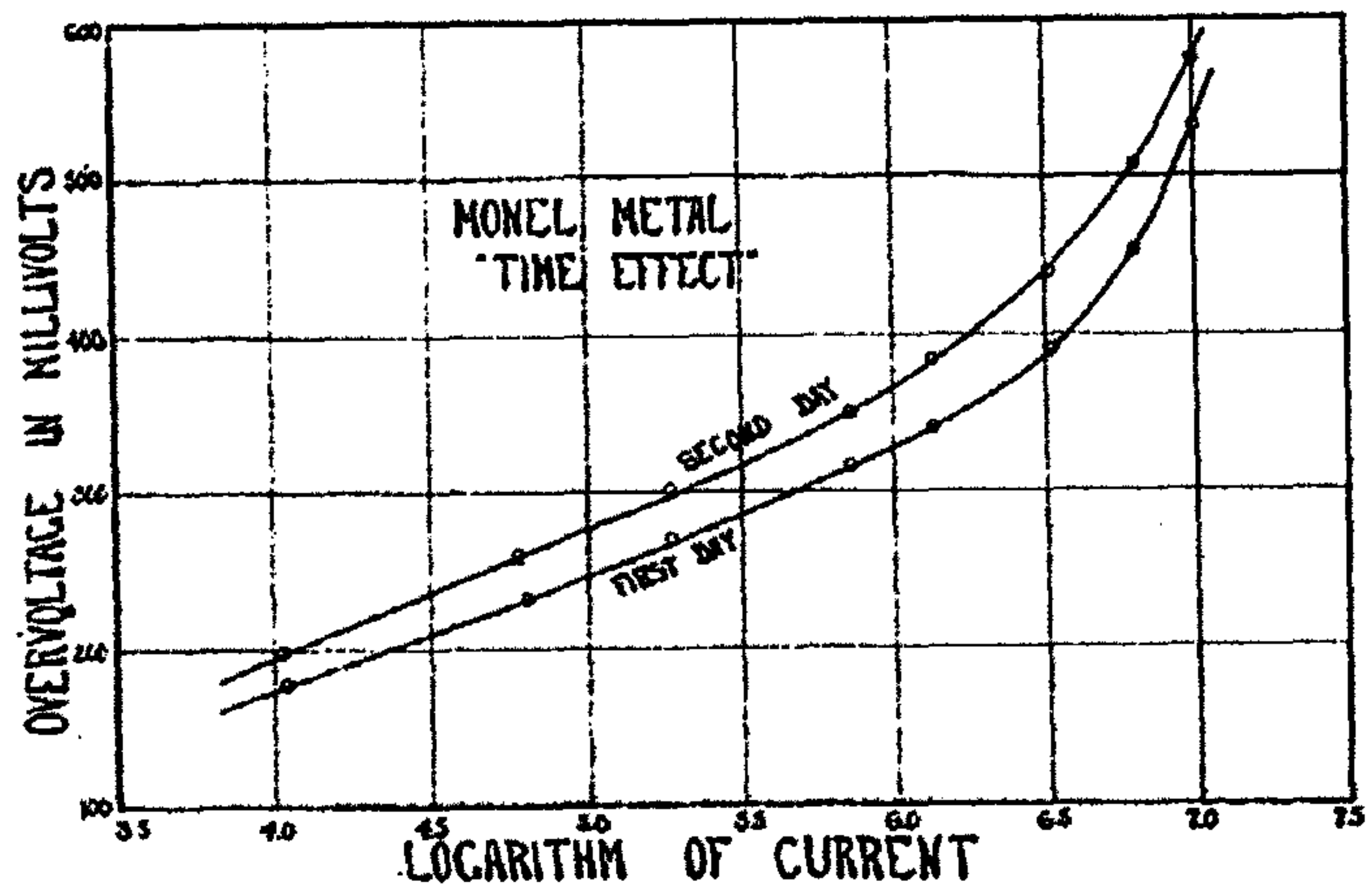

FIG. 9

Effect of Time on Overvoltage. (Current in 10^{-9} Amperes).

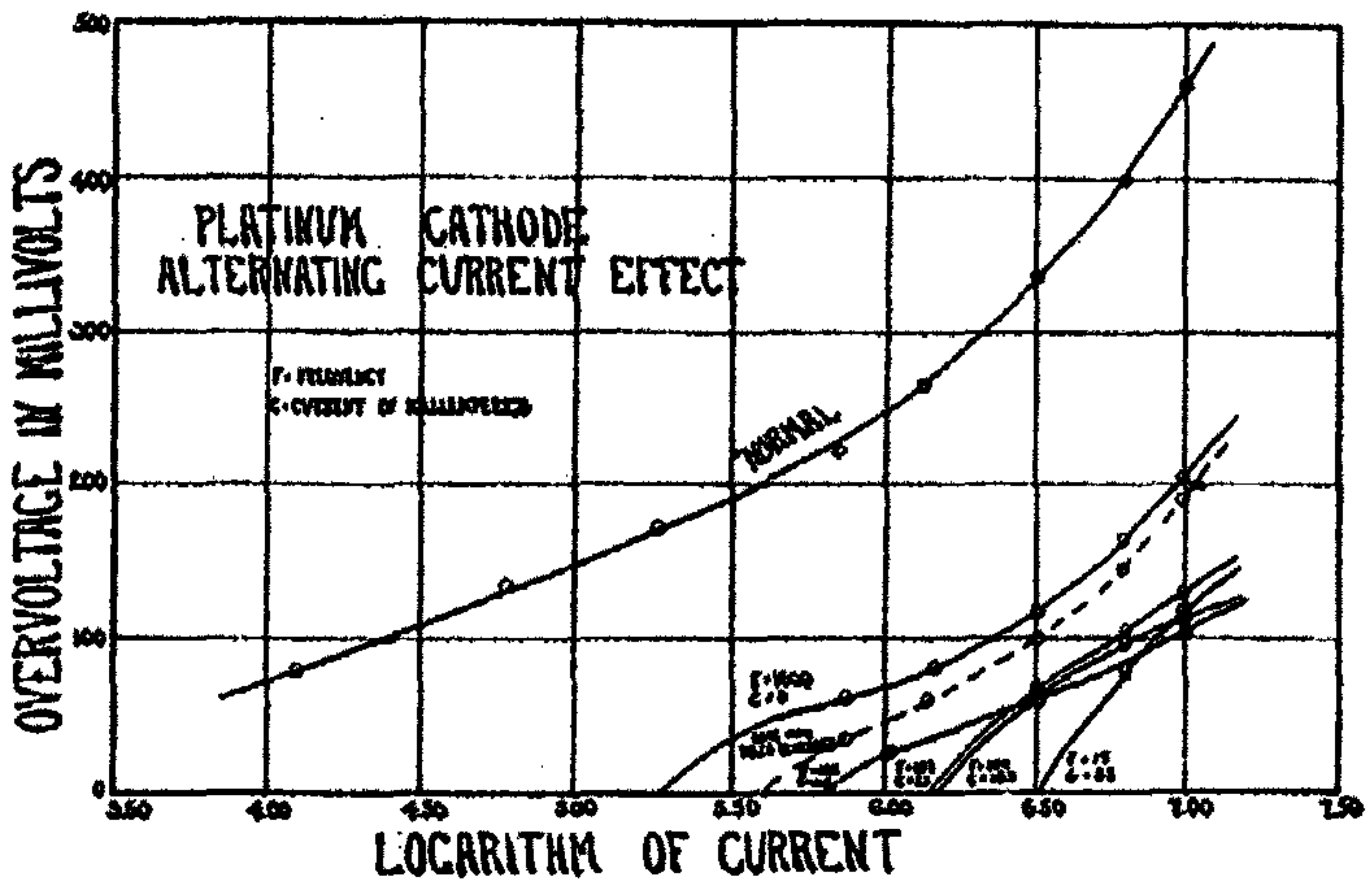

Fig. 10

Effect of a Superimposed Alternating Current on Overvoltage. (Logarithm of Current in Terms of Billionths of an Ampere for an Electrode of 84 sq. mm. Area. C = Current in Milliamperes).

That there are exceptions to the above rule is shown by the fact that the overvoltage of rough copper (Fig. 12), of smooth copper, and of copper deposited from acid and from alkaline solutions, was raised by a superimposed alternating current except at the lowest current densities used. This seems to indicate that the positive phase of the current is not particularly effective as a depolarizing agent on copper, and that the negative phase acts to increase the effectiveness of the direct current in increasing the overvoltage.

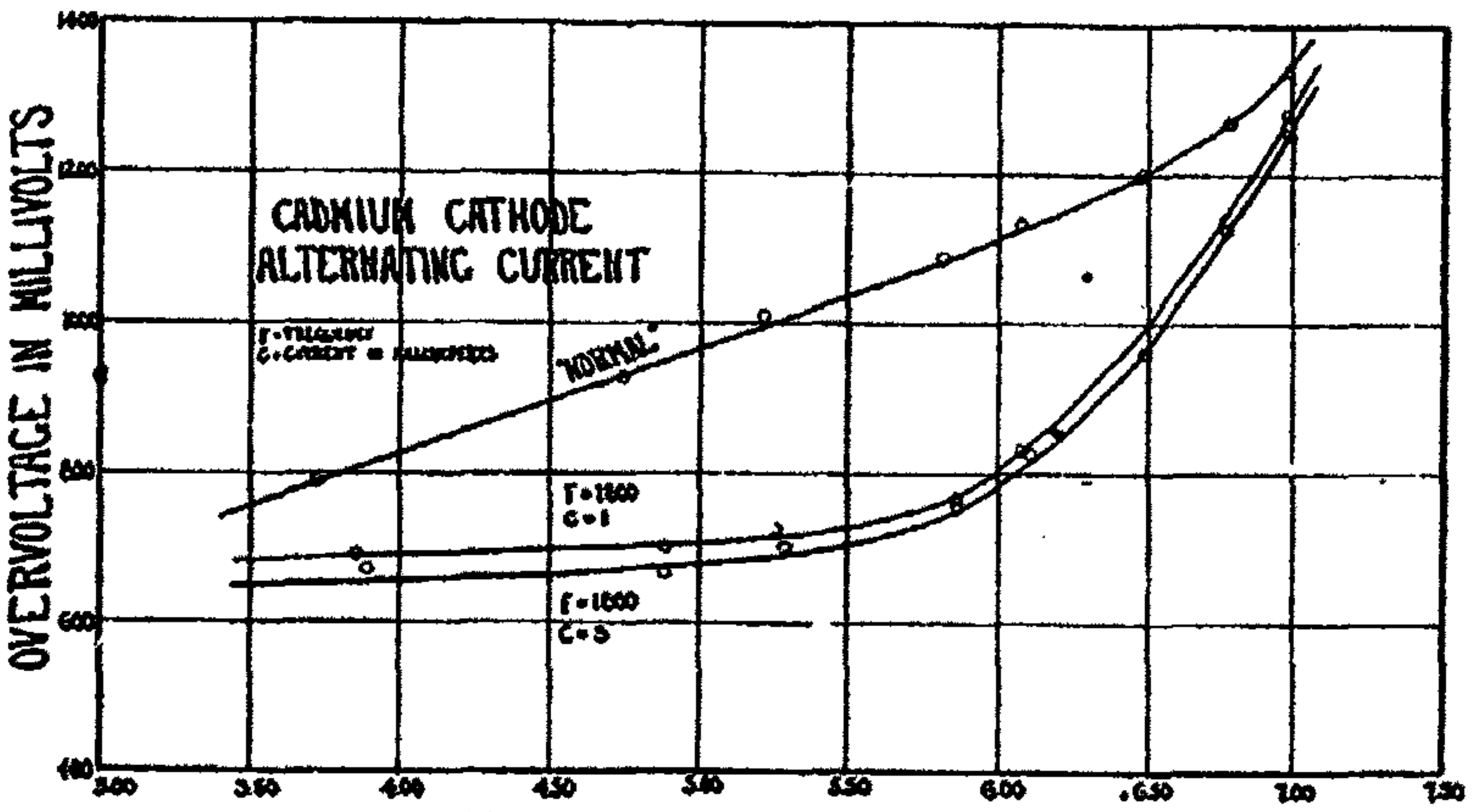

Fig. 11

Effect of a Superimposed Alternating Current on Overvoltage (Log. of current in 10^{-9} Amperes. C = Current in 10^{-3} Amperes).

9. Overvoltage and Current Density

The relation between the overvoltage and the current density was determined for 12 metals at 25°C. In general order of increasing overvoltage these were platinum, tungsten, molybdenum, monel metal, nickel, gold, silver, copper, tantalum, mercury, cadmium, and tin. Fig. 13 gives the overvoltage as plotted against the logarithm of the current density, as obtained by increasing the current. The curves obtained when the current was again decreased lie slightly above these in every case, but are omitted to avoid confusion in the diagram. Thus there is a hysteresis comparable to that obtained by raising and lowering the temperature. Similar data were obtained from rough cathodes for all of the metals except mercury, tungsten, tantalum, molybdenum, and monel metal. In every case the rough cathode gives a lower overvoltage than the smooth at the same apparent current density. Roughening the surface has two effects: it increases the actual area for a definite apparent area, and it supplies points from which hydrogen is more easily liberated. Fig. 14 illustrates this effect for I polished copper, II copper

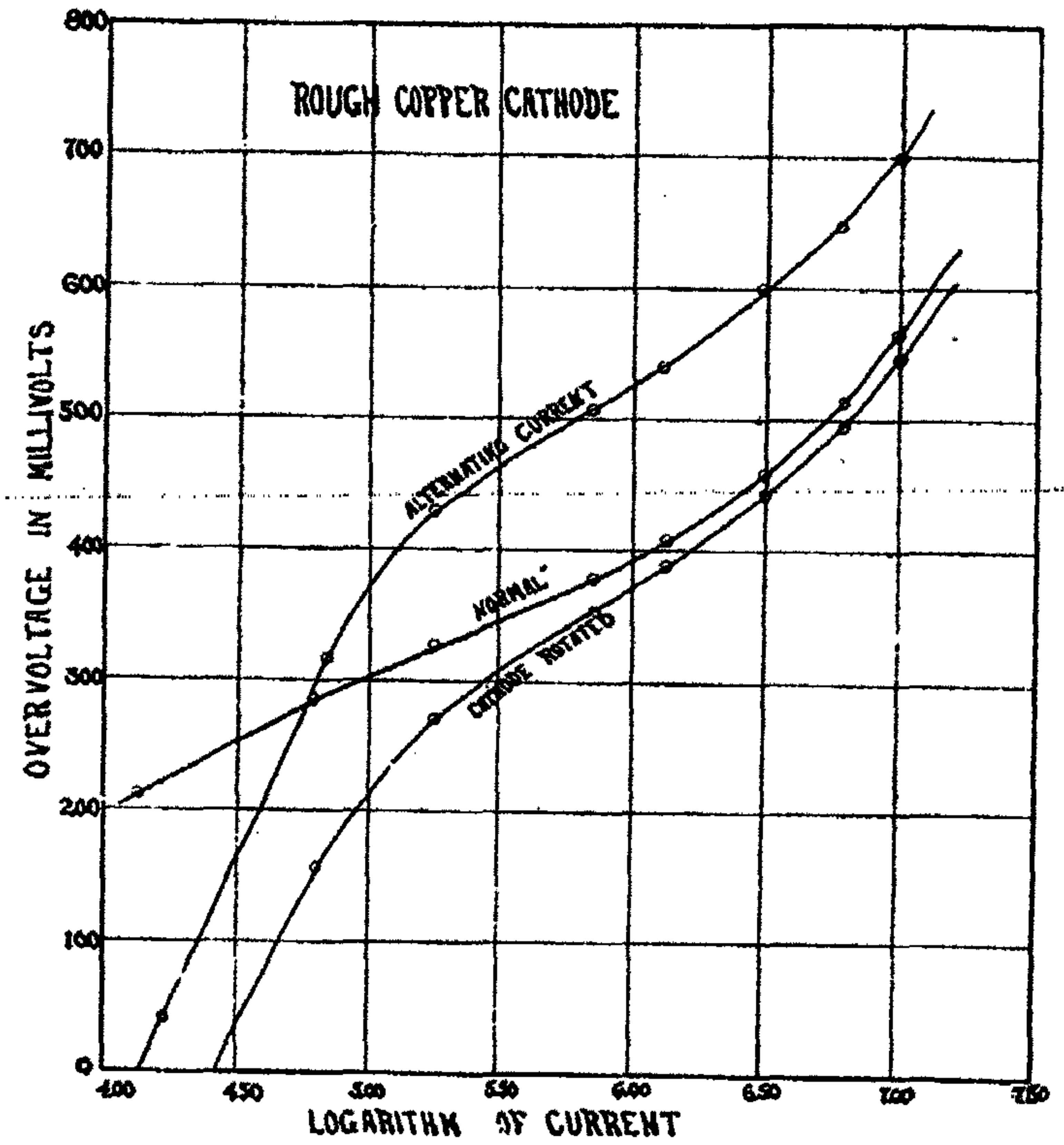

Fig. 12

Effect of a Rotating Cathode and of a Superimposed Alternating Current on Overvoltage (Current in 10^{-9} Amperes).

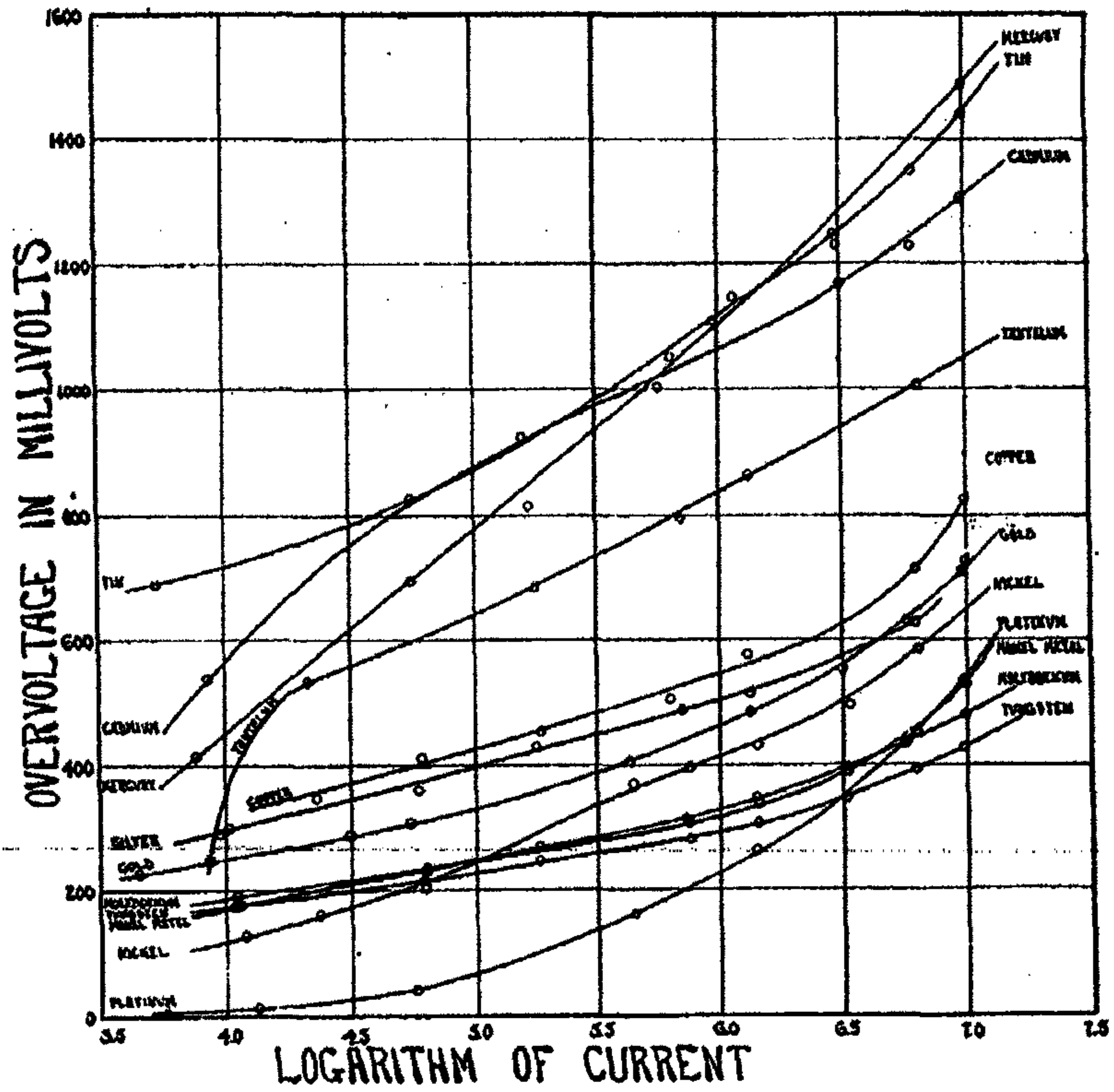

Fig. 13 A
Effect of Current Density on Overvoltage (Current in Billionths of an Ampere on an Electrode of 84 sq. mm. Area).

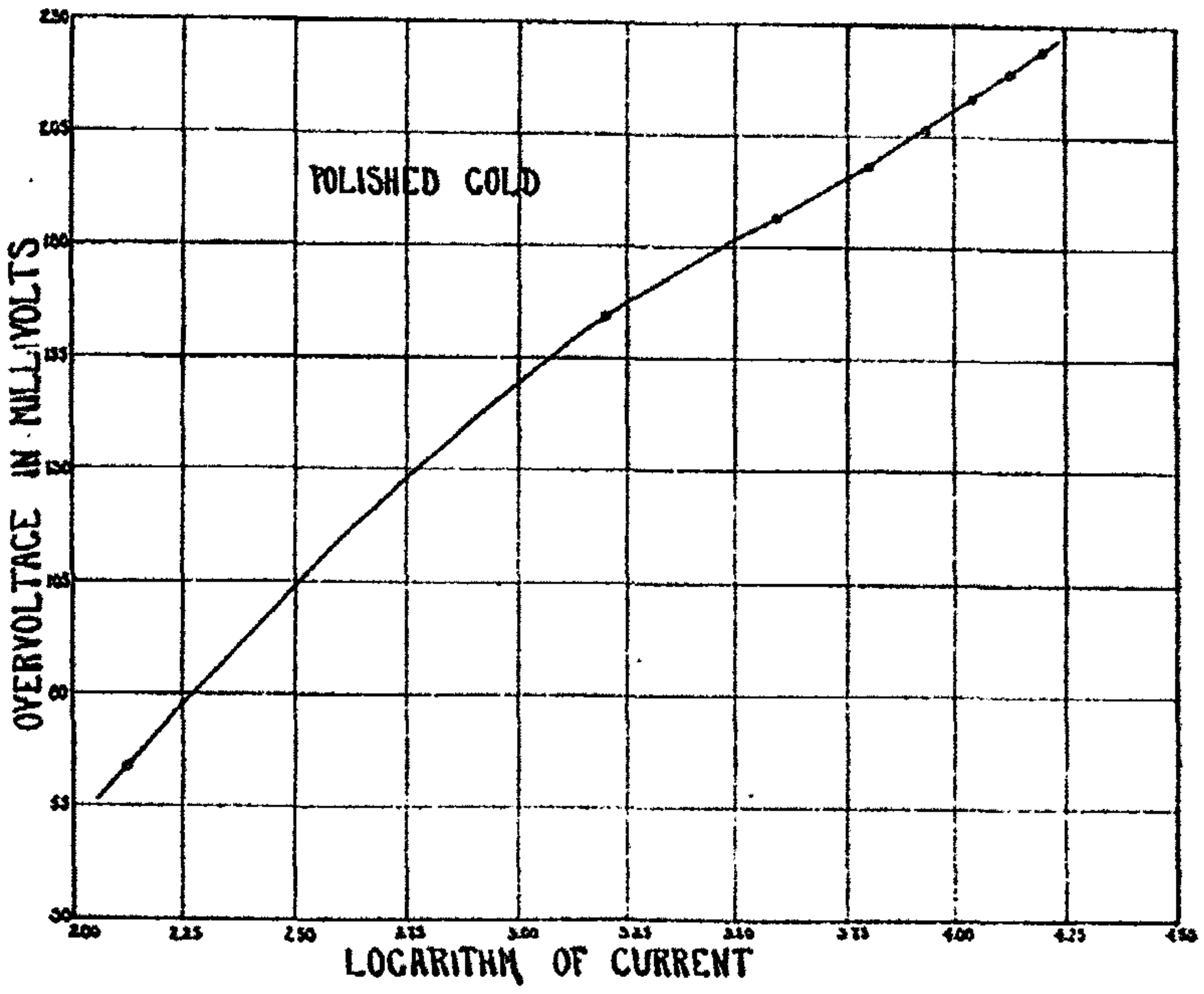

Fig. 13 B
Effect of Low Current Densities on the Overvoltage of Gold. (Current in 10^{-9} Amperes).

from ammoniacal solution, and III copper from acid solution. The overvoltages given by III are from 100 to 200 millivolts lower than those given by I.

The curves of Fig. 13 indicate that at 25° and with the 12 metals represented, the overvoltage is in general not far from a linear function of the logarithm of the current density, though there are in some cases considerable variations from linearity which indicate that there are conditions under which the relation does not hold. It is important in this connection that similar experiments should be carried out at different temperatures.[1]

It is apparent that in general the overvoltage increases as the cohesion in the metal decreases.

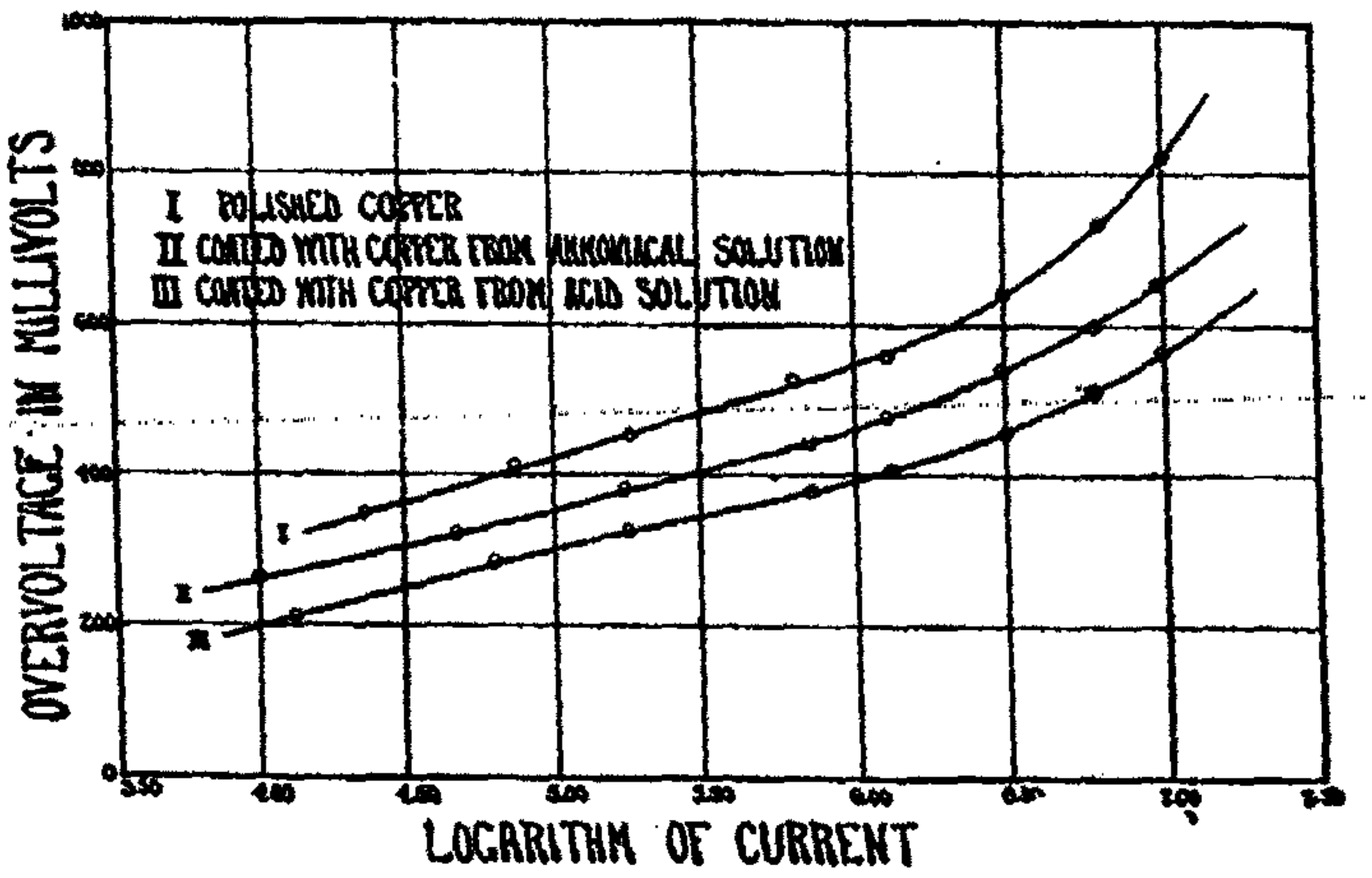

Fig. 14
Effect of Nature of Surface on Overvoltage. (Current in Billionths of an Ampere).

10. Relation to the Periodic System

An earlier paper by Harkins[2] indicates that overvoltage is related to the periodic system of the elements in the sense that members of the same family of elements have nearly the same overvoltage. Thus it was found that arsenic, antimony, and bismuth, have overvoltages which differ little, and the same was found true of copper, silver, and gold, of zinc, cadimum and mercury, and of tin and lead. The present paper shows that this is true for copper silver, and gold, and for cadmium and mercury, over the whole range of current density. In addition it is found that the same relation holds for molybdenum and tungsten, metals for which the overvoltage increases very slowly as the current density rises, so slowly that at high current densities they have a lower overvoltage than platinum. The overvoltage curve for monel metal is almost the same as that for molybdenum and tungsten, and it should be noted that its slope is much less than that of the curves for its components, copper and nickel, and in general lies far below both of them.

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[1] This has been done by Bircher and Harkins.

[2] J. Am. Chem. Soc., 32, 518-30 (1910).

Summary

1. The overvoltage on a metal cathode is found for inactive metals to be on the whole a linear function of the logarithm of the current density, this line being specially straight in the cases of mercury and tantalum. At low current densities the overvoltage falls off much more rapidly, than corresponds to this relation. The overvoltage of molybdenum and tungsten increases very slowly, while that of platinum, nickel, and mercury, increases rapidly with the current density. Curves for tin, cadmium, copper, silver, gold, and monel metal, in addition to those cited above, are given.

2. The overvoltage of mercury, a metal of high overvoltage, is practically constant between 1/36 and 3 atmospheres pressure.

3. The overvoltage of a metal with a high overvoltage (mercury) is found, contrary to the deduction made by Rideal on the basis of a desorption theory, to decrease rapidly by 2 millivolts for each degree increase of temperature, which indicates that the effect is related to the changes of surface energy.

4. Rotating the cathode at high speed, 2000 to 6000 revolutions per minute, or bubbling hydrogen nitrogen, carbon dioxide, air or oxygen, over the electrode, reduces the overvoltage greatly at low, and to some extent at high, current densities. The extent of the lowering depends also on the surface, being, for example, much larger for smooth tin than for rough copper. The overvoltage of rough nickel was greatly raised by rotation.

5. Alternating currents with frequencies of from 15 to 1800 and current densities of from 1 to 200, were found to give rise to undervoltages on platinum, tungsten, and molybdenum at low current densities of the direct current, and to lower the overvoltage in all cases except on a smooth or rough copper cathode on which the overvoltage was raised. The general effect is what would be expected if the hydrogen were oxidized, presumably while still in the atomic state.

6. The overvoltage increases with the time during which the metal is used continuously as a cathode.

7. Roughening the surface is found to decrease the overvoltage in all cases. The effects cited in this and the preceding paragraph were already known when this work was begun, but the present paper shows the extent of the variations which occur.

8. The paper illustrates the relation between overvoltage and the ordinary periodic system.

The object of the paper has been to present facts concerning the phenomena of overvoltage. Many theoretical papers on this subject have been written. Some idea of the various theories may be obtained by consulting the papers of Bennett[1], Bancroft[2], MacInnes, Adler, and Contieri[3], and Newbery[4].

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[1] Bennett: J. Phys. Chem., 20, 296-322 (1916).

[2] Bancroft: J. Phys. Chem. 20, 396-401 (1916).

[3] MacInnes, Adler and Contieri: J. Am. Chem. Soc., 41, 194, 2013 (1919).

[4] Newbery: J. Chem. Soc., 105, 2428 (1914).

STUDIES IN ADSORPTION FROM SOLUTION FROM THE STANDPOINT OF CAPILLARITY—II[1]

BY W. A. PATRICK AND N. F. EBERMAN

Introduction

In a former paper[2] dealing with adsorption by silica gel of a large number of substances from solution, the adsorption was explained by a lowering of solubility due to the high curvature of the surface of the adsorbed solute in the capillaries of silica gel. This, it was pointed out, is strictly analogous to adsorption from the gaseous phase and should obey the laws largely enunciated by Patrick and McGavack[3] in a study of the adsorption of sulfur dioxide by silica gel. It is the purpose of this paper to further extend the above view to adsorption from solution in general and to apply the capillary theory of adsorption from a more quantitative and rigorous standpoint.

The empiric formula of Patrick and McGavack[4] has satisfactorily explained the adsorption by silica gel of sulfur dioxide, ammonia[5], carbon

$$V = K\left(\frac{P\sigma}{P_o}\right)^{1/n}$$

dioxide and nitrous oxide[6], butane[7], water vapor[8], and the solution of ammonia in water.[9] In this formula V is the volume of liquefied gas (obtained by dividing the weight of gas by the density) or liquid adsorbed per gram of gel, P is the equilibrium pressure, σ is the surface tension of the liquefied gas or liquid, K and $1/n$ are constants and P_o is the ordinary saturation pressure of the adsorbed substance at the temperature. Now in order to apply this formula to adsorption from solution, let us write it:

$$V = K\left(\frac{S\sigma}{S_o}\right)^{1/n} \qquad (1)$$

where V is the volume of liquid (usually) solute adsorbed per gram of gel, S is the equilibrium concentration of the solute in the surrounding solvent, K and $1/n$ are constants as before, σ is the interfacial tension, and S_o, for want of a better term, will be called the "solubility," or "solution power" (of the solvent). Being analogous to P_o, it might be thought that S_o should be the ordinary maximum solubility of the solute in the solvent at the temperature in question. But since there exist cases in which adsorption occurs from liquids miscible, so to speak, in all proportions (see later), it is obvious that

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

[2] W. A. Patrick and D. C. Jones: J. Phys. Chem., 29, 1 (1925).

[3] J. Am. Chem. Soc., 42, 946 (1920).

[4] Loc. cit.

[5] Patrick and Davidheiser: J. Am. Chem. Soc., 44, 1 (1922).

[6] Patrick, Preston and Owens: Unpublished paper to appear soon.

[7] Patrick and Long: Unpublished paper, to appear soon.

[8] Patrick and Opdyke: Unpublished paper, to appear soon.

[9] Patrick and Neuhausen: J. Phys. Chem., 25, 693 (1921).

S_0 cannot represent the ordinary solubility,—for then, in the above case, S_0 should come out infinity. It will be seen, however, that in all the calculations made, even with liquids completely soluble in each other, S_0 has a definite finite value. Just what physical meaning to ascribe to this quantity S_0, will be discussed later after the experiments have been described.

Experimental

The data which follow pertain to the adsorption of water from its solution in n-butyl alcohol. This system was selected because water is soluble in butyl alcohol to the extent of about 20%. In this case adsorption could be readily studied over the entire range of concentration, and the values of S_0 found could be compared to the ordinary finite solubility (in distinction from infinite solubility in the case of liquids miscible in all proportions,—although this state of affairs will also be referred to). Furthermore, water is readily adsorbed by silica gel, since the latter consists of aggregates of spherical silica particles surrounded by concentric shells of water molecules[1].

The general procedure consisted in treating solutions of known concentration of water in butyl alcohol, ranging from zero to about fifteen percent water, with a certain amount of gel, and, after equilibrium was attained, analyzing the solution for water to determine the equilibrium concentration (S) as well as the amount (i.e. – volume = V) of water taken up per gram of gel.

The gel was prepared as usual[2], and a granular form used which passed through a 12 and was retained by a 16 mesh sieve. The water content was determined by heating to constant weight, and found to be 5.2%. This gel was kept in a well stoppered separatory funnel arranged for delivery into a narrow mouthed flask which contained the solution. This same gel was used throughout the following experiments and was kept in a desiccator.

The n-butyl alcohol was obtained from the Commercial Solvents Company, and fractionated to remove the water. The fraction taken was that boiling between 118.2°–118.6° at 775.5 mm. pressure, according to the vapor pressure curve given by Landolt-Börnstein. The method of analysis used was the determination of the density of the aqueous-alcoholic solution by means of an Ostwald pyknometer. First, a density-concentration curve was made for 26.2°—the temperature of the thermostat used. Adsorption experiments were then made at 1°, 26.2° and 50°. The adsorption flasks were allowed to remain at the temperature, with very frequent shaking, for at least four hours. Determination of density after this time showed that four hours was more than sufficient time for equilibrium to be attained. A sample of the liquid above the gel was then carefully drawn into the weighed phknometer, immersed in the thermostat until constant volume, and weighed. These results are given in Table I and Fig. 1.

(In Table I it is well beyond the limits of error in the subsequent calculations to assume the grams water adsorbed equal to the number of cc. adsorbed.)

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[1] Patrick and McGavack: loc. cit.

[2] Patrick and McGavack: loc cit.

The ordinary solubility of water in n-butyl alcohol was also determined by the above methods and found to be 17.8% (weight) at 1° and 19.5% at 26.2°. Besides this, an approximate value for the critical solution temperature was determined by heating butyl alcohol and water in a closed tube in a bath and observing the disappearance of the meniscus. The tube was then shaken and allowed to cool slowly in a bath with an accurate thermometer until the first haziness appeared, when the temperature was noted. The C. S. T. found this way was 134.8° — very close to the value for iso-butyl alcohol, which is given in tables as 131.5°. This is to be expected, inasmuch as the physical properties in general of normal and iso-butyl alcohol are very similar, whereas the secondary has quite different properties.

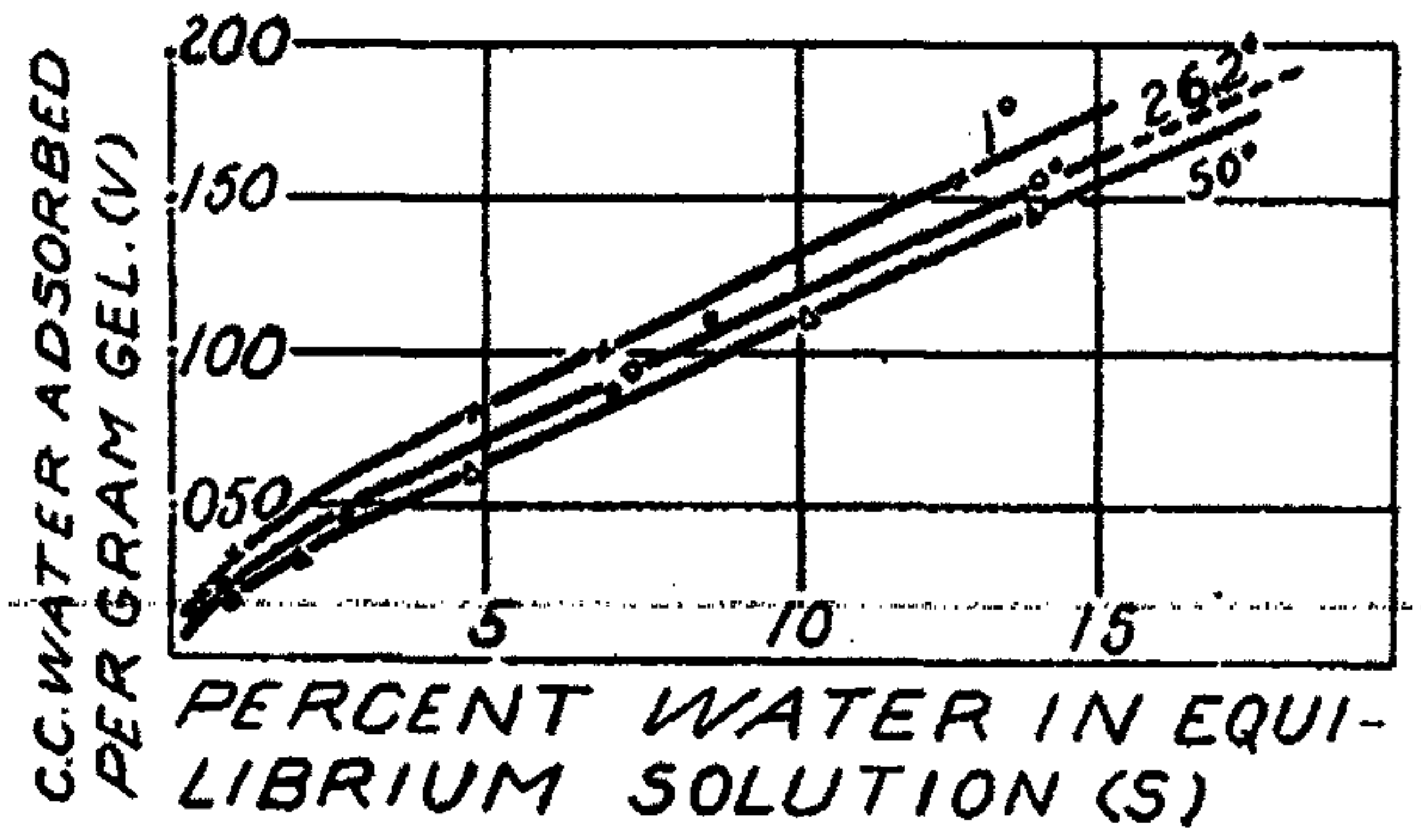

FIG. 1
Adsorption of Water from Butyl Alcohol

TABLE I

Temperature 26.2°

S (% wt)	V
0.83	.0214
0.92	.0191
2.76	.0455
6.90	.0870
7.24	.0938
8.44	.1113
14.00	.1573
14.25	.1607

Temperature 1°

S (% wt)	V
0.40	.0235
1.05	.0300
4.80	.0812
6.75	.1020
12.60	.1568
14.04	.1620

Temperature 50°

S (% wt)	V
2.10	.0314
4.83	.0618
6.75	.0859
10.17	.1083
13.87	.1460

Calculations

In order to solve for S_o from the data of Table I, it will be necessary to resort to the following mathematical treatment to obviate the presence of three constants—K, S_o, and $1/n$ in the equation

$$V = K \left(\frac{S\sigma}{S_o}\right)^{1/n}$$

Putting this equation in the logarithmic form, we have

$$\log V = 1/n \log (S\sigma) + (\log K - 1/n \log S_o) \qquad (2)$$

If we now plot log V against log (Sσ), a straight line should be obtained with a slope of 1/n and an intercept on the log V axis of ($\log K - 1/n \log S_o$). These results are given in Table II, in which the volumes (V) and concentrations (S) are read from the 26.2°. isotherm of Fig. 1. The question now arises, what value are we to ascribe to σ, the interfacial tension? The answer to this question depends upon whether the phase which separates out in the pores is pure water or water containing some butyl alcohol. According to Freundlich[1],

$$\sigma_{BW} = \sigma'_W - \sigma'_B \qquad (3)$$

where

σ_{BW} = interfacial tension of butyl alcohol-water

σ'_W = surface tension of water saturated with butyl alcohol

σ'_B = surface tension of butyl alcohol saturated with water.

TABLE II

σ=2.0	T=26.2°	σ=2.8	T=1°
log V	log (Sσ)	log V	log (Sσ)
−1.60206	0.36173	−1.60206	0.32222
−1.30103	0.79518	−1.30103	0.84510
−1.12494	1.02119	−1.12494	1.10037
−1.00000	1.18469	−1.00000	1.27600
−0.90309	1.30963	−0.90309	1.41162
−0.82391	1.41497	−0.82391	1.52114

It is also known that a capillary active substance lowers the surface tension much more than a capillary inactive substance raises it. This is illustrated by curves given by Freundlich[2].

According to this state of affairs, if we assume the phase which separates out in the capillaries to be pure water, our interfacial tension will be, according to equation (3)

$$\sigma_{BW} = 75 - 25 \quad \text{or about } 50\ \frac{\text{dynes}}{\text{cm}}; -$$

assuming that the small amount of water in the butyl alcohol has not appreciably raised the latter's surface tension (= 25)—according to the above tenets. On the other hand, if the phase which is adsorbed is water containing, at least at its surface, some butyl alcohol, the interfacial tension will be

$$\sigma_{BW} = 30\ (\text{about}) - 25 \quad \text{or about } 5\ \frac{\text{dynes}}{\text{cm}}.$$

(The value 30 is an approximation taken from curves given by Freundlich). Which of the above values to use becomes evident upon consulting Table I

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[1] "Kapillarchemie," p. 132.

[2] "Kapillarchemie," p. 137.

which gives the amount of water removed by the adsorption. In all cases, this is very slight, amounting to about .2 gm. water from a solution containing 15% water. This indicates the interfacial tension must be very small indeed, else much more water would be removed. For it can be shown that in the case of two liquids, other things being equal, that liquid which has the higher interfacial tension will be more readily condensed in a capillary. Unfortunately, the tensions σ'_W and σ'_B (equation 3) have not been determined for our system. In lieu of this, and the fact that iso-butyl alcohol is very similar in physical properties to n-butyl alcohol, we will use Antonow's[1] value of the interfacial tension of iso-butyl alcohol—water (as defined by equation 3) of approximately 2 $\frac{\text{dynes.}}{\text{cm}}$ At all effects, this will give us relative values for S_0, since σ_{BW} is a constant throughout the calculations. Furthermore, from the above discussion it is obvious that the value 2 cannot be very far from the truth.

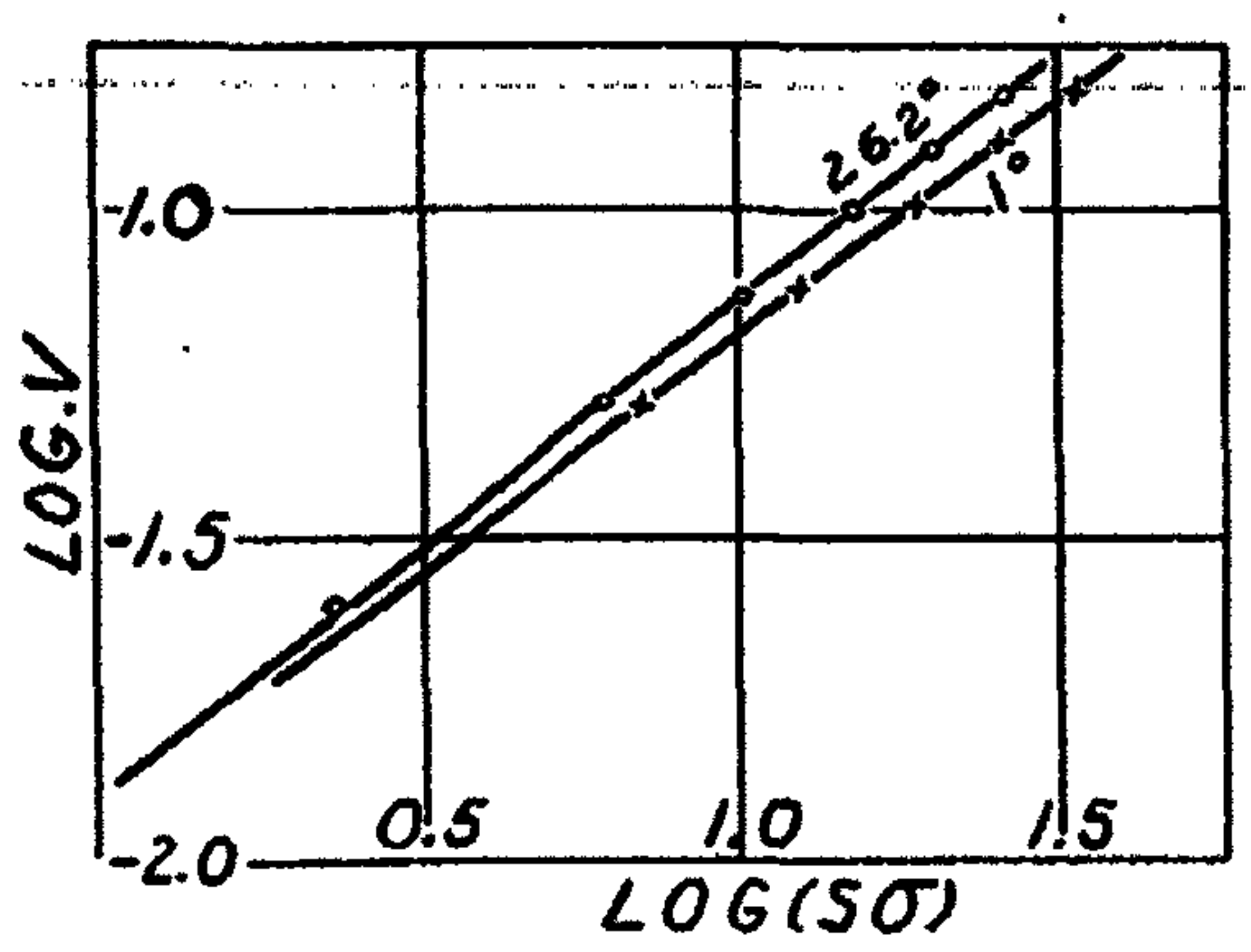

Fig. 2

From Table II we plot on large graph paper the curves given in Fig. 2 and measure the slopes and intercepts. (The interfacial tension at 1° was found by assuming a straight line function with the temperature, and that the tension at the C.S.T. of 134.8° was zero). In the case of the 26.2° curve (Fig. 2), we have $1/n = .767$. Now it is true that when $S = S_0$

$$V_0 = K\sigma^{1/n} \tag{4}$$

where V_0 represents the internal volume of the gel, which in this case is approximately .2 cc. per gram gel. This value .2 cc. is found by extrapolating the 26.2° isotherm of Fig. 1. If this is done, it is seen that when S is a concentration of about 19.5% (the saturation value found by experiment at 26.2°), the volume of water corresponding is about .2 cc. It is to be expected that the conical capillaries will fill to different volumes, depending upon the value of the interfacial (or surface) tension. Thus in the case of the system under consideration—that is, one in which the interfacial tension is very low—it is entirely probable that the capillary effect would cease at a smaller radius

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[1] J. Chim. phys., 5, 372 (1907).

of the conical capillaries,—therefore giving a less value for V_o than with adsorption of a pure substance such as sulfur dioxide, in which case V_o is about .4 cc.

Hence, from equation (4)

$$K = \frac{.2}{2.767,} \quad \text{whence } \log K = 0.92986$$

And, from equation (2)

$$-0.92986 - .767 \log S = -1.9$$

where -1.9 is the measured intercept of the curve (Fig. 2)

$$\text{Whence } S_o = 18.88$$

Similar calculations with the 1° curve give a value of S_o of 17.74.

It is seen, then, that S_o comes out *less* than the ordinary saturation value of 19.5%. That it should be *less* is to be expected, since, with adsorption with liquids miscible in all proportions, a finite value would be found. For example, experiments performed by D. C. Jones[1] upon the adsorption of butyl alcohol from benzene—liquids miscible in all proportions—give a value of about 5% for S_o. *Wherever adsorption takes place, therefore, a value of S_o can be found.* In all cases calculated so far, this value has come out *less* than the ordinary solubility value at the temperature.

From this standpoint then, the "solubility" as determined above has a definite conception based primarily upon the dissolving power of the solvent as uninfluenced by molecules of the solute subsequently entering.

Theoretical

Since adsorption by silica gel is fundamentally caused by the capillaries in the adsorbent exerting their manifold influences, it should be possible to treat the above experimental results, as well as the results of adsorption in general from liquid or gas, according to the known laws of capillarity, without having recourse to empirical formulae. This can readily be done as follows. Let us relate the internal volume of a gram of gel with the radius (average of course) of the capillaries by the equation

$$V = K\, r^{1/n} \tag{5}$$

which is the most general form.

Now, the well known Thomson[2] formula relates, in turn, the radius of the capillaries (i.e. the radius of curvature of the liquid within them) with the equilibrium vapor pressure of the liquid within the system. This formula may be written

$$\ln \frac{P_o}{P} = \frac{2\sigma M}{D_l r R t} \tag{6}$$

where P_o is the saturation pressure of the gas at the temperature, P the equilibrium pressure, σ the surface tension of the liquefied gas (in this case), M the molecular weight, D_l the density of the liquefied gas and r the radius of curvature. In case of adsorption (or capillary condensation) from solution, equation (6) should be written:

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[1] D. C. Jones: Unpublished results.

[2] Phil. Mag. (4), 42, 448 (1881).

$$\ln \frac{S_0}{S} = \frac{2\sigma M}{D_l rRT} \qquad (7)$$

By combining equation (6) or (7) with (5), one can readily eliminate r, and obtain a direct relation between V and P (or S) not very different in its essential relationship from the empiric equation (1). Now it is obvious that if we plot radius, as found by equation (6) or (7) against volume (V) as measured, we should obtain a parabolic curve (according to equation 5) which should be the same curve for all substances adsorbed by the same sample of gel whether from the gas or from solution—regardless of temperature. For, if adsorption consists in capillary condensation, the same volume of internal gel space must hold the same volume of liquid regardless of circumstances.

These V-r curves for a large number of substances are plotted on Fig. 3. The data are taken from results obtained by Patrick and McGavack, Patrick and Long, and Patrick and Opdycke.[1]

A glance at these curves shows a number of significant relations. First of all, it shows that the curves cannot be represented by the relation $V=K r^{1/n}$ until the radius reaches the value, in most cases of about .5 $\mu\mu$. Before this is reached, the curves have the form

$$V=K r^n$$

Thus the complete curve would require at least a cubic equation in V and r. Now, the shape of the curves is that which, upon the basis of the supposed structure of the gel, would be expected. At low volumes adsorbed, a small increase in the volume adsorbed would bring about a relatively large change in the radius of the V-shaped capillaries which are being filled, (i.e.—the radius of the capillary at the point to which the liquid has filled is much greater than when the capillary was filled to a lower point),—at high volumes adsorbed, the same small increase in volume adsorbed would bring about a much less change in the radius of the V-shaped capillary. Furthermore, with large volumes adsorbed and the effective capillary radius becoming larger and larger, the total capillary *effect* is becoming less. Thus the curves eventually turn parallel to the r axis.

As before stated, if all the substances adsorbed are really liquefied in the capillaries, all these curves should coincide, regardless of temperature. That the water content of the gel has practically no effect, is seen by the curves for butane at 30° with gels of three different water contents. These three curves coincide with each other, and also happen to lie on the −54° isotherm for SO_2. When the statement is made, however, that *all* the curves should coincide, it must be remembered that this is made under the assumption that the physical properties of a liquid in a capillary are the same as of a liquid under ordinary conditions. For, it is seen that r is calculated from formula (6) which involves the ordinary values for surface tension, density and molecular weight. That these properties suffer no change in a capillary is most probably not the case, for matter existing with high curvature is well known to exhibit very different properties than matter en masse. Quite recently,

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[1] Loc. cit.

for example, Fisher[1] has shown that it is not correct to assume that water in a capillary tube possesses the same density as water in bulk.

What property (or properties) of a liquid which, if an erroneous value is assumed, brings about the greatest effort in the non-coincidence of the curves of Fig. 3 can be approximately determined by a process of elimination. For example, let us assume that the adsorbed liquid be polymerized. Then M in formula (6) or (7) would be greater. Consequently r will be greater, and the curve concerned higher, i.e.—further from the r axis. But, polymerization would obviously be greater at low temperatures than at high, and therefore the correction would be greater at low temperatures than at high,—which in turn would place the curves (say of SO_2 at different temperatures) further apart. Hence polymerization is improbable.

By a thorough consideration of all the factors involved, we are led to the firm belief that the surface tension of a liquid is a function of the curvature; that a liquid existing in small drops has a much lower surface tension than ordinarily, and that the liquid has a much greater surface tension if its surface is highly concave—as in the capillaries under consideration. This is entirely in agreement with the viewpoint of Freundlich, derived from independent considerations.[2] Furthermore, this variation of surface tension with curvature is also a function of the temperature. It would seem, from the curves, that the change of surface tension with the radius should be greater at high temperatures than at low. This is in accord with the results of Patrick and Preston on the adsorption of carbon dioxide by silica gel[3]. That the surface tension of a liquid in a capillary is greater than ordinarily, practically follows from all our adsorption experiments. For, if condensation of a gas *does* take place in a capillary above the critical temperature[4] and, in other cases, at pressures always below the saturation pressure; and, if adsorption *does* take place from liquids above the critical solution temperature,—it follws that the critical temperature for a fluid in a capillary is higher. If the critical temperature is higher, the surface tension must be correspondingly higher, inasmuch as the temperature-surface tension curve, which is generally linear, cuts the temperature axis at or near the critical temperature.

Since the surface tension term occurs in the numerator of formula (6), the values of r found by means of this equation would be greater in proportion as the surface tension of the liquid adsorbed in the capillaries would be greater. Experiments are now being made in this laboratory to test out formula (6) experimentally. That the radius would be greater due to increased surface tension would not only harmonize our experimental results to a greater degree, but would lead to a more reasonable value for the size of the spaces (i.e.—capillaries) between the spherical silica particles in silica gel. Zsigmondy,[5] for instance, from ultramicroscopic observations and from calculations[6]

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[1] J. Phys. Chem., 28, 360 (1924).
[2] Freundlich: "Kapillarchemie," loc. cit. p. 63.
[3] Patrick Preston and Owens:
[4] Patrick, Preston and Owens: loc. cit.
[5] "Colloids and the Ultramicroscope," p. 232.
[6] Z. anorg. Chem., 71, 356 (1911).

based on the lowering of vapor pressure in capillary systems, ascribes the value 5 μμ to the silica particles. This would give very small spaces between the spheres—about 1 μμ as a maximum radius (or space). Our curves (Fig. 3) indicate radii up to about 4 μμ. With these limits of capillary space—comparable to molecular dimensions—the large amounts of substances adsorbed cannot be harmonized. Therefore it is most probable that the values for the radii, as indicated by Freundlich[1], Zsigmondy and the results of our own experiments, are much too small. In a later paper, experiments dealing with the variation of surface tension of a liquid with the curvature will be described.

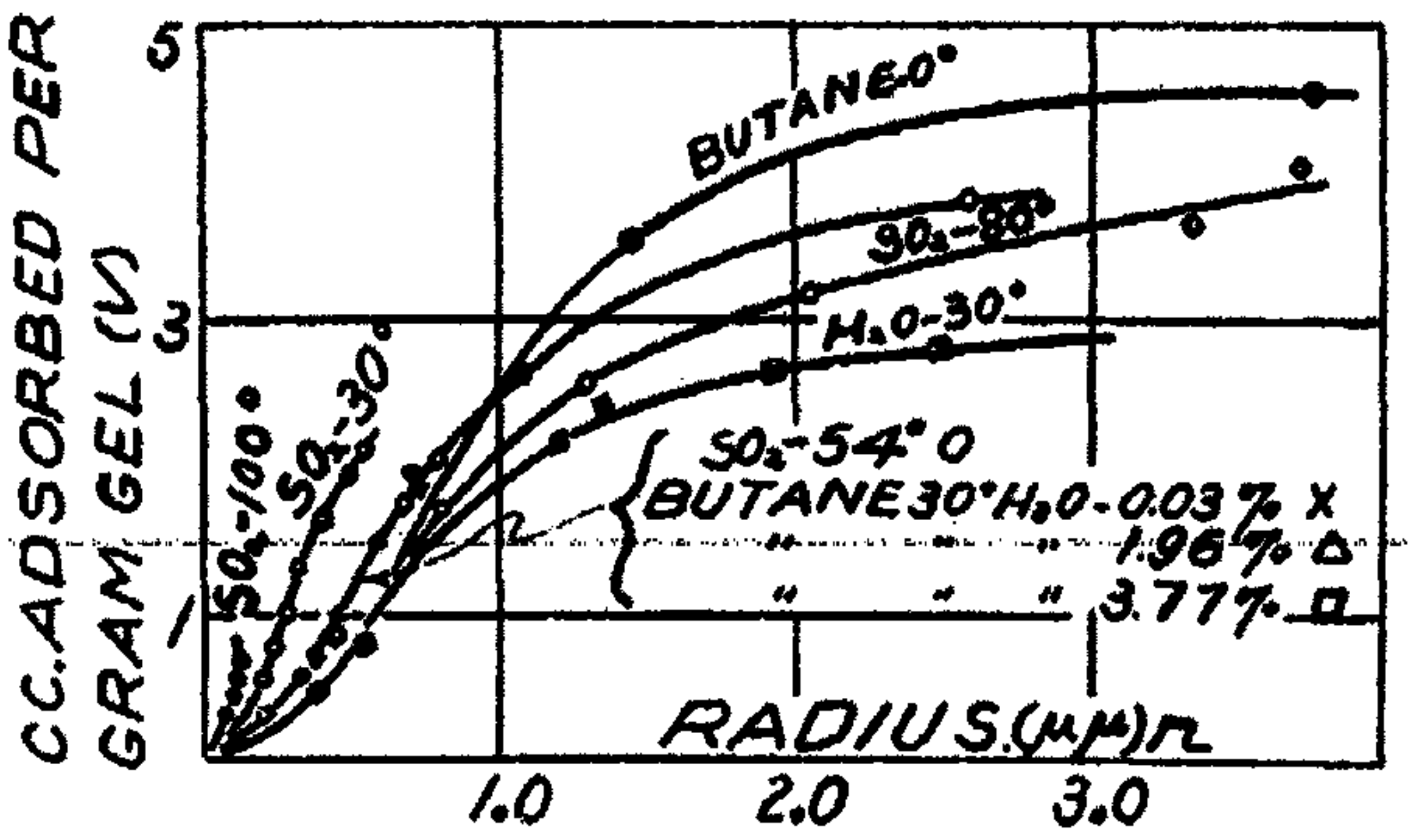

FIG. 3

It is obvious that the "solubility" S_o can be calculated for any adsorption (from solution) measurements from the theoretical equations (5) and (7) instead of using the empirical relation—(1). (In order to do this, equation (7) was solved for S_o. All the other factors in this equation are known except the radius r. This radius, however, can be approximately determined from the water vapor curve Fig. 3, where the radii are read off from the corresponding values of V from Table I. In this manner S_o comes out about 14%; as before,—less than the ordinary saturation value which, at 26.2° is 19.5%.

Summary

1. The adsorption of water from n-butyl alcohol by silica gel has been studied.

2. The empirical formula $V = K\left(\frac{S\sigma}{S_o}\right)^{1/n}$, analogous to the formula for adsorption of gases, is applied to adsorption from solution in several cases in order to calculate the "solubility" S_o.

3. The term S_o is defined.

4. A theoretical adsorption formula is derived from the laws of capillarity, and applied to the system butyl alcohol-water.

5. Reasons are given to show that the surface tension of a liquid in a capillary tube is greater than that of the same liquid under ordinary conditions, and that the change is greater the higher the temperature. It is shown how the above variation affects the adsorption formulae under consideration.

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[1] "Kapillarchemie," p. 917.

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. *By J. W. Mellor. Vol. V. 25×17 cm, pp. x+1004. New York and London: Longmans, Green and Co., 1924. Price: $20.00.* This volume deals with boron, aluminum, gallium, indium, thallium, scandium, cerium, and the rare earth metals, and an instalment on carbon. It was new to the reviewer that boron was first called boracium by Humphry Davy and that he afterwards suggested changing the name to boron in order to emphasize the analogy with carbon, p. 3. Under these circumstances there seems to be no justification in clinging to glucinum in preference to beryllium.

The uses of borax are given on p. 75. "Borax and boric acid have an extraordinary number of applications in different industries. They are used as constituents in making enamels for iron, and other metals; in the manufacture of pottery glazes; in making glass, artificial gems and strass; and in the manufacture of pigments for glass painting. Borax is used in making Guignet's green. It is employed in the tannery, and in the currying shops for dissolving dirt and blood from skins and thus ensuring a more rapid liming. It is used for cutting oils and fats used in stuffing leather and in bleaching and mordanting leather. It is used in the laundry in washing and starching; it helps to give linen a high gloss. Many commercial starches contain borax; and borax is also used in making some soaps. Borax is used as a wood preservative against dry rot, and on account of its antiseptic qualities it is introduced in cosmetics, mouth-washes, tooth-powders, and salves. It is used as a constituent of powders for killing insects, etc. It is employed as a preservation for meats, fish and other food-stuffs. A varnish for stuffing hats is made from borax and shellac. A mixture of casein and borax is a substitute for gum and it is moisture-proof. The paper mills use borax in making a kind of parchment, and borax is used in making sizes and coatings for glazed papers and playing cards. Borax is used as a stiffening agent for the wicks of stearin candles; and it is also used in calico-printing. On account of the solvent action of fused borax on metal oxides, it is used for keeping a clear surface in the welding and brazing of metals. It is also used as a flux in many other operations; and in blowpipe analysis. Borax is employed in making manganese borate to be used as a drying agent for oils".

It is claimed that the Parthians used aluminum sulphate to make their wooden turrets fireproof, p. 148. Aluminum is apparently the ideal substance for sounding-boards, p. 180. "Aluminum differs from all other metals in the absence of the comparatively continuous and uniform higher partial tones which give in other metals the tone-color called metallic; and further that it possesses an elasticity capable of synthetic vibration uniformly through a wide range of tone-pitch, which renders it superior in this respect to wood". The uses of aluminum are given on p. 223.

Chromium oxide is given, p. 263, as the coloring matter of the ruby; but there is no discussion why the color should be red. The suggestion has been made that the blue of the sapphire is due to an unspecified but different oxide of chromium. This does not seem probable in view of the very different behavior of the ruby and the sapphire to radium emanation and to ultraviolet light.

On p. 264 we read that, "according to Rankin and Merwin, alumina occurs in two distinct forms: α-alumina is the ordinary crystalline variety represented by corundum; and β-alumina, which is formed in small quantities in hexagonal crystals often in groups of overlapping triangular plates when pure alumina is melted and cooled slowly. The presence of magnesia (say 0.5 percent) assists the transformation of α-to β-alumina, whereas the presence of lime or silica facilitates the formation of the α- variety. It has not been possible to convert β-alumina to α-alumina by holding the former at temperatures above or below the melting-point, and it is therefore suspected that β-alumina is monotropic with respect to α-alumina". This last conclusion does not follow and is probably unsound.

Air-dried alumina shows marked selective adsorption of air, the gas adsorbed being 41% nitrogen and 59% carbon dioxide with no oxygen, p. 269. If the alumina is dried at 110°, the composition of the adsorbed gas is 83% nitrogen and 19% oxygen with no carbon dioxide, p. 269.

"According to E. Stern, in 1913, about 3300 tons of monazite were consumed annually in producing the 300 tons of thorium nitrate used in making incandescent mantles; about 315 million mantles were made in that year. About 100 tons of ceria were obtained as a by-product. Of this, about 3 tons were used in making gas mantles; 200 tons in making pyrophoric alloys; and 300 tons of cerium fluoride in impregnating arc-light carbons. A mixture of 100 grms. of thorium nitrate; 0.8 to 0.1 grm. cerium nitrate; 0.2-0.5 grm. beryllium nitrate; and 0.10 to 0.25 grm. of magnesium nitrate is employed for impregnating the mantles. Mantles for high-pressure gas may have 2.8 per cent. of ceria. For stamping the mantles before burning off, a solution containing didymium nitrate is used. A little yttria earth, along with thoria and zirconia, is employed in making the filaments for Nernst's lamps. The pyrophoric alloys are used in the manufacture of modern automatic gas lighters, petrol lighters, cigarette lighters, for indicating the path of projectiles in the so-called tracer shells and tracer bullets, etc. Here, the 'flint and steel' of our forefathers is revived; the steel is replaced by the so-called pyrophoric alloys. It has been known for a long time that metals other than steel give pyrophoric sparks when struck. Thus, G. Chesneau observed that sparks can be detached from uranium by friction with hard steel, and these sparks instantly ignite mixtures of methane and air, and alcohol, benzene, or light petroleum poured on cotton. The estimated temperature is over 1000°. The sparks detached from steel have not so high a temperature since they ignite none of these gases and vapours. The term pyrophoric alloy is applied to those brittle metals or alloys which, when struck with hard steel, furnish a shower of small particles which are heated sufficiently to allow them to ignite. The cerium family of metals also gives sparks, but the metals are too soft to be useful. C. A. von Welsbach found that cerium, or mischmetall, when alloyed with iron, cobalt, or nickel, becomes brittle enough to enable the alloys to be employed for the purpose," p. 610.

"The oxidation of cerous to ceric oxide takes place more rapidly in the presence of alkali hydroxides, but in the presence of alkali carbonate a still higher oxide is produced. The oxidation to the peroxide in the presence of air occurs only with cerous hydroxide and not ceric hydroxide. The ready oxidation of cerous hydroxide renders it a strong reducing agent, for, as W. Biltz and G. A. Barbieri showed, it reduced cupric to cuprous salts; mercuric to mercurous salts, etc. This reducing action of the cerous salts distinguishes them from the salts of all the other rare earths, and shows that in this respect they are more nearly allied to the manganese salts," p. 628.

"The colloidal solutions of ceric hydroxide, made by the dialysis of a solution of ceric ammonium sulphate, change in a marked manner with time, the ageing being accompanied by a diminution in viscosity, a gradual loss of the faculty of gelatinization, and by a diminution in the sensitiveness towards electrolytes. The change is irreversible, and is accelerated by the rise of temperature. It is supposed that the ageing is due to the gradual dehydration of the sol particles. The ageing of ceric hydroxide sols is very largely modified under the influence of β- or γ- rays from radium. The first effect consists in an accelerated rate of diminution of the viscosity, but this effect is succeeded by a second, in which the viscosity of the sol increases to a value very large in comparison with that of the freshly dialyzed sol. The progress of the second stage is not dependent on the continued exposure of the sol to the action of the active rays, for if the exposure be made intermittent, it is found that the course of the viscosity—time curve is quite unchanged. A further curious effect is observed when the source of the radiation is removed before the end of the first stage in the ageing process. Under these circumstances, the second stage in the ageing process sets in, and the viscosity of the sol increases very considerably, attains a maximum value, and subsequently decreases almost as rapidly as it increased before the attainment of the maximum. The jelly obtained when the radiation is allowed to act sufficiently long appears to be perfectly stable. Similar changes in the viscosity are produced by the addition of electrolytes, although the effects are not readily distinguishable. The ageing of sols is supposed to be due to the gradual formation of larger colloidal particles by a process of aggregation, but it is probable that the effects described by the authors are connected with changes in the degree of hydration. It is probable that ceric hydroxide and other metallic hydroxide sols are highly hydrated, and in this way differ from hydrophobic colloids, such as the metallic and the sulphide sols. Under the influence of electrolytes or β- or γ-rays, the electrical charge of the colloidal particles is neutralized, and this is accompanied by a diminution in the degree of hydration, and results in a lowering of the viscosity, gradual when the sol is subjected to β- or γ-rays and immediate when an electrolyte is added. The increase in viscosity in the second state of the ageing process is then due to the aggregation of the electrically neutral particles, a process which takes place with a velocity comparable with that of crystallisation and similar processes. The attainment of a maximum viscosity and the subsequent fall which is observed when the added electrolyte is very small in quantity or the time of exposure to the rays is comparatively brief is explained by assuming that this peptization is due to the action of the electrically charged colloid particles which are enclosed by the jelly resulting from the aggregation of the electrically neutral particles. In support of this view, it has been found that ceric hydroxide jelly may be readily peptized by the addition of the corresponding sol," p. 633.

There is an interesting case of selective wetting in connection with diamond mining, p. 716. The heavier portions of the diamantiferous gravel "fall through a grating and are conveyed to percussion or shaking tables smeared with greases. The diamonds adhere to the grease, and the other constituents flow as tailings over the end of the percussion tables. The tailings may be dribbled on to a second shaking table; and the reject from this may be examined and any diamonds picked out. The grease is scraped from the tables, and is placed in a pot which is immersed in a cauldron of boiling water. The grease is recovered to be used again, and the diamonds are then examined on a sorting table, where the true diamonds are separated from pyrites, barytes, etc., by hand-picking."

"The diamond is used as a gem-stone; for bearings, etc., in watches, electric meters, and scientific instruments; for testing the scratching hardness of minerals, etc.; for cutting glass; drilling glass and pottery; and as a powder, in cutting diamonds, drilling rock,—for which purpose carbonado is preferred because it has no tendency to cleavage, etc. Graphite is used in making refractory goods—e.g. bricks, crucibles—when the crystalline or flaky variety is preferred. A mixture of plastic clay with 50 to 75 per cent of Cingalese graphite is moulded, dried, and fired in muffles in a reducing atm. It is used as a resistor in electric furnaces—e.g. kryptol is a mixture of graphite, carborundum, and clay so compounded as to give a granular mass; but graphite alone gives as good or even better results. Graphite is used in the manufacture of lead pencils. A mixture of graphite and clay, very carefully graded and washed, is moulded by expression, fired, and fitted into the wooden casing. Graphite—particularly the colloidal form—is used as a lubricant with or without tallow, grease, palm oil, etc. Graphite is used in the foundry as a facing for moulds; in making paints, particularly for coating iron surfaces; in electrotyping; for commutator brushes; in making battery plates; as a polishing medium—e.g. for gunpowder—in making stove polish; as a preventive of boiler scale; etc. Amorphous graphite, and charcoal are used for decolorizing sugar, fats, glycerol, etc.; in the filtration and disinfection of liquids; for the separation and recovery of gases and vapours; the purification of gases; the storage of gases; as a catalyst in many reactions; in the production of high vacua; as an absorbent in gas masks for noxious gases, and in the removal of industrial stenches. The charcoal mask was recommended by J. Stenhouse in 1854. Charcoal is used as a constituent of some explosives; as a depilatory in the tannery; in making crucibles; battery plates; in the manufacture of indian ink, printers' ink, black paints; etc. The manufacture of carbon electrodes for electric furnaces and arc lighting is one of the most important branches of the carbon industry, and is growing rapidly as electric furnaces are increasingly applied in the metallurgical industries. As experience in the manufacture of carbon electrodes grows, the specifications as to purity, electrical resistance, hardness, and density become more and more stringent. Carbon electrodes were used by H. Davy about 1806. Carbon filaments are employed in incandescent electric lamps. The light emitted by a hot body increases rapidly with rise of temp. A platinum wire heated by the electric current gives a good light, but this metal melts at too low a temp. to render it satisfactory. Carbon filaments were then tried and they gave better results, but they had a comparatively short life. Improvements in the manufacture of the filaments considerably increased the length of their practical life. The useful life of a carbon filament lamp depends more on the vaporization than on the melting point of the carbon. Different kinds of carbon have different vapor pressures. The graphitized filaments have the longer life," p. 833.

While we have no direct method of determining the molecular weight of graphite or diamond, "Nernst's observations on the specific heat of the diamond fit formulas deduced on the assumption that the molecule of the solid is monatomic; while the specific heat of graphite fits better the assumption that the molecule is polyatomic, C_n, where *n* is greater than unity." p. 839.

"According to M. Tanret, if a mixture of solutions of chloral hydrate, $CCl_3.CH(OH)_2$, and of potassium permangante be made alkaline, say with potassium hydroxide, gas is evolved, the liquid becomes discoloured, and sesquioxide of manganese is precipitated. If several grams of chloral hydrate be acted upon, and the temperature not raised above 40°, the reaction will last for some hours; then on filtering the liquid the filtrate will be found to contain chloride, carbonate, and formate of potassium. The gas evolved is carbon monoxide. The reaction occurs equally well with very dilute solutions, and even if borax be substituted for potassium hydroxide. This decomposition leads to a theory to account for the action of chloral hydrate upon the animal system; it is suggested that when this substance is taken into the circulation, it is submitted to oxidizing agencies; the alkalinity of the serum determines its decomposition; the carbon monoxide displaces the oxygen from the arterial blood, and produces an effect similar to that resulting from poisoning by carbon monoxide. The lowering of the temperature of the body and the prolonged action of the chloral hydrate, owing to slow decomposition, tend to make this theory more tenable than the assumption of its conversion into chloroform. The slow decomposition of chloral by an oxidizing agent also explains the continuity of its action as a hypnotic, which would not be the case if it were transformed into chloroform," p. 913.

Wilder D. Bancroft

Chemistry in the Twentieth Century. *Edited by E. F. Armstrong. 26×20 cm; pp. ix+281. New York: The Macmillan Co., 1924. Price: $5.25.* The aim of this volume is to present to the reader, by means of a series of monographs, a statement of the present position of chemical science in Great Britain. There is an introduction by the editor, E. Frankland Armstrong, and the individual papers are: the rôle of chemistry in physical science, by J. I. O. Masson; the structure of the atom, by E. N. daC. Andrade; crystallography, by T. V. Barker; X-ray analysis of crystals, by Sir William Bragg; the rare gases of the atmosphere, by M. W. Travers; the chemistry of carbon compounds, by J. F. Thorpe; milestones in organic chemistry, by H. E. Armstrong; the chemistry of colloids, by William Clayton; catalysis, by T. P. Hilditch; the fats and oils, by John Allen; the sugars and carbohydrates, by J. C. Irvine; cellulose, by C. F. Cross; colour in nature, by Reginald Furness; coal-tar colours, by E. A. Bearder; syntheses in the terpene series, by G. G. Henderson and Alexander Robertson; the alkaloids, by F. L. Pyman and T. A. Henry; the nitrogenous constituents of the living cell, by R. H. A. Plimmer; biochemistry and fermentation, by Arthur Harden; chemistry in agriculture, by H. J. Page; alloys, by C. H. Desch; pottery and refractories, by Joseph Burton; explosives, by Sir Robert Robertson; the chemistry of photography, by Walter Clark.

On p. 17 the editor says that perhaps some day the chemist may even succeed in having a loaf of bread delivered to the customer wrapped in clean paper. That stage has been reached to some extent in this country. On p. 24 we read that "the foremost aim of physical science today may be taken as the discovery of a fundamental unit of matter; of a fundamental unit (if there be one) of action or energy; and ultimately, of the cause-and-effect connection between these two units. Although we do not at all presume to determine the deeper exploration of the future, it seems justifiable for us now to say that the first of these units is nearly in our grasp, the second is apparently drawing within range; but the definite capture of both involves that of the third, which is no nearer than the horizon."

"An objection to the theory that the mass of all nuclei is due to protons immediately occurs" namely, that the atomic weight of hydrogen is not 1, but 1,0077, in terms of oxygen as 16. This has been met by arguments which lead to speculations of the first importance. The hypothesis to be justified is that packing the protons close together to form heavier nuclei, the size of which is but little larger than their own, leads to a slight loss of mass. The electromagnetic theory of mass does, in fact, indicate such loss, since the inertia of an electric charge depends upon the space in which it is concentrated, but the problem arises as to what has become of the mass. On all older theories mass is indestructible, but according to Einstein's theory of the equivalence of mass and energy a loss of mass can be compensated by a release of an amount of energy which calculation shows to be very large. In fact, it follows from the theory that if four protons, which when separated have a total mass 4.0308, should combine to form a helium nucleus, 5×10^{-5} ergs of energy would be set free. This may not sound very much, but it is equivalent to saying that if a gram-molecule of helium could be made out of the necessary hydrogen atoms 7×10^{11} calories would be set loose, or some hundred million times as much heat as is produced by the burning of an equal weight of coal. To put the matter in an engineering form, one ounce of helium in the course of formation from hydrogen should yield a million horse power for seven hours. This exceeds the transformations dreamt of by the alchemists; but, so far, we cannot see our way to making hydrogen nuclei stick together with the cement of two electrons. Perhaps we shall one day get, with great difficulty, a few atoms of helium so to form, which will satisfy the man of science; perhaps we shall get a controlled rate of formation in appreciable quantities, which will satisfy the engineer; perhaps we shall get an uncontrolled and cumulative rate of formation which will destroy the experimenter, and satisfy certain religious sects who object to experiments as impious; or will destroy the world and satisfy nobody. This is mere speculation, but one can scarcely refrain from speculation at the thought of these enormous supplies of energy associated with so small a weight of matter. In any case nuclear chemistry, which is at its very beginning, is bound to furnish sensational results," p. 49

When discussing crystallography, Barker says, p. 73, that "in a series of investigations, in collaboration with Miss F. Isaac, it was shown, by measuring the refractive index of the solution in contact with the crystal, that there are two degree of supersaturation, the metastable and the labile. A solution in the former condition will not crystallize spontaneously, however violently stirred, but will quietly deposit material on any crystals that happen to have been introduced. A solution in the labile state, on the other hand, immediately liberates a shower of crystals on shaking, the result being a sharp drop in the refractive index."

In regard to the Lodge-Cottrell process, Clayton says, p. 133, that "owing to the rapidly alternating polarity of the particles, they clump together to form flakes or drops, as the case may be, and these clumps are heavy enough to settle out provided the gas velocity is sufficiently low." This is not at all what happens. A direct current is used and the particles are carried to the larger electrode. It is very misleading for Hilditch to say in regard to contact catalysis, p. 137, that "according to one view, the chemical combination of two substances in presence of a specific third material is due to the condensation of the two former at the surface of the third, resulting in a highly concentrated surface layer of each of the interactants." This seems to imply that the high concentration is the important thing.

It is very interesting to note, p. 175, that "in general the distribution of pigments in flowers coincides exactly with that of oxydases. The oxydases, it is true, are more widely distributed than are the chromogens; but the distribution is in conformity with the oxydase-chromogen hypothesis, as will be illustrated by several typical examples, culled from the many available. The flowers of *Primula sinensis* and of *Dianthus barbatus* (Sweet William) show most epidermal oxydase in the most deeply coloured varities, less in the less deeply coloured, and none at all in the white varieties. The white flowers of certain *Primula sinensis*, *Pisum sativum*, and *Lathyrus odoratus* have all been shown to contain oxydases, and the white colour is attributed to the absence of chromogen. In the Mont Blanc Star, the distribution of oxydase again parallels that of pigment. One flower had irregular magenta-flaked petals with one exception, this particular petal being of a uniform magenta colour. The latter petal gave a well-marked oxydase reaction, the magenta patches on the others demonstrated a fair reaction, whilst the white portions did not respond to the test. Similarly, Sweet Williams were grown in full-coloured, white, and almost white varieties, the latter showing rosy dots or lines. The fully-colored flowers responded definitely to the tests for the presence of oxydases, whilst the white flowers also gave a definite but limited reaction—the white colour being probably due, as explained above, to the absence of chromogen. The white flowers with rosy dots showed oxydases only in the parts of the petals corresponding to the pigmented dots."

"There is one aspect of the importance of the industry which is deserving of mention. A few years ago the manufacture of artificial silk from cellulose acetate became a commercial proposition and its production on an industrial scale commenced. Very grave obstacles were encountered, however, which were gradually overcome and ultimately an excellent saleable material was evolved. It was then found that, unlike the other varieties of artificial silk, this new one was not susceptible to the usual dyeing processes and, indeed, that it could not be dyed by any known process so as to yield shades of a useful degree of fastness. Without a suitable method of dyeing it was clear that the new fibre could have but a very limited utility, and consequently a great deal of attention was directed to the problem with the result that very praiseworthy progress has been made. If the problem has not yet been completely solved it is at least now possible to dye cellulose acetate silk in practically any hue required, and there is little danger of the young industry being stunted from difficulties in this direction," p. 182.

"In recent years very striking results have been obtained in the study of the effect on plant growth of small quantities of elements other than those known to be essential. Bertrand and Mazé, in France, have studied this subject extensively, and they conclude that in small doses manganese, zinc, fluorine, and iodine produce definite increase in growth in water cultures; in this country, similar results have been obtained with manganese by Dr. Brenchley in water cultures; but in field trials the results were negative, probably owing to the presence of sufficient manganese in the soil already. Silicates also appear to have a beneficial effect. This is especially noticeable on the phosphate-starved plots at Rothamsted; Hall and Morrison conclude that silicates act by causing an increased assimilation of phosphoric acid by the plant. The view has also been advanced, however, that silicates are able to replace phosphates to a certain extent in the plant. This problem is now under investigation at Rothamsted. Voelcker has carried out a long series of pot experiments as Woburn on a variety of inorganic substances. These were all toxic above a certain concentration, but in some cases there was evidence of a stimulating effect when the concentration is low. This appears to be the case with salts of lithium and with borates. The study of the action of the latter has recently been again taken up at Rothamsted, with very striking results. It has been found that in water or sand culture certain leguminous plants, such as the broad bean, are quite unable to make satisfactory growth or to flower and set seed if they are entirely deprived of boron. The most minute trace of boric acid (1 part in 2.5 million parts, or even less) suffices, however, to bring about normal healthy growth; moreover, a plant which is almost *in extremis* from lack of boron can be cured and started into healthy growth by the addition of a quantity of boron of the above order. Similar results have been obtained with other leguminous plants such as runner beans and red clover, but in the case of a cereal crop such as barley the effect is not produced. It is at present impossible to say what part these minute traces of boron play in the growth of the plant, nor is there any evidence that plants grown in the field ever suffer from lack of boron, which is present in traces in most soils. Results of this sort do, however, suggest the possibility that the deterioration of soil continually receiving only artificial fertilisers may be due to the gradual removal from the soil of some element which is beneficial to the crop in minimal amounts, and which is present in dung," p. 228.

"Before leaving the consideration of the physical properties of the soil, mention may be made of the striking results that have recently been obtained at Rothamsted in the study of the effect of farmyard manure and of chalk on the mechanical properties of the soil. Practical men have long known that both these materials exerted a beneficial effect on the tilth and ease of cultivation of heavy soils. Quantitative expression is given to this fact by measurements which have been made, by means of the dynamometer, of the power consumption in ploughing land which has been dunged or chalked. It has been found that if the draw-bar pull exerted in ploughing unmanured land on the Rothamsted farm be represented by 100, that exerted in ploughing dunged land was 78-82, while for chalked land the figure was 85. This represents an appreciable saving in power, and in cost of cultivation," p. 230.

"The shortage of farmyard manure arises, not from any shortage of straw, but from a shortage of animals, caused in no small degree by the replacement of the horse by mechanical traction. Earlier work at Rothamsted by Hutchinson on the breakdown of cellulose in the soil and on the relation of carbohydrate material to nitrogen fixation and nitrate assimilation led Hutchinson and Richards to study the conditions under which straw could be caused to rot down. As a result of this work they found that by treating wet straw with a certain amount of combined nitrogen and maintaining the reaction of the mixture faintly alkaline it was possible to convert the straw into a product which had all the outward appearance of farmyard manure and was of very similar composition. Field trials gave very promising results, and the process was patented. The commercial development of the process is now in the hands of the Agricultural Development Company, a non-profit-making syndicate which owes its origin to the public-spirited action of Lord Elveden, who had already given considerable support to the earlier work on which the process is based. The process has now been further improved in several respects, and a number of large-scale trials have taken place in various parts of the world. In this country, straw is the raw material to which the process would ordinarily be applied; but many other waste plant products from outlying parts of the Empire have been tested and successfully converted into synthetic farmyard manure in the laboratory. The further development of this process promises to be of great value to agriculture both in this country and overseas," p. 240.

Wilder D. Bancroft

The Story of Early Chemistry. *By John Maxson Stillman. 22×15 cm; pp. xiii+566. New York: D. Appleton and Company, 1924. Price: $4.00.* Professor Stillman died just before the first proofs of this book were received from the printers and the volume has been seen through the press by his colleague Professor Young. No one who had the privilege of knowing Stillman, no matter for how short a time, ever forgot him. Young says in the foreword that "there was something in Stillman's art as a teacher that almost invariably commanded the respect, admiration, and devotion of his pupils. . . . If it is to be explained at all, I think it was due to a fine power of his, of keenly discerning the deeper spiritual characteristics and mental traits of each of those with whom he came into contact, and thus of subtly distinguishing between individuals and meeting each on his own ground. . . .

"It was out of Professor Stillman's labors as a teacher that 'The Story of Early Chemistry' was born and grew to what it is. For much of his life he had given increasing attention to the history of chemistry, and for many years taught the subject to small classes. Gradually covering new ground and extending his knowledge of the field, he finally gained a breadth of view which he felt might justify some contributions to the literature of the subject."

The book deals with chemistry up to the death of Lavoisier; in other words, through the beginning of modern chemistry. The chapters are entitled: the practical chemistry of the ancients; the earliest chemical manuscripts; theories of the ancients of matter and its changes; the early alchemists; chemical knowledge in the Middle Ages; chemistry in the thirteenth century; chemistry of the fourteenth and fifteenth centuries; the progressive sixteenth century; chemical currents in the sixteenth century; chemistry of the seventeenth century; the eighteenth century—rise and fall of the phlogiston theory; the development of pneumatic chemistry in the eighteenth century; early ideas of chemical affinity; Lavoisier and the chemical revolution.

"There has been much speculation as to the sources whence the ancient Egyptians obtained the tin for their bronzes. No nearby sources have been discovered. Geologic evidence is to the effect that tin occurred in Persia, and it may have been from this region that the earliest supplies came. It is also possible that sources of tinstone from farther south on the African continent may have been drawn upon, but any evidence to that effect is also lacking.

"The Greek name 'kassiteros' is allied to the more ancient names for tin among Assyrians, Acadians and Babylonians. The Sumerians in Southern Babylonia (Shinar), evidently possessed a knowledge of tin as a constituent of bronze as early as about 3000 B. C., and it is not impossible that this region was the earliest source of tin for Egypt and the Mediterranean countries. Just when the sources of tin in Britain became available to the ancient world about the Mediterranean is difficult to determine. References in ancient authors, however, make evident that certainly by the fifth century B. C. tin was received from that region. The price of the metal was lowered and the uses of bronze much expanded by the opening up to trade of the rich deposits of the British Islands," p. 4.

On p. 48 we read that the 'ammoniacal' salt of Dioscorides is not, as was sometimes supposed, our sal-ammoniac; but was common salt from Egypt in the vicinity of the temple of Ammon. Our word ammonia is apparently a corruption of Armenia, p. 245.

The views of Dioscorides on wine and beer would have delighted the modern prohibitionist, p. 55. "Fermented liquors, wines, meads and beer were known in all countries from the most ancient times. Their use at the time of Dioscorides and Pliny was extensive and excessive. They naturally entered largely into medicine. It is worthy of note that Dioscorides ascribes injurious action to their continual use, and advises they be used only as occasional stimulants. The effect of new wine in accelerating the pulse may be avoided, he says, by adding water and boiling until this is again evaporated. That the reason for this lies in the elimination or reduction of the alchool content was beyond the understanding of the time.

"Beer, from grain, especially barley, he considers as especially deleterious, as it bloats, promotes obesity, attacks the kidneys through its diuretic properties, and irritates the nervous system and the brain."

Stillman does not attempt to settle the dispute whether the Greeks did or did not get their theories of the nature of matter from the philosophers of India, p. 104. "These two nations developed the most consistent and logical theories, strangely parallel indeed in their development. Scholars are not agreed upon the question as to whether the development of the philosophy of nature in the two ancient civilizations has been entirely independent. Certain it is that, up to the present time, no historical evidence has been discovered which indicates any direct contact of Hindu and Greek thought, though it is not thereby rendered impossible nor even improbable that through Persian mediation Hindu concepts may have found their way to Greek thinkers, if only in the form of imperfect and incomplete suggestions. Scholars differ on this probability."

Stillman points out, p. 127, how far Aristotle's method of developing a theory was removed from the inductive methods of modern science, and on p. 144 we read that the inductive method of modern science is not the method of Plato. The reviewer believes that modern science talks about the inductive method but uses the deductive method.

Stillman tells us, p. 279 that "so far as present knowledge authorizes we may assume that Geber was a European chemist, probably a Spaniard, who wrote largely from his own experience as a practical chemist and metallurgist, and that his theoretical views upon alchemy were those of the thirteenth century, which were largely the result of Arabian development. No Arabian originals are known which might have been translated by him nor which present so advanced a knowledge of chemical processes. On the other hand he makes no claim to originality, and seems to have endeavored to give a clear description of the practice of his time."

He also thinks well of Paracelsus, p. 323. "Much more important than any specific chemical advances due to Paracelsus was his influence in attracting the attention of physicians and chemists to the importance of chemistry in the development of medicine in connection with his campaign against the blind worship of traditional authorities. In his life-long and intense struggle against the conservatism of the medicinal faculties and profession, he constantly emphasized the duties of the physicians to depend upon experiment and independent observation rather than on the dogmatic medicine of Galen and Avicenna, and emphasized the great value of new medicine derived from the development of chemistry.

"He possessed a breadth of view as to the field of chemistry and its possibilities, and stimulated chemists to seek a more important field for their activities than the search for gold making or the philosopher's stone. Not that he disbelieved in the possibility or reality of transmutation. On the contrary it received full attention and credence from him in his chemical philosophy."

The reviewer was much pleased to learn the origin of the word gas, p. 323. "The term gas as a generalization for aerial fluids was first suggested by van Helmont (1577-1644), himself very familiar with the works of Paracelsus and to some extent a champion of his views. He tells us that he derives this word from the Greek *chaos*, and it is more than probable that it was the use of the word by Paracelsus in this sense that suggested the word gas to van Helmont."

Of interest also is van Helmont's experiment, p. 382, in which a willow tree gained one hundred and sixty-four pounds when grown in a weighed amount of earth which remained unchanged. Since the pot was supplied only with rain water or distilled water, van Helmont concluded that one hundred and sixty-four pounds of willow tree had been produced from pure water.

"If we recall that at that time there was no knowledge or suspicion of the presence of carbon dioxide or of nitrogen compounds in the atmosphere, and that nothing was known of their relation to vegetation, and again if we consider the large number of substances obtained by the distillation of wood, we cannot regard van Helmont's conclusion as anything but a reasonable deduction from the facts as he knew them. Furthermore, his conclusion was confirmed from certain facts of which he knew but had not personally experimented upon. Such was the often repeated account of certain springs which have the power of converting wood or charcoal into stone, a process usually interpreted at that time as a kind of transmutation. As charcoal is producible from water alone, and as charcoal can be changed to stone, this proved to van Helmont that the stone also is materially water. Also the fact that fishes spend their lives in the water and obtain their development by things occurring in the water is interpreted by van Helmont to mean that they, like his willow tree, are also ultimately produced from water."

We wish that Professor Stillman could have been spared to writes more books for us; but this one is a fitting close to a busy and well-spent life.

Wilder D. Bancroft

The Simple Carbohydrates and the Glucosides. *By E. Frankland Armstrong. Fourth edition. 25×16 cm; pp. xi+293. New York and London, 1924. Price: $5.00.* In the preface the author says that "a natural period in the history of chemical discovery, especially in the sugar group, was brought to a close through the death of Emil Fischer in 1919. This monograph is very largely a record of his monumental work. . . . It is remarkable that just at the close of Fischer's activity, the outlook suddenly became widened by the disclosure, both in his laboratory and by Irvine in that built by Purdie at St. Andrews, of a form of hexose molecule other than the isodynamic, stereoisomeric alpha and beta forms. The new form, gamma glucose, is characterised by its relative instability and the readiness with which it undergoes oxidation.

"That a discovery of so refined a character, so long delayed, would rapidly find practical application was scarcely to have been expected; there is, however, reason to think that it may prove to be of primary importance in connection with the fell disease, diabetes."

The subject is presented under the headings: introduction; glucose; stereoisomerism—isomeric change—structure; the chemical properties of glucose and the hexoses; the hexoses pentoses, and carbohydrate alcohols; the disaccharides; hydrolysis and synthesis; the polysaccharides; the relation between configuration and biological behaviour; the natural glucosides; the synthetic glucosides; the function of carbohydrates and glucosides in plants.

The α- and β- methyl glucosides, p. 12, and the α- and β- glucoses, p. 40, are striking cases of slowly interconvertible liquid modifications. The glucoses are especially interesting because, p. 41, "a solution of glucose containing α and β forms can be made to give wholly α- or wholly β-glucose on concentration, according to the temperature at which crystallisation takes place. The α form, which is then the less soluble, is that obtained at lower temperatures; but, above 98°, the β form, being the less soluble at the higher temperature, alone separates." It is a pity that we have no diagrams for this equilibrium. The interconversion of glucose, fructose, and mannose in presence of dilute alkali, p. 56, is another case of the same type.

On p. 50 is an interesting paragraph. "From the biological point of view, the fact that glucose exists in solution not as a single substance but as an equilibrated mixture of stereoisomeric butylene oxide forms, readily convertible into one another, is of fundamental and far-reaching importance. If one of the stereoisomerides is preferentially metabolised in the plant or animal, in the course of either synthetic or analytic processes, the possibility of controlling the equilibrium in the one or other direction, so as to increase or limit the supply of this form, places a very delicate directive mechanism at the disposal of the organism. This question is undoubtedly one which demands the close attention of physiologists."

"The ketose sugars without exception are decomposed when their aqueous solutions are exposed in quartz tubes to sunlight. Carbon monoxide is evolved and the corresponding alcohol containing one carbon atom less is formed. The aldose sugars are practically unaffected under these conditions. Exposure of the ketoses to the ultra-violet light from a mercury lamp brings about the same decomposition, but other actions also take place involving the formation of hydrogen, methane, formaldehyde and non-volatile acids. The aldoses are decomposed in a similar manner to the ketoses by ultra-violet rays but are less susceptible to attack," p. 57.

"The combination O.C.O.C.O determines the extraordinary instability of sucrose in presence of acids as compared with that of maltose, lactose, etc. The amylene oxide ring, in contrast to the butylene oxide ring, opens by the agency of very weak acids thus disturbing the glucosidic linking which then undergoes hydrolytic cleavage. The initial condition of the fructose formed is transient as it rapidly passes to the stable butylene oxide form," p. 123.

"Today's knowledge enables it to be stated that the active forms of sugar in metabolism are not the stable butylene oxide forms but the 2 ring forms, whatever they may be, under acid and neutral conditions and the open ring enolic form or even the very closely allied aldehyde or ketone itself when the reaction is alkaline. The effect of the addition of an aldehyde to a fermenting mixture of yeast juice and glucose in presence of a suitable amount of phosphate is greatly to diminish the time required for the attainment of the maximum rate of fermentation: it is considered that the aldehyde acts as an acceptor for hydrogen, a conclusion supported by the fact that methylene blue produces a similar effect. In an ordinary fermentation of glucose it is probable that hydrolysis of hexose phosphate results in the formation of fructose which in its turn yields a hydrogen acceptor and assists the increase in the rate of fermentation. Acetaldehyde and methylene blue are something like 50 times as effective as fructose in accelerating the fermentation of glucose. In the presence of acetaldehyde fructose is fermented more rapidly than glucose.

"In view of the preceding there can be little doubt that one function of phosphoric acid in the plant is in some way to modify the sugar as in fermentation. Probably the intermediate product of the hydrolysis of glucose phosphate is γ-glucose," p. 176.

The saponins "are soluble in water, giving clear solutions which froth strongly on agitation, form emulsions with oils or resins, prevent the deposition of finely divided precipitates, and occlude electrolytes and also many soluble dyestuffs. The saponin of soapwort, for example, in its colloidal form gives a blue adsorption compound with iodine, although the crystallisable constituent does not," p. 216.

"The recognition of the potent effect of the constituents of glucosides in acting as stimuli and starters of active metabolism may be of importance in studying the nutrition of animals. It is well known that the herbage of one pasture may have the power of fattening an animal whereas similar grass on an adjoining field, though equally readily consumed by the animal, fails to bring it into condition for the market.

"This is especially the case in Romney Marsh, where one field will fatten six or eight or more sheep to the acre whereas an adjoining field will do little more than keep the sheep in a growing condition. Hall and Russell, who investigated this difference in 1912, found that the floral type in the two fields was constant but that a leafy habit of growth obtained in the fattening field and a stemmy habit in the poorer fields. The ordinary methods of chemical analysis failed to reveal any difference either in the herbage or the soils. Since this date much evidence has accumulated in favour of the importance of quality as well as of quantity in animal feeding and the subject is one of the greatest importance to agriculturalists.

"Subtle differences between the grasses of these two fields have hitherto defied detection, but it is not impossible that the presence or absence of certain glucosides or similar constituents may have some bearing on the difference," p. 230.

Three changes take place simultaneously in the potato tuber during storage: "starch is being transformed into sugar, sugar into starch and also by the process of respiration into carbon dioxide. A decrease in the temperature hinders all three reactions but it has least effect on the formation of sugar from starch. Accordingly, when the potato is stored at 0° sugar is formed till the amount increases to 3 per cent. At −1° all enzyme action ceases. At +3° there is still formation of sugar but the enzymes acting to destroy it tend to keep the amount down to 0.5 per cent. At +6° the rate of formation of sugar from starch and that of the reverse change are equal; above this temperature the formation of starch predominates. In consequence no sugar is stored and any sugar previously present is destroyed," p. 237.

"In the case of plants which are killed by frost it is supposed that as a result of the removal of the water as ice the concentration of the cell fluid becomes such that the soluble proteins are precipitated from solution. This salting out of the proteins is prevented by the presence of non-electrolytes such as sugar: Lidforss, to whom this explanation is due, has shown that the leaves of winter plants are free from starch but contain much sugar. The warm days of early spring bring about the regeneration of starch and partial disappearance of sugar; in consequence the cell is but ill protected against the effects of a subsequent frost," p. 238.

"During ripening, the skin of the banana changes from green to yellow, deep brown, and finally black; the fruit is then fully ripe. This change is due to an oxydase acting on some aromatic substance liberated from a glucoside. The black colour is quickly produced when a yellow banana skin is disintegrated by mincing or when the entire skin is exposed to the vapour of some hormone. Under natural conditions the stimulus which leads to blackening is given from within the fruit by the liberation of the characteristic ester of the banana, which acts as a powerful hormone. In the case of most fruits, it would seem that the final appearance which is associated with ripeness is conditioned by stimulus from within rather than by any environmental influence," p. 239.

Wilder D. Bancroft

The Corrosion of Metals. *By Ulick R. Evans. 22×15 cm; pp. xi+212. New York and London: Longmans, Green and Co., 1924. Price: $5.00.* The author is a firm believer in the electrochemical theory of corrosion, though he prefers to call it the newer electrochemical theory, p. 9. By this he merely means that he is laying more stress on differences of oxygen concentration and less on differences of metal surface than Cushman and Walker did. He also emphasizes the fact that direct oxidation at higher temperatures is quite different theoretically from oxidation at ordinary temperatures in presence of moisture, p. 12.

It is rather a pity, p. 36, that he prefers to discuss the anodic corrosion of zinc in a chloride solution as due to the discharge of chlorine which then reacts with the zinc. It is true that he makes clear that this is not what happens; but it is usually safer to state things as they are. One wonders whether the difference in rate of going passive of pure, rolled nickel anodes and impure, cast anodes is really only a matter of current density, p. 48.

The author brings out clearly, p. 62, that over-voltage may easily overbalance the effects due to heterogeneity. "The corrosion of zinc was not aided by contact with compact cadmium or compact lead (metals with high overpotential values); but was accelerated by contact with dark spongy lead. Cadmium, which was itself almost unaffected by hydrochloric acid, liberated hydrogen when brought into contact with nickel or iron. Iron gave off hydrogen slowly by itself, but much more quickly in contact with nickel; contact with copper or lead was not found to have any appreciable effect. Nickel, lead, and tin, as already explained, only liberate hydrogen when in contact with black platinum, and even then only extremely slowly. . . . .

"Although impurities of low overpotential value usually increase corrosion by acids, those having high values may actually diminish it. Amalgamated zinc, for instance, is practically unattacked by dilute sulphuric acid owing to the high overpotential of mercury, although it evolves hydrogen readily if touched with copper; amalgamated iron withstands the effect of fifteen percent sulphuric acid for a day or two, but the protective effect may vanish quite suddenly, probably because the mercury gathers itself spontaneously into globules. The presence of arsenic in dilute sulphuric acid reduces greatly the corrosion of iron by that acid, probably owing to the high overpotential of the arsenic deposited on the metal. Arsenic fails to protect iron against corrosion by an acid solution of ferric chloride (an oxidizing agent which corrodes without the evolution of hydrogen), nor does amalgamation protect zinc from the same reagent."

"Whilst heterogeneous structure on a coarse scale certainly affords a condition favourable to corrosion, a fine duplex structure, such as is present in alloys or impure metals, does not necessarily lead to rapid attack. Here the anodic product (a soluble salt of the metal) and the cathodic product (alkali) are produced so close together that the insoluble precipitate is formed almost in contact with the surface, and may produce a 'blanket' over it. Furthermore, if the alkali from the cathodic areas gains direct access to the anodic areas it may produce passivity there; the whole surface may thus become 'equipotential' and corrosion-currents may cease to flow altogether. Consequently an article consisting of a large piece of the metal A in mechanical union with a large piece of the metal B will behave differently from a similar article constructed wholly of an alloy consisting of a mosaic of A and B. Murray has found that the so-called 'double fagoted iron' (consisting of alternate layers of wrought iron and mild steel) rusts quicker in damp air than simple mild steel; microscopic examination has shown that rusting commences where the pearlite areas of the steel touch the ferrite areas of the pure iron. But within the steel itself, pearlite and ferrite are in contact, and yet along these lines of contact no special corrosion can be observed," p. 70.

There is an excellent discussion, pp. 72-82, of corrosion due to differential aeration. The effect of stirring on the corrosion of copper is taken up on p. 103 and, on p. 105, we find McKay's work on the different behavior of stagnant and moving solutions.

Since nearly everybody is apparently willing to accept the electrochemical theory of corrosion when properly worded, it is time for those interested in the subject to get together and to devise methods for studying the behavior of protecting films and for developing an accelerated test. These two problems are not taken up in this book because they are the unsolved ones. The reviewer is quite confident that the accelerated test of the future will be an electrolytic one; but he recognizes fully the immense amount of work to be done before any such test can be accepted as absolutely satisfactory.

Wilder D. Bancroft

What Industry Owes to Chemical Science. *By Richard B. Pilcher and Frank Butler-Jones. Second edition, revised and enlarged. 19×13 cm; pp. xv+158. New York: D. Van Nostrand Company, 1924. Price: $2.00.* The first edition was reviewed over five years ago (23, 660). The new edition differs but slightly from the old one, and the titles of the chapters are the same in the two editions. The chief value of the book is that it gives numberless examples of industrial applications and the teacher can choose from these the ones which will be helpful to him.

Wilder D. Bancroft

SOME OBSERVATIONS ON THE PREPARATION AND PROPERTIES OF SILICIC ACID GEL

17-1835

BY H. A. FELLS AND J. B. FIRTH

Graham[1] was the first to show that on mixing with vigorous agitation a ten per cent solution of sodium silicate with a ten per cent solution of hydrochloric acid, a clear colloidal solution of silicic acid is obtained which may be freed almost completely from electrolytes by dialysis. On standing this solution coagulated to a firm elastic gel which on drying over sulphuric acid gave a hard glassy mass. Little further work was done until van Bemmelen[2] carried out extensive researches on the hydration and dehydration of the gel and showed that the two curves do not follow the same path. He also investigated the influence of the concentration of the liquid from which the gel was prepared and the time of drying, upon the porosity and adsorptive capacity.

Zsigmondy[3] examined the structure of silica gel by the ultramicroscope. The diameter of the pores is calculated to be $5\mu\mu$ for a depression of vapour pressure of 6 mm. It is shown that, for dry silicic acid gel saturated with benzene, the true size of the particles is very small and the observed coarse structure is due to the accumulation of liquid in some of the parts separated by air.

Patrick[4] investigated gas adsorption by silica gel and measured the amount of sulphur dioxide, carbon dioxide and ammonia adsorbed at different temperatures and pressures.

Bachmann[5] showed that the weight of different liquids taken up by silica gel is proportional to their density. Measurements with water, benzene, chloroform, ethyl iodide and acetylene tetrabromide gave concordant results.

McGavack and Patrick[6] have studied the adsorption of sulphur dioxide by silica gel at temperatures ranging from -80° to $+100^\circ$ and show that the maximum adsorption is obtained with gels of about seven per cent water content.

Holmes[7] gives directions for the preparation of silicic acid gels setting in any required time. The gels produced by decomposing sodium silicate with various acids are described. The influence of the concentration of the solutions and the temperatures on the time of setting is also studied.

Experimental

Preliminary Experiments

The sodium silicate used in the experiments herein described was the pure water glass sold for domestic purposes. It was clear and colourless, free from

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[1] Phil. Trans. **151**, 183-224 (1861); Ann., **121**, 1-177 (1862); Proc. Roy. Soc. (1864).

[2] Z. anorg. Chem. **13**, 233-396 (1896); **18**, 117 (1898).

[3] Z. anorg. Chem. **71**, 356-377 (1911).

[4] Inaugural Dissertation Göttingen (1914).

[5] Z. anorg. Chem. **79**, 202-208 (1913).

[6] J. Am. Chem. Soc. **42**, 946-978 (1920).

[7] J. Phys. Chem. **22**, 510-519 (1918).

traces of iron and on treating with hydrochloric acid gave no indication of carbon dioxide. On analysis the sodium silicate was found to contain one part of Na_2O to two parts of SiO_2 (analysis gave the values 1 : 1.98). For the preparation of the gels pure hydrochloric acid was used throughout.

A number of preliminary experiments were carried out in which the sodium silicate solution was carefully diluted to a density of 1.116 and the acid used was of a strength 1.64N. It was found that when equal volumes of the silicate solution and acid were rapidly mixed in a boiling tube, the silicate solution being added to the acid, a soft semi-fluid gel separated out in about fifteen minutes which occupied about one-third the volume of the mixed solutions. On standing this gel gradually became firmer but also became opalescent. After 7-8 days the clear liquid above the first-formed gel set to a very clear firm gel; whilst the first-formed gel became very cloudy in appearance.

The result was similar when the acid was added to the sodium silicate solution, and also when sodium silicate solution of a density 1.15 was used.

The two gels thus obtained i. e., the first-formed somewhat cloudy gel and the second very clear gel were further examined. Samples of each gel were taken and dried in a steam oven, heated in an air oven for 4 hours at 140°C, and then analyzed.

The following are typical results for (a) sodium silicate solution of density 1.116 (b) sodium silicate solution of density 1.15.

			(a)	(b)		(a)	(b)
Lower first formed gel.	SiO_2 1.0,	H_2O	0.0955,	0.1008	NaCl	0.7028,	0.5495
Upper gel formed after several days.	SiO_2 1.0,	H_2O	0.1445,	0.1621	NaCl	1.3950,	1.6095

When the sodium silicate solution was added to the hydrochloric acid in the proportion of 3 : 2 by volume a thick precipitate formed immediately, the whole volume becoming practically solid, whilst when the ratio of silicate solution to acid was 2 : 3 the mixed solution remained clear and set in from two to three weeks. Sodium silicate solution of a density 1.116 required an equal volume of hydrochloric acid of strength 1.36 N to neutralize it, using phenol phthalein as indicator. When the hydrochloric acid solution was run into the sodium silicate solution the whole mass set just before the pink colour was discharged; whereas when the operation was reversed the mass, set just as the pink colour appeared in the solution. From these results it would appear that a very slight alkalinity in the neighbourhood of neutralization point brings about an immediate setting of the gel.

Influence of Concentration of the Acid on the Time of Setting

In this series of experiments sodium silicate solution of a density of 1.15 was added to an equal volume of hydrochloric acid, the strength of which was varied from concentrated acid of a density 1.165 to acid of a strength less than normal.

Pure concentrated hydrochloric acid (density 1.165) when added to an equal volume of water glass gave a firm clear gel in ten to fifteen minutes. As the strength of the acid solution was gradually diminished the time of setting *gradually* increased until when the concentration of the acid was 6 N the time of set was from two to three hours. Further dilution beyond this point produced a more rapid increase in the time of set, thus when the concentration of the acid was 2 N a firm gel was not obtained until a period of from two to three weeks had elapsed after mixing. When the concentration of the acid was reduced to 1.5 N a firm, rather opalescent, gel formed immediately on mixing. Acid of this strength was just sufficient to leave the resulting mixture feebly alkaline (i. e., practically neutralized). As the strength of the acid was further diminished the time of set again increased becoming very indefinite for concentrations below normal.

Influence of Temperature

A series of gels were prepared at temperatures ranging from 0° to 45°C. Sodium silicate solution of density 1.15 and hydrochloric acid of strength 6 N was used throughout the series.

The sodium silicate solution was gradually added to an equal volume of acid, the liquid being vigorously agitated during the mixing by means of a mechanical stirrer. If the rate of stirring was not sufficiently rapid to ensure a rapid distribution of the added silicate solution, there was a tendency to local formation of gel as a flocculent mass, particularly during the addition of the last portions of the silicate solution. When the two solutions had been thoroughly mixed, the stirring was stopped, and the solution maintained at the required temperature in an efficient water bath, until a firm gel had been obtained.

Over the range of temperatures investigated, the time of setting did not show any distinct variation with temperature, the times being similar in all cases.

The gels thus obtained were broken up into small lumps and repeatedly digested with distilled water until the washings gave no opalescence with silver nitrate, a condition which was usually attained in about twelve hours. The resulting product was first dried in a steam oven and then in an air oven at 120° to 135°C for about four hours. It was then heated in an air oven at 300°-320°C for two hours and finally at 600°C for 20-30 minutes. The gel was then stored in air-tight tubes.

The gel was then divided into two portions according to the size of the granules by sifting through a 2 mm wire mesh. The water content of the fine and coarse fractions was then determined for gels prepared at the various temperatures, a weighed portion of the gel being heated in small blast furnace until a constant weight was obtained. The results are given in the following Table I.

TABLE I

Temperature at which Gel was prepared.	Percentage of water contained in the gel.	
	Coarse particles.	Fine particles.
0°	← 2.33 →	
18°	5.20	3.18
35°-40°	4.23	3.80
40°-45°	4.70	3.84

The rate of sorption of water vapour and sorption capacity of each gel were also determined. A weighed quantity of the gel freshly heated at 600°C, contained in a crucible was placed in an atmosphere saturated with water vapour at room temperature. A glass vessel of the type usually employed as a desiccator was used for this purpose; a little distilled water being placed on the bottom. The crucible was removed after definite intervals and weighed until further exposure produced no increase in weight. The maximum amount of water sorbed is given in Table II and the rate of sorption curves are given in Fig. 1.

TABLE II

Temperature at which Gel was prepared		Maximum amount of water taken up per 100 grams of gel.	Duration of Experiment in hrs.
0°		50.42	65
18°	Fine granules.	72.54	43
	Coarse granules.	67.35	43
35-40°	Fine granules.	67.72	72
	Coarse granules	67.40	72
40-45°	Fine granules	62.22	46
	Coarse granules	59.85	46

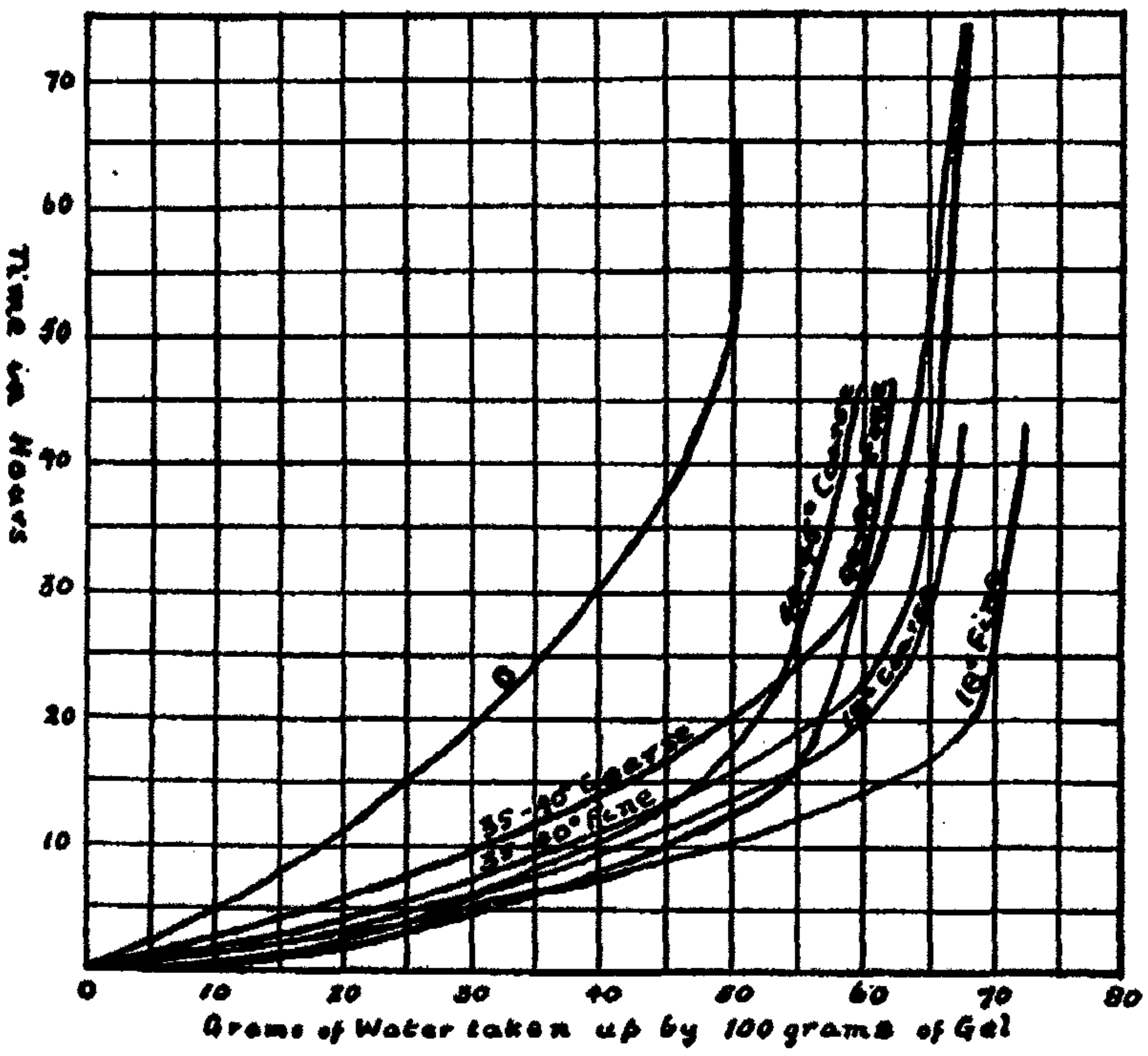

FIG. 1

The rate of sorption of water vapour was also determined by passing a fairly rapid stream of air saturated with water vapour at 18°C. over a quantity of freshly heated gel. The gel prepared at 18°C (about 2 grams), was contained in a narrow tube 5 mm bore and fitted with two taps. Air which was saturated with water vapour by first bubbling through water, was passed over the gel. At definite intervals the current of air was stopped, the taps closed and the tube re-weighed. The results were as follows:—

Time in hours.	0.5	1	1.5	2	3	6	10	20	40
Water taken up, per 100 grams of gel.	17.7	26.9	33.1	37.7	42.5	51.1	61.2	69.8	72.4

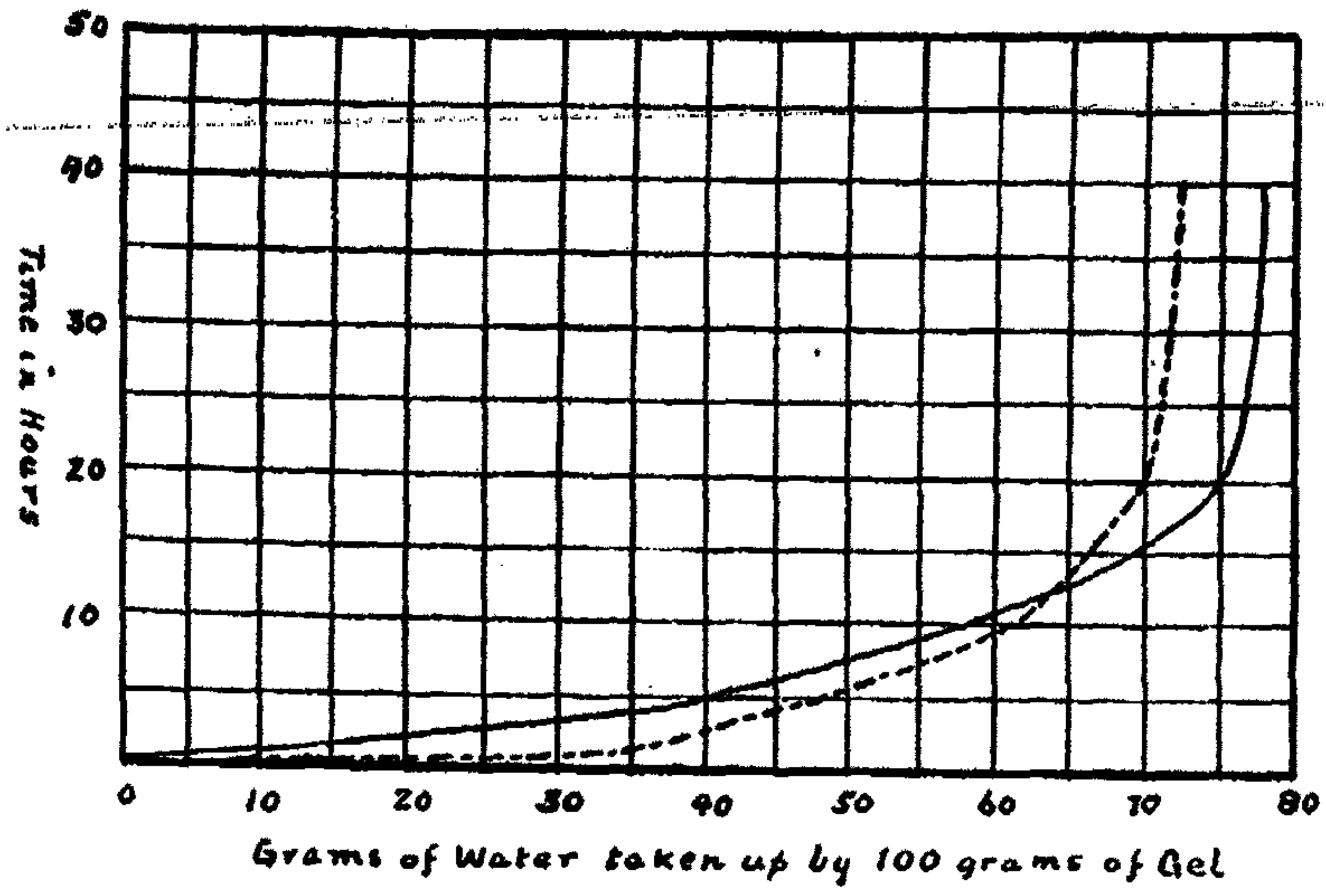

FIG. 2

Drying of the Gel before Extraction of the Sodium Chloride

For some later experiments the authors desired to prepare gels impregnated with certain substances. These substances are introduced in many cases as soluble compounds by dissolving the desired substance in either the silicate solution or the acid prior to mixing the solutions. The added substance, however, decomposes on strongly heating, leaving the desired residue evenly distributed throughout the gel. Under such circumstances, owing to the solubility of the added substances, it was impossible to follow the usual procedure of washing out the sodium chloride before heating. It was therefore desirable to examine the product obtained when the gel as produced, is first dried and subsequently heated at 600°C. *before* the extraction of the sodium chloride is carried out. Gels were prepared at 18°C. by mixing equal volumes of 6 N by hydrochloric acid and sodium silicate solution of density 1.15. The resulting gel was then transferred to a shallow evaporating basin and slowly dried in a steam oven: as the gel dried the surface of the gel became covered with a mass of very fine crystal-like needles, which, as the drying proceeded, increased in size until eventually the product resembled a ball of fluff with a hard silica core at the centre. On examining these needles they were found not to be real crystals but very fine capillary tubes. Microphotographs of these needles are shown in Figs. 3 and 4. The needles are soluble in water and on evaporation gave the characteristic cubic crystals of sodium chloride. Fig. 5 shows one of these needles in which the centre portion has been dissolved by the introduction of a trace of water; on allowing the water to evaporate cubic crystals are deposited.

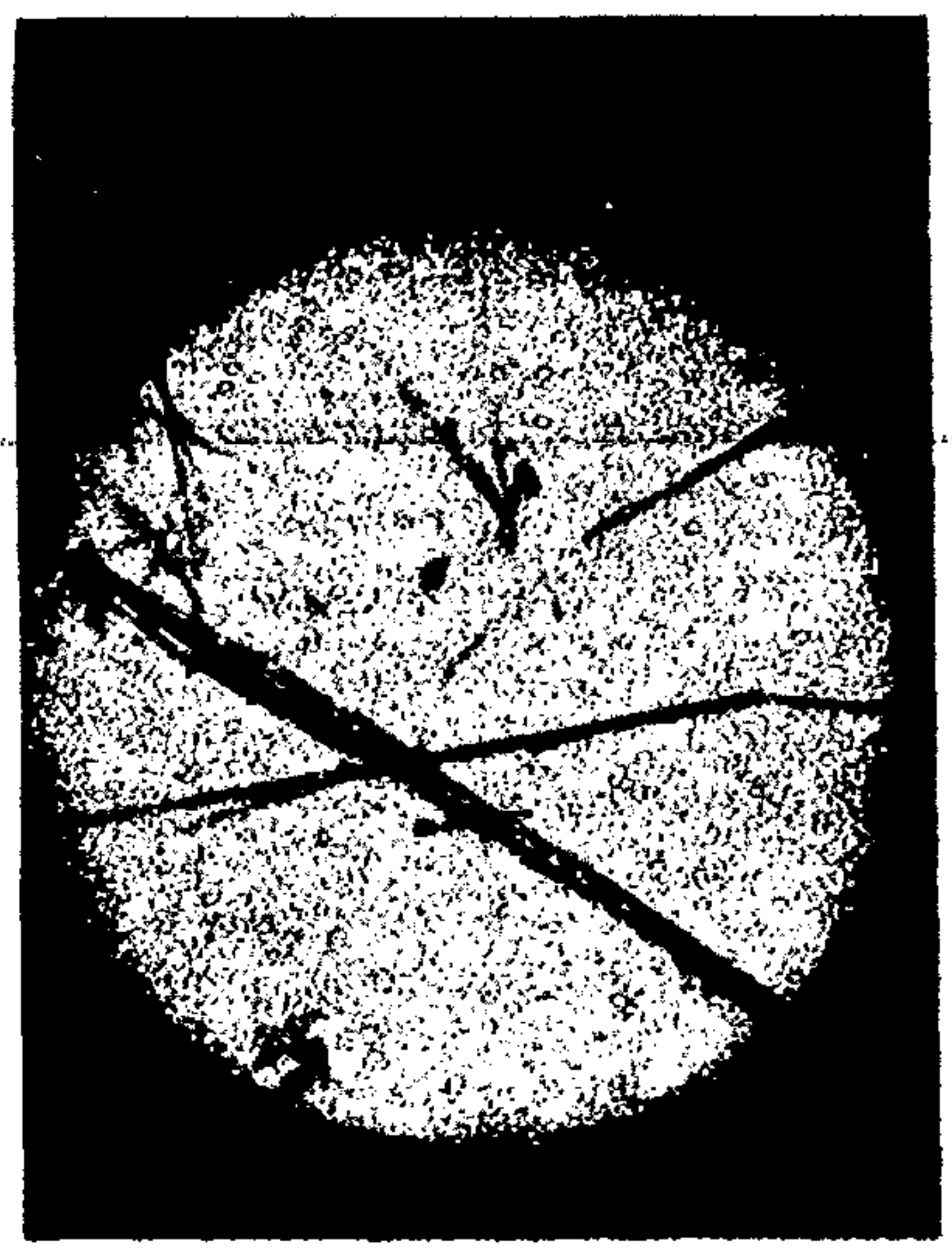

FIG. 3

FIG. 4

In some experiments needles over two inches in length were obtained. They are exceedingly friable and difficult to manipulate without breaking. A quantity of these needles was carefully collected and analysed and the following is a typical analysis

$$\text{Na} = 39.46 \qquad \text{Cl} = 60.49$$

From these observations it is therefore apparent that these needles are pure sodium chloride.

The product obtained after drying at 100°C was then heated at 300°C for two hours. The product was then thoroughly digested with warm distilled water, filtered and the operation repeated until the filtrate gave no opalescence with silver nitrate, i. e., was as free as possible from sodium chloride. This process required from 3 - 4 hours, which indicates that the sodium chloride is much more easily removed after heating. The resulting gel was then dried and heated at 600°C for about twenty minutes. The water content of a sample of this gel was 1.65 per cent. The gel differed from the previous gels in that the particles were much finer and more uniform in size, being on the average about

3 mm diameter. The rate of sorption and sorptive capacity of this gel was then determined by the flow method, exactly as previously described and the results are shown by a continuous line in Fig. 2.

For the purpose of comparison the results for the corresponding gel in which the sodium chloride was removed before drying is indicated by a broken line. It should be noted that the original water content of the two gels was 1.65 and 5.20 per cent respectively and that although the percentages of water taken up were 77.91 and 72.54 the final ratio of $SiO_2 : H_2O$ is very similar in both cases, being 1:0.82 and 1:0.84 respectively.

Discussion and Summary

The results show that when a silica gel is formed in two fractions, the first, a somewhat cloudy gel, formed almost immediately, and the second portion a clear firm gel which may take several days to set. The concentration of the sodium chloride and also the degree of hydration is much greater in the last formed gel.

It is shown that an immediate set is obtained on mixing the silicate solution and hydrochloric acid solution, when the mixed solution is just slightly alkaline, that is a slight excess of hydroxyl ions produces the quickest set, whilst if the concentration of the hydroxyl ions is increased the time of set rapidly increases. In acid solutions the quickest set is obtained with pure concentrated acid. The time of set *gradually* increases until the strength of the added acid is about 6 N, under which conditions the time of set is about three hours. As the concentration of the added acid is reduced below 6 N the time set increases more rapidly until for 3 N acid 18 - 24 hours elapse before the gel sets. The time of set increases very rapidly as the acid is further diluted until in the vicinity of the neutralization point it becomes very indefinite. It would appear, therefore, that the hydrogen ion concentration is not a vital factor, but rather the concentration of the undissociated molecules of the acid. It seems probable that the molecules of the acid exert a catalytic influence on the silicic acid produced; the influence being in the nature of a dehydrating action.

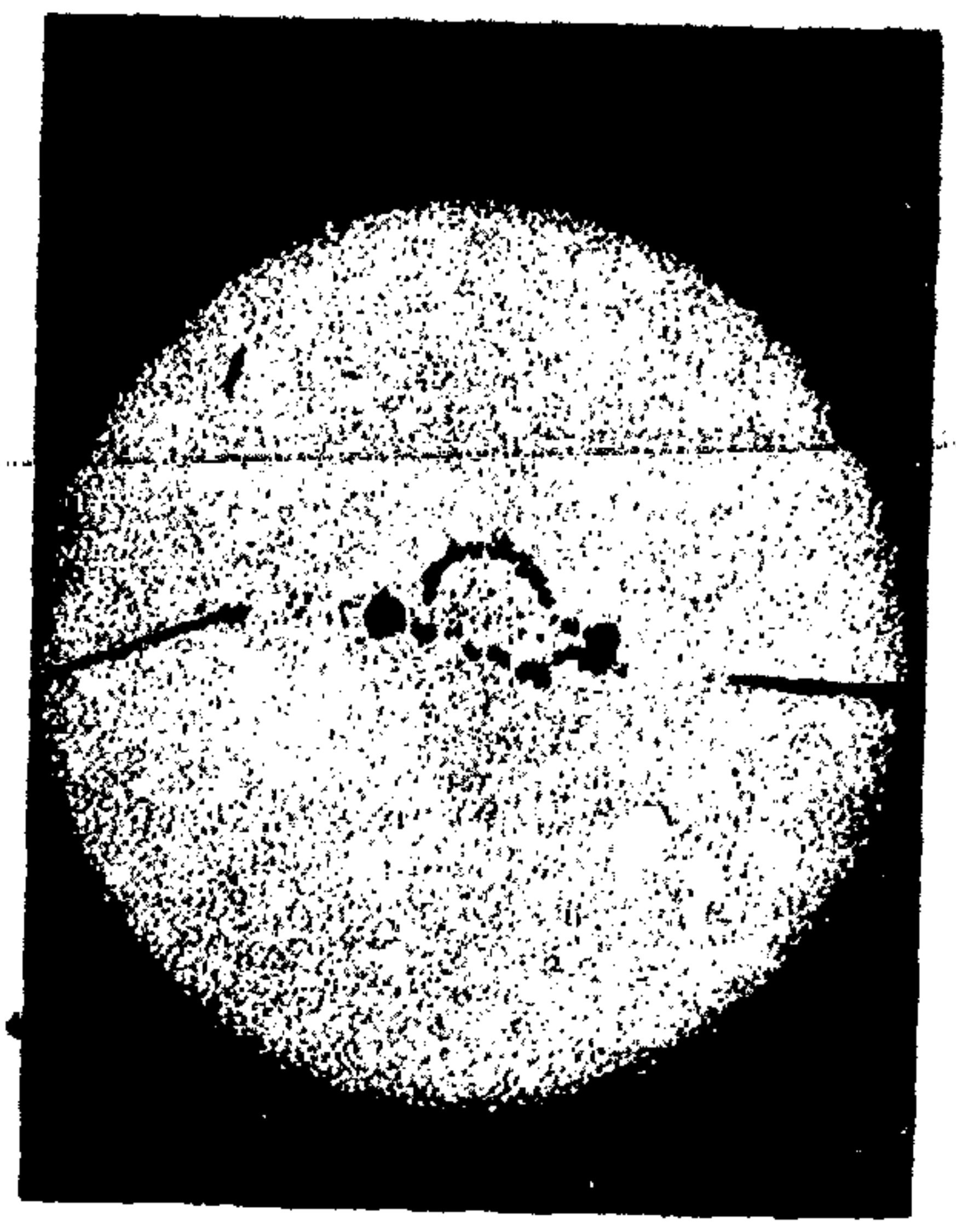

Fig. 5

Gels prepared at different temperatures show a similarity of water content after the final heating at 600°C., with the exception of that prepared at 0°C., which is appreciably lower than that for those prepared at higher temperatures. The rate of sorption of water vapour and sorptive capacity, have been determined by the static method. The gel prepared at 0°C. shows a slower rate and also an appreciably less capacity than those prepared at higher temperatures.

Of the other gels, that prepared at 18°C., shows the highest capacity, taking up approximately 70 per cent by weight of water, whereas the gel prepared at 45°C took up about 60 per cent of its weight of water. The difference in the size of the granules influences mainly the rate of sorption but does not affect to any great extent the total amount of water taken up. The determination made by the method of flow, for the gel prepared at 18°C, shows that the rate of sorption is much more rapid than by the static method, particularly in the earlier stages. This is of course as would be expected.

It has been shown that on drying the gel as produced, i. e., without the preliminary removal of the sodium chloride formed; that the sodium chloride, which is gradually removed from the gel during drying, forms fine capillary needles which grow out from the surface of the gel. It would appear that the sodium chloride and water are simultaneously removed at a considerable number of minute pores at the surface of the gel. As the drying continues the sodium chloride, as solution, exudes from these pores, the water evaporates immediately and the sodium chloride is deposited, hence the needles gradually increase in length. It was further observed that as the drying proceeded, the larger first-formed crystals became detached from the gel, whilst the later formed needles were much finer. The breaking off of the larger needles is readily understood when one considers the vast reduction in the surface of the gel as the drying proceeds; whilst the finer needles are the result of the contraction of the pores. These observations indicate that the surface of the finer gel contains a veritable mass of minute pores. These pores are probably the open ends of exceedingly fine capillaries in the gel. A comparison of the sorptive capacity of the two gels in which the sodium chloride was removed before drying and after drying respectively, shows very close agreement.

Hence within the limits of the present experiments the removal of the sodium chloride *after* heating has not materially altered the sorption capacity of the gel for water.

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October 18, 1924.

THE EFFECT OF THE ADDITION OF SOME ALKALOIDS ON THE RATE OF SOLUTION OF IRON IN DILUTE HYDROCHLORIC ACID

PART I

M. B. RANE AND MATA PRASAD

The action of acids on metals has been studied by various workers. Divers and Shimidzu[1] investigated the action of mixtures of sulphuric and nitric acids on zinc and found that the rate of solution of zinc depended on the surface of the metal exposed and the concentration of the acid, but was independent of the quantity of the acid used. Spring and Aubel[2] examined the action of various acids on zinc containing lead and found that the rate of evolution of hydrogen was slow at first, but increased rapidly afterwards till it reached a maximum and then decreased in such a way that the reaction was proportional to the decreasing concentration of the acids.

Veley[3] found that the rate of reaction of the acids on metal was affected by the dimunition in the concentration of the acids in the immediate neighborhood of the metals and by the gas bubbles that adhere to the surface. Friend and Dunnett[4] also observed that the rate of solution of iron in dilute sulphuric acid was greatly altered when the reactants were kept in motion.

A systematic study of the rate of solution of iron in hydrochloric acid was made by Conroy[5]. He measured the rate of solution of iron at successive intervals of time, by noting the volume of hydrogen evolved in a given time, and found that the rate rose to a maximum after a certain time depending upon the temperature and the concentration of the acid. Incidentally he found that the rate of solution of iron was diminished by the presence of small quantities of arsenious oxide.

Arsenious oxide is a well-known poison and the inhibiting effect observed by Conroy may be attributed to the poisoning action of arsenic. The authors were, therefore, led to examine if other poisonous substances also affect the rate of solution of iron in hydrochloric acid in a similar manner as arsenic.

The inhibiting effect of arsenious oxide has not been satisfactorily explained. It is likely that arsenious acid forms a thin metallic film on iron and thus protects it from being affected by the acid. The effect of poisons on the corrosion of iron and other metals and on the solution of iron by acids are somewhat analogous in character to the phenomenon of possivity. In order to obviate the likely formation of a metallic film as postulated in the theory generally put forward to explain the inhibiting action of such sub-

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[1] J. Chem. Soc. 47, 597 (1885).

[2] Ann. Chim. Phys. (6) 11, 505.

[3] J. Chem. Soc. 55, 361 (1889).

[4] J. Chem. Soc. 121, 41 (1922).

[5] J. Soc. Chem. Ind. 20, 316 (1901).

stances as arsenic oxide in the above phenomenon, it was considered desirable to study the behaviour of such poisons as the organic alkaloids under the same circumstances.

Experimental

In the present investigation the effects of various alkaloids on the rate of solution of iron in hydrochloric acid have been studied. Two sets of experiments were undertaken in the investigation.

The first consisted of the measurement of the rate of solution of pure iron in hydrochloric acid of various concentrations. These experiments had to be performed as there were no reliable data on the subject, the only work of importance being that of Conroy who unfortunately used commercial iron.

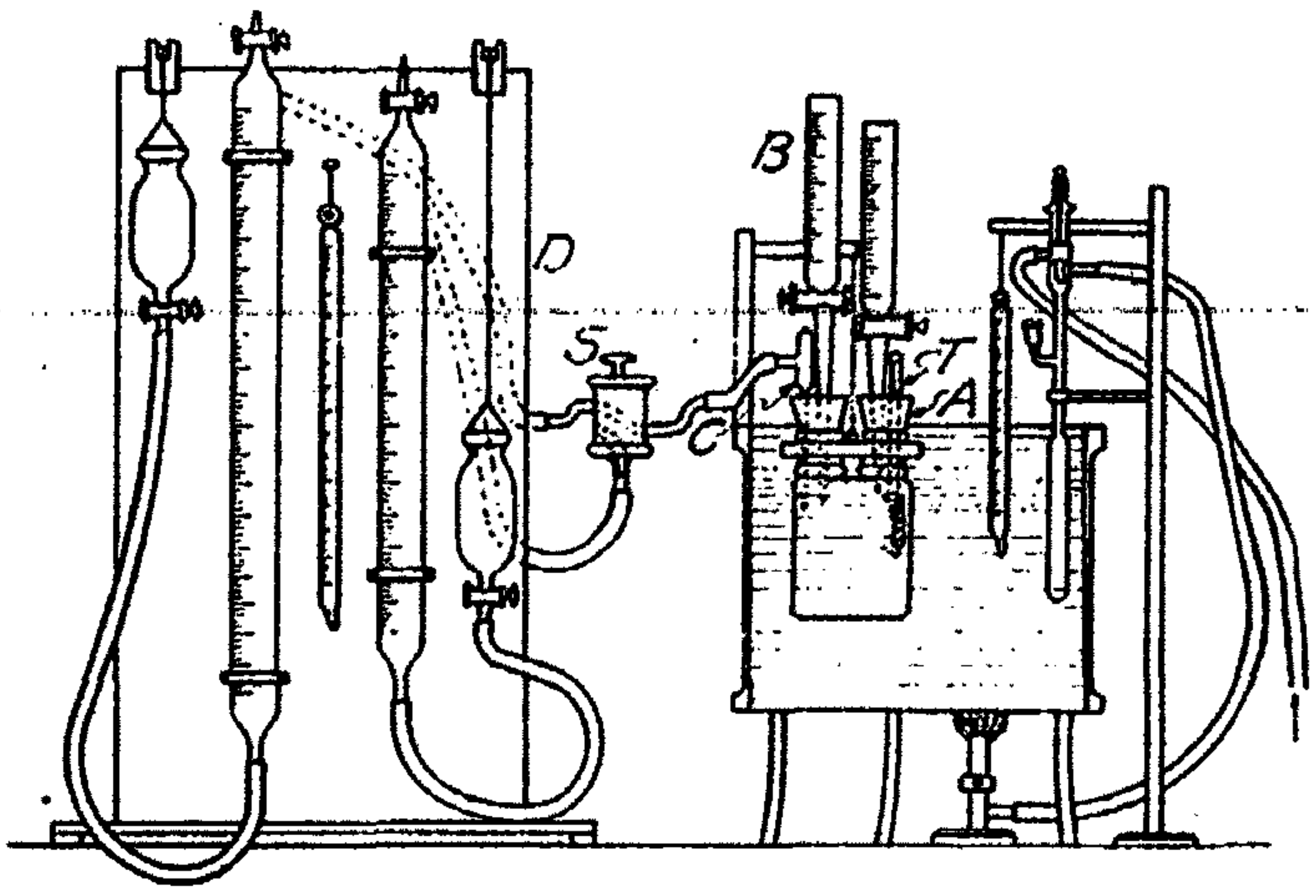

Fig. 1

The second set of experiments was performed after the addition of a given quantity of a known alkaloid and the changes in the rate of solution of iron in hydrochloric acid were noted by measuring the quantities of hydrogen evolved at various intervals.

The apparatus used is a modification of Conroy's apparatus and is shown in Fig. 1. The rubber stopper A of the Woulff's bottle has two holes. Through one passes a small burette for adding the alkaloid when needed and through the other passes a thermometer T for registering the inside temperature of the bottle and for carrying a small glass hook for suspending the coil of iron wire. The burette B in the other stopper serves the purpose of adding strong hydrochloric acid as will be shown later. The gas is led out through a delivery tube C and is collected in burettes D over water under reduced pressure. A system of two burettes is connected to the delivery tube by a two-way stop-cock S so that the gas evolved can be measured continuously in one or the other burette.

The bottle is placed in a thermostat maintained at a constant temperature of 45°C and kept suspended in it from a support fixed to the side of the thermostat. As the rate of evolutions of hydrogen by the action of acids on metals is greatly influenced by the motion of reactants[1], the bottle is given a regular and constant shaking by means of a mechanical attachment to the crank-shaft of a hot-air engine.

As pure electrolytic iron was not available, the best iron wire that could be had was employed. The specifications of the wire were:

Wire No. 20	S.W.G.
Diameter	0.0927 cms.

The analysis of the wire gave the following result:—

Iron	99.619 per cent.
Manganese	0.310 per cent.
Carbon	0.071 per cent.

400 cc. of the acid were placed in the bottle which was suspended in the thermostat as described above. It was kept there for sufficient time till it acquired the temperature of the bath. The thermometer T indicated that the temperature of the acid inside the bottle was the same as that of the bath. 87 cms of iron wire were coiled and inserted in the bottle through the glass hook. The gas evolved was measured after an interval of every 20 minutes. The temperature and pressure at which the gas collected were also noted and the volumes were reduced to N.T.P.

Friend and Dunnett have observed some anomalies in the curves obtained by plotting the rate of solution of iron in sulphuric acid against the concentration of the acid. The effect of concentration of the hydrochloric acid on the rate of solution of iron is investigated by the authors and the results obtained are shown in Table I.

TABLE I

Amount of Hydrogen evolved at N.T.P. per hour

Time	Concentration of HCl. N cc.	1.5N cc.	2N cc.	2.5N cc.	3N cc.	4N cc.
1st hour	91.7	117.4	137.6	141.6	144.1	194.0
2nd "	143.6	171.3	200.1	221.3	234.3	247.4
3rd "	177.4	211.2	275.1	337.6	352.7	384.0
4th "	224.3	305.3	430.3	500.8	549.3	
5th "	286.7	388.6	406.1	352.7	337.0	
6th "	248.4	325.6	114.4			

It will be seen from the above table that the rate of solution of iron increases as the concentration of the acid is increased and no anomaly is observed.

Also in each case the rate first rises, goes up to a maximum, and then decreases with a great rapidity. These results are similar to those obtained by Conroy and exhibit no periodicity[2].

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[1] Cf. Friend and Dunnett: J. Chem. Soc. **121**, 141 (1922).

[2] Cf. Ostwald: Z. physik. Chem. **35**, 33, 204 (1900); Hedges and Myers: J. Chem. Soc. **125**, 608 (1924).

There are two factors which are affecting the rate of solution of iron and they are:—

1. The diminution in the percentage of the free acid in the solution due to the reaction.

2. The increase in the surface of the wire which when taken out of the acid and examined, is found to be more porous than before the experiment.

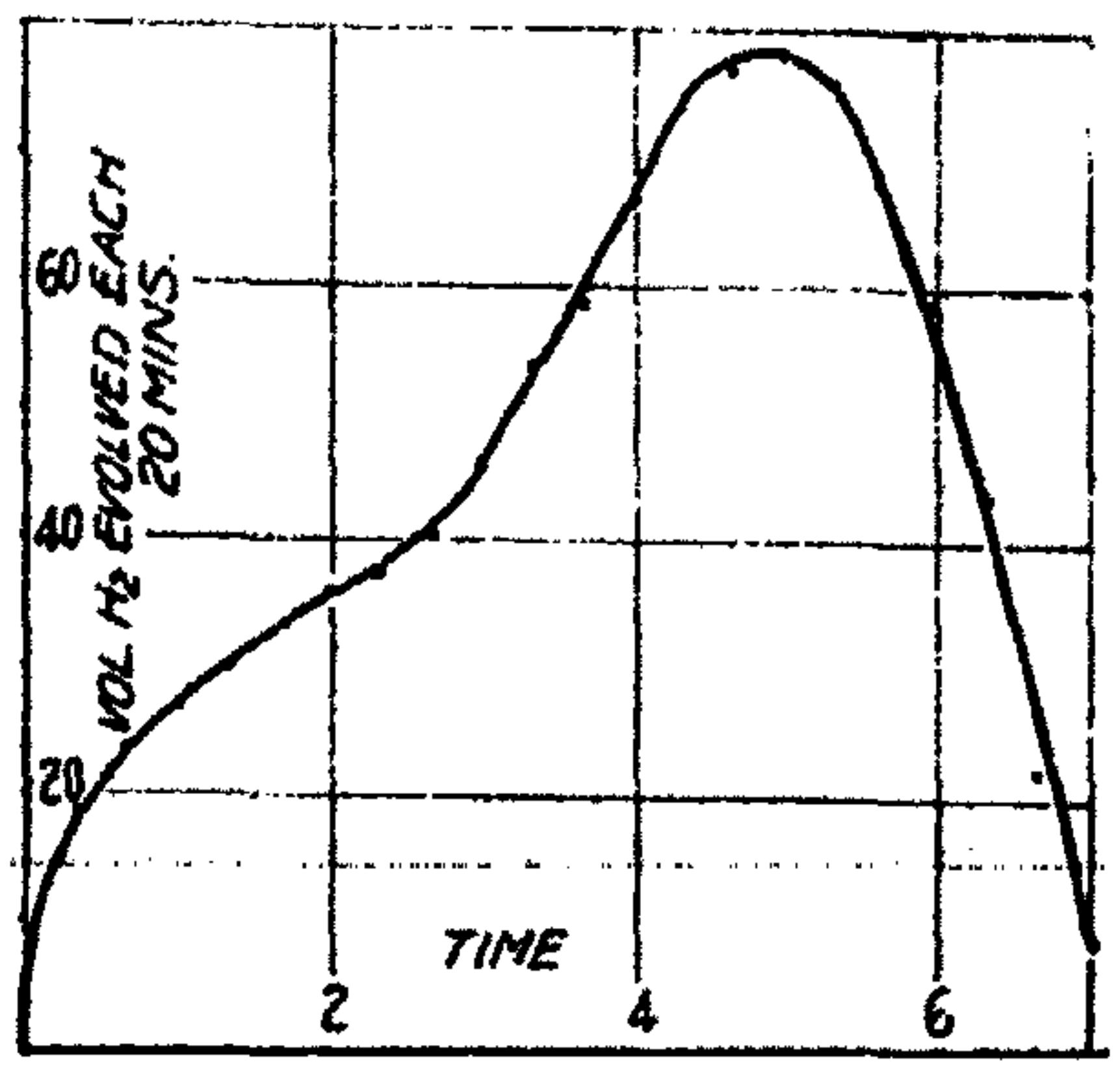

Fig. 2

To counteract the effect of the first factor, a strong solution of hydrochloric acid was prepared and placed in the burette B. After every 20 minutes the amount of the acid consumed was calculated and was added to the bottle. There was certainly a very slight increment in volume thereby (never exceeding 3 cc. in all) but it has been shown by Veley, Divers and Shimidzu, and others that the volume of the acid is ineffective in influencing the rate of reaction.

In subsequent experiments 300 cc. of the normal hydrochloric acid and 50 cms. of the wire were used. The results of the variation in the rate of evolution of hydrogen with time on keeping the concentration of the acid constant are shown in Table II.

TABLE II

Time in Minutes	Volume of the gas evolved per 20′ at N. T. P. cc.	Time in Minutes	Volume of the gas evolved per 20′ at N. T. P. cc.	Time in Minutes	Volume of the gas evolved per 20′ at N. T. P. cc.
0′— 20′	18.68	140′—160′	41.21	280′—300′	77.72
20′— 40′	23.63	160′—180′	45.67	300′—320′	75.27
40′— 60′	27.11	180′—220′	53.52	320′—340′	67.28
60′— 80′	30.09	200′—220′	58.22	340′—360′	58.08
80′—100′	31.37	220′—240′	66.23	360′—380′	42.90
100′—120′	35.76	240′—260′	73.63	380′—400′	21.68
120′—140′	37.54	260′—280′	76.20	400′—420′	8.29

By plotting the volume of the gas evolved each 20 minutes against time, a curve is obtained as shown in Fig. 2. This curve is almost similar to the curve obtained by plotting the values given in Table I.

Effect of Alkaloids

The effect of the alkaloids available in the laboratory was examined. The alkaloids tried in the preliminary experiments were codeine, cinchonine, brucine, strychnine, nicotine, and cocaine. In all the cases the inhibiting effect was observed.

A detailed study of only the first three alkaloids has been made in this part of the effect of the addition of the varying amounts of alkaloids on the rate of solution of iron has been examined. In most of the experiments the alkaloids were added initially to the acid and in some cases they were added after the reaction had proceeded for sometime. The solutions of all alkaloids were prepared in normal hydrochloric acid and the total volume of the acid and the alkaloid solution was 300 c.c. in all cases. The results of the investigation are indicated in Tables III-V.

TABLE III

Effect of Codeine on the Rate of Solution of Iron

Time	Volume of the gas evolved on the addition of the following quantities initially						
	Grams 0.0200	Grams 0.0150	Grams 0.0100	Grams 0.0050	Grams 0.0020	Grams 0.0008	Grams 0.0002
	cc.	cc.	cc.	cc.	cc.	cc.	cc.
0′– 20′	1.76	2.91	6.16	6.53	8.27	9.55	12.81
20′– 40′	5.80	10.61	12.99	16.50	17.89	20.52	23.15
40′– 60′	11.50	17.36	16.02	21.94	22.02	23.24	29.55
60′– 80′	16.20	18.62	22.10	23.37	24.40	26.63	32.39
80′–100′	18.07	19.29	24.33	26.46	25.39	28.77	35.03
100′–120′	19.89	21.89	24.42	28.23	30.89	31.83	37.20
120′–140′	20.30	23.17	24.55	29.38	31.74	34.93	40.91
140′–160′	20.50	23.22	25.29	30.50	33.58	36.94	41.16
160′–180′	21.66	23.90	25.52	31.31	35.02	38.95	46.70
180′–200′	21.91	24.80	25.99	33.08	38.73	46.22	51.12
200′–220′	21.09	25.31	28.79	33.50	41.35	48.08	54.71
220′–240′	22.75	26.93	30.95	35.17	43.80		

TABLE IV

Effect of Cinchonine on the Rate of Solution of Iron

Time	Volume of the gas evolved on the addition of the following quantities initially				
	0.0200 grams	0.0020 grams	0.0002 grams	0.00015 grams	0.0001 grams
	cc.	cc.	cc.	cc.	cc.
0′– 20′	1.07	2.63	5.81	5.77	6.84
20′– 40′	1.41	7.55	14.10	16.54	19.86
40′– 60′	3.31	12.27	24.97	28.65	29.42
60′– 80′	5.45	18.76	31.44	31.09	34.04
80′–100′	6.20	21.73	34.10	33.12	35.83
110′–120′	7.12	24.33	37.88	35.29	36.59
120 –140	9.63	26.93	36.83	35.70	37.10
140′–160′	9.44	28.24	41.97	37.05	39.05
160′–180′	10.33	29.80	42.23	40.15	40.73
180′–200′	11.67		46.75	43.86	43.27
200′–220′	11.73		50.02	48.43	47.40
220′–240′	13.71		45.73	53.09	52.73

TABLE V

Effect of Brucine on the Rate of Solution of Iron

Time	Volume of the gas evolved on the addition of the following quantities initially			
	0.0020 grams	0.0002 grams	0.00015 grams	0.0001 grams
	cc.	cc.	cc.	cc.
0′– 20′	5.61	12.33	12.66	12.68
20′– 40′	13.90	19.18	18.35	21.08
40′– 60′	17.80	23.74	25.02	25.70
60′– 80′	20.25	26.79	29.54	29.46
80′–100′	23.33	28.35	32.57	33.84
100′–120′	24.32	31.48	36.66	36.09
120′–140′	28.19	29.37	38.77	38.23
140′–160′	28.57	32.54	41.80	42.91
160′–180′	31.03	35.45	45.53	47.18
180′–200′	37.47	39.64	50.68	50.90
200′–220′	43.30	45.44	55.00	57.93
220′–240′	47.10	50.57	59.46	63.20

Discussion of Results

It will be seen from the Tables I and II that the evolution of hydrogen is similar in both the cases. In the latter case the concentration of hydrochloric acid is maintained constant while in the former no such allowance is made. This indicates that the rise and fall in the rate of solution of iron in hydrochloric acid is not much affected by the slight variations in the concentration of the acid due to neutralisation. The rise in the rate of reaction is due to the iron which becomes more and more porous as the reaction proceeds and thus offers a larger and larger surface for reaction. The rate of reaction increases up to a certain limit when the iron reaches its maximum limit of porosity and consequently the largest surface. The curve, shown in Fig. 2, gives an idea of the manner in which the surface of iron changes. After the maximum surface is reached, the further action of the acid lessens the active mass of the iron and the rate decreases as would be required by the law of mass action.

It is clear from the Tables III, IV and V that the rate of evolution of hydrogen falls off by the addition of alkaloids even in such small quantities as 0.0001 grams. The inhibiting effect is greater as the amount of the alkaloid used is larger. The inhibiting effect varies with the nature of the alkaloid. The following table gives the effect observed when 0.02 grams of various alkaloids were added to the bottle after the reaction has proceeded for two hours. In these experiments the length of the wire used is 87 cm., and the volume of the normal hydrochloric acid is 400 c.c.

The alkaloids can, therefore, be arranged in the following series according to their poisoning action upon iron: brucine > strychnine > cinchonine > nicotine > codeine > cocaine > conine.

TABLE VI

Effect of 0.02 grams of Alkaloids on the Rate of Solution of Iron

Time	Volume of the gas evolved in each hour on the addition of alkaloids							
	Without the alkaloid	Brucine	Strychnine	Cinchonine	Nicotine	Codeine	Cocaine	Conine
	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
1st hour	91.7	—	—	—	—	—	—	—
2nd hour	143.6	—	—	—	—	—	—	—
3rd hour	177.4	35.78	39.81	62.48	91.20	91.70	120.40	160.30
4th hour	224.3	35.78	43.33	68.53	109.80	—	125.00	205.10
5th hour	286.7	36.28	46.86	72.06	110.40	95.74	138.00	276.70
6th hour	248.4	37.79	49.89	72.56	133.00	99.79	145.60	252.00

To see if the above phenomena is any way similar to passivity of iron, the following test[1] indicative of passivity was made.

Two similar coils of iron wire were taken and dipped into two beakers, one containing normal hydrochloric acid and the other normal hydrochloric acid and alkaloid. They were taken out after sometime and dipped into beakers containing 0.5% copper sulphate solution. The deposition of copper was almost the same on the two coils.

Next, two similar coils after introducing them in hydrochloric acid for some time were taken out and dipped into two beakers, one containing the copper sulphate solution and the other the copper sulphate solution and the alkaloid. It was observed that the copper deposited exceedingly slowly on the coil which was placed in the mixed solution of copper sulphate and the alkaloid while the deposition was very rapid on the other coil.

It would appear from these experiments that the effect of the alkaloid in inhibiting the evolution of hydrogen by the action of hydrochloric acid is somewhat analogous to the phenomena of passivity. It is intended to carry on further work in the direction of making measurements of the electromotive force and other physical properties induced in the iron by the action of the alkaloids. By this means it is hoped that a rational interpertation of the effects observed would be forthcoming.

The authors take this opportunity of expressing their thanks to Dr. S. S. Bhatnagar for taking interest in the work.

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[1] Dunstan and Hill: J. Chem. Soc. 99, 1835 (1911).

THE ADSORPTION OF VAPORS BY METALLIC OXIDES: ITS BEARING ON THE CATALYSIS OF ESTER FORMATION

J. N. PEARCE AND A. M. ALVARADO

The catalytic dehydrating and dehydrogenating power of metallic oxides has been known for many years. In fact, the phenomenon of dehydration was first observed by Priestley[1] while passing alcohol vapors through an earthen tube heated to redness. It remained for Deimann[2] to observe the catalytic dehydrating effect of the tube itself, and to separate and identify the gases. He found that when alcohol vapor is passed over heated alumina it is converted into ethylene and water. He reports also the presence of a certain amount of hydrogen in the issuing gases.

In 1908 Sabatier and Mailhe[3] report the use of thorium oxide as a catalyst in the decomposition of alcohol. They found that at 340° this oxide gives fifty percent more ethylene than does alumina; also that in addition to its greater activity it behaves exclusively as a dehydrating agent. Unlike most other oxides whose activities are greatly influenced by the mode of preparation, the activity of thoria is, according to Sabatier[4], not sensibly diminished when it is ignited at red heat. The recent work of Kramer and Reid[5] has shown that the method of preparing this oxide does influence its activity. Some of their preparations were almost inactive; indeed, commercial thoria and discs cut from Welsbach mantles were found to be inactive. Gilfillan[6] has found that strong calcination or prolonged heating at lower temperatures inactivates thoria for the dehydration of ethyl alcohol, but under certain conditions produces a considerable amount of aldehyde by dehydrogenation. When alcohols[7] are heated to temperatures ranging from 300° to 350° in the presence of ThO_2, Al_2O_3 and WO_3 they are converted into ethylene hydrocarbons; at temperatures below 250° they are converted into ethers. Sabatier and Mailhe consider that these transformations are analogous to those that take place when the alcohols are heated with sulphuric acid, and that sulphuric acid is not a true catalyst because its activity is destroyed by the presence of the water produced. They believe that the most probable mechanism of the reaction is one which involves the formation of complex compounds such as, $ThO(OC_nH_{2n+1})_2$. This may then break up directly to give ethylene and water, or it may react with another molecule of alcohol to give ether; in either

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[1] Priestley: Phil. Trans. 73, 429 (1783).

[2] Deimann: Crell Ann., 2, 312, 430 (1795).

[3] Sabatier and Mailhe: Compt. rend., 147, 106 (1908).

[4] Sabatier: "La Catalyse", 2nd ed., 26 (1920).

[5] Kramer and Reid: J. Am. Chem. Soc., 43, 880 (1921).

[6] Gilfillan: J. Am. Chem. Soc., 44, 1323 (1922).

[7] Sabatier and Mailhe: Compt. rend., 150, 823 (1910).

case the metallic oxide is regenerated in an active condition. Senderens[1] has found that at 240° to 260° Al_2O_3 with methyl and ethyl alcohols gives very good yields of the corresponding ethers, and he states that the reaction involved is most probably represented thus:

$$2C_2H_5OH \xrightarrow{Al_2O_3} (C_2H_5)_2O + H_2O, \text{ and}$$

$$2CH_3OH \xrightarrow{Al_2O_3} (CH_3)_2O + H_2O.$$

As will be observed the reaction thus represented is purely one of dehydration. He states that the ease with which Al_2O_3 transforms methyl and ethyl alcohols into the corresponding ethers would lead one to expect that all alcohols could thus be transformed to their respective ethers. This is not the case, however, since he found that propyl alcohol forms a condensible ethylene hydrocarbon to such an extent that only a thirty percent yield of propyl ether is obtained. Further, isobutyl alcohol was transformed completely into di-isobutylene, no ether being formed. When tungestic oxide (WO_3) is substituted for Al_2O_3 only very small amounts of methyl and ethyl ether are formed, while no ether is formed when ThO_2 is used.

Senderens[1] has also prepared ketones of various types by heating the corresponding acids and esters in the presence of various catalysts, particularly with Al_2O_3 at 300°. He has proposed to represent the chemical changes taking place thus,

$2CH_3COOH \longrightarrow H_2O + CO_2 + (CH_3)_2CO$, or the reaction may take place in successive steps,

$$\begin{array}{l} CH_3COOH \\ CH_3COOH \end{array} \longrightarrow H_2O + \begin{array}{l} CH_3CO \\ CH_3CO \end{array} > O.$$ The anhydride may then decompose into carbon dioxide and acetone,

$$(CH_3CO)_2O \longrightarrow CO_2 + (CH_3)_2CO.$$

In confirmation of the possibility of the latter reaction he states that acetic anhydride when passed over Al_2O_3 at 300° actually gives CO_2 and acetone, the evolution of CO_2 being more abundant as the temperature approaches 380°. The yield of ketone is very small when propionic and isobutyric acids are treated in a similar manner. Under like conditions the ethyl esters yield acetone, CO_2, C_2H_4 and H_2O. He proposes to express the reaction for ester decomposition by the equation,

$$2RCOOC_2H_5 \longrightarrow 2C_2H_4 + CO_2H_2O + RCOR.$$

When ThO_2 is used as catalyst good yields of diethyl, dipropyl and diisopropyl ketones were obtained from the corresponding acids at 380° to 420_2.

When formic acid[1] is heated alone at 260° it decomposes into carbon monoxide and water. If ThO_2 is present the temperature of decomposition is lowered to 200° and there is formed H_2O, CO_2 and HCHO from two molecules of the acid, the relative quantities depending upon the temperature. In the

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[1] Senderens: Bull. (4) 5, 480 (1909); Compt. rend., 140, 995, (1905); 148, 227, 297 (1909); 150, 11, 702 (1910); Ann. Chim. Phys., 28, 243, 344 (1918).

presence of Al_2O_3 at 200° to 250° ethyl formate decomposes into ethyl ether, CO and H_2O. With the same catalyst at 400° ethyl succinate yields CO_2, C_2H_4 and tetrahydroquinone. It has been shown[1] that acetic acid alone may be heated in a sealed tube without decomposition; if Al_2O_3 is present it decomposes at 350° to give H_2O, CO_2 and acetone. Ethyl acetate alone is stable at 430°, but in contact with Al_2O_3 it decomposes at 350°, the products being H_2O, C_2H_4, CO_2 and acetone. In a later paper Senderens[2] showed that if the aromatic and aliphatic acids are heated in the presence of ThO_2, ZrO_2, and UO_2 they are transformed into ketones.

Mailhe[3] represents the possible reactions between an alcohol and an acid when passed over a metallic oxide, MO, thus,

(1) $(RCO_2)_2M+H_2O \longrightarrow MO+RCOR+H_2O+CO_2$,
(2) $MO+2C_nH_{2n+1}OH \longrightarrow M(OC_nH_{2n+1})_2+H_2O$,
(3) $M(OC_nH_{2n+1})_2 \longrightarrow MO+H_2O+C_nH_{2n}$, or
(4) $M(OC_nH_{2n+1})_2 \longrightarrow 2RCO_2H+MO+RCO_2C_nH_{2n+1}$.

The formation of the alcoholate according to (4) is limited by the decomposition of the unstable metallic alcoholate by water, whereby the alcohol is regenerated. On the contrary, all of the possible reaction products are formed when acetic acid and alcohol are heated with ThO_2 at 400°. If, however, the acid employed is one whose salt does not readily decompose according to (1), then the principle reaction is that of ester formation (4), the reactions represented by (2) and (3) being negligible. Thus the methyl, ethyl, propyl, isobutyl, isoamyl and allyl esters of benzoic acid are obtained in practically theoretical yields by passing a mixture of one mol of the acid and twelve mols of the alcohol over ThO_2 at 350°. The equilibrium limit of ester formation is rapidly attained when the alcohol and acid are present in molar proportions.

Sabatier[4] summarizes the catalytic action of alumina, thoria and titania on ethyl acetate at temperatures around 400° in the following equations:

$$2CH_3CO_2C_2H_5 \xrightarrow{Al_2O_3} (CH_3)_2CO+2C_2H_4+CO_2+H_2O,$$

$$2CH_3CO_2C_2H_1 \xrightarrow{ThO_2} (CH_3)_2CO+C_2H_4+CO_2+C_2H_5OH,$$

$$CH_3CO_2C_2H_6 \xrightarrow{TiO_2} CH_3CO_2H+C_2H_4.$$

An extended investigation of the activity of oxide catalysts at temperatures between 300° and 400° by Sabatier and Mailhe[5] show that a majority of oxides promote two reactions simultaneously, one the process of dehydration, the other the process of dehydrogenation. The analyses of the gaseous products obtained in the passage of the vapor of ethyl alcohol over various oxides at

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[1] Senderens: Compt. rend., **146**, 1211 (1908).
[2] Senderens: Compt. rend., **150**, 702 (1910).
[3] Mailhe: Chem. Ztg., **35**, 485, 507 (1911).
[4] Sabatier: "Le Catalyse en Chimie Organique", 341 (1920).
[5] Sabatier and Mailhe: Ann. Chim. Phys., (8) **20**, 289 (1910).

340° to 350° showed that with certain catalysts ethylene only is produced. In general the effluent gas is a mixture of ethylene and hydrogen in varying proportions depending upon the catalyst used. They have tabulated the different metallic oxides in the order of decreasing power of dehydrating ethyl alcohol, thus

Oxide prepared below 350°	Vol. of gas per min.	100 c. c. %C_2H_4	contain %H_2
ThO_2	31.0	100.0	traces
Al_2O_3	21.0	98.5	1.5
W_2O_5 (blue)	57.0	98.5	1.5
Cr_2O_3	4.2	91.0	9.0
SiO_2	0.9	84.0	16.0
TiO_2	7.0	63.0	37.0
BeO	1.0	45.0	55.0
ZrO_2	1.0	45.0	55.0
U_3O_8	14.0	24.0	76.0
Mo_2O_5 (blue)	5.0	23.0	77.0
Fe_2O_3	32.0	14.0	86.0
V_2O_3	14.0	9.0	91.0
ZnO	6.0	5.0	95.0
MnO_2	3.5	0.0	100.0
SnO	45.0	0.0	100.0
CdO	11.2	0.0	100.0

These data indicate that ThO_2 behaves almost exclusively as a dehydrating agent under the given conditions; its power as a dehydrogenating agent is practically nil. Alumina and tungstic oxides are only slightly less active dehydrating agents. The oxides of tin and cadmium are exclusively dehydrogenating agents, their dehydrating action is entirely suppressed. Between the two extremes the dehydrating and dehydrogenating power of the metallic oxides varies rapidly. In general, the greater the catalytic dehydrating activity of a metallic oxide, the smaller is its dehydrogenating activity toward alcohol. A study of the adsorption powers of these oxides for acetic acid, alcohol, water and ethyl acetate should throw some light upon the mechanism of ester catalysis.

There is, however, an apparent lack of agreement among experimenters as to whether Al_2O_3 is a catalyst for dehydration or for dehydrogenation. Senderens[1] has attempted to explain this lack of agreement by stating that if in the preparation of the catalyst the calcination is strong and long continued the catalytic dehydrating power of the alumina is diminished, and with this change in character there is an increase in its tendency to dehydrogenate alcohols.

As has been stated, Sabatier[2] has found that widely different decompositions are induced in esters by alumina, thoria and titania. The equations which he

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[1] Senderens: Compt. rend., **146**, 125 (1909).

[2] "La Catalysé en Chimie Organique", 341 (1920).

presents to represent these reactions might lead one to believe that each catalyst under a given set of conditions is capable of inducing a definite specific reaction. He and Mailhe[1] explain the difference in the decomposition products of esters by various catalysts as being due to the relative instabilities of the intermediate compounds formed between the catalyst and the acid and between the catalyst and the alcohol. In a careful investigation of the action of alumina, titania and thoria on alkyl acetates, Adkins and Kraus[2] have found no evidence that these oxides catalyze specific decompositions of ethyl acetate. The results which they did obtain indicate that in determining the order of the efficiency of these catalysts for these reactions, the method of preparation of the catalyst is of equal, if not of greater importance, than the particular metallic element present in the catalyst. They state that the course of the decomposition is not determined by the relative instability of the salts of the acid and of the alcohol.

Briggs[3] considers that the activation of charcoal for the adsorption of gases is dependent upon interstices of molecular dimensions formed by the elimination of carbon atoms from the carbon molecule or space lattice. In this he refers to the cavities of molecular size and not to those much larger, microscopically visible pores or capillaries which have apparently little to do with adsorption. Starting with this idea Adkins[4] has advanced an hypothesis which considers that the catalytic activity of alumina is conditioned by its molecular porosity, or the distance between the aluminum atoms, and that this part is determined by the size, shape and position of the radicles attached to the aluminum atom when the aluminum compound passes into the solid state of the catalyst. All of the experimental evidence obtained with alumina catalysts, prepared in various ways, was found to be in complete harmony with this hypothesis. He was able to activate alumina preferentially either for dehydration or for decarboxylation by modifying its mode of preparation. In terms of this hypothesis he states that decarboxylation is favored by large molecular pores in the alumina and that ethylene formation is favored by small pores.

In a recent critical study Pease and Yung[5] have found that alumina at 300° to 400° dehydrates alcohol to give pure ethylene. If the reaction is carried out at lower temperatures, 240° to 260°, ether is produced. Ether itself was found to be dehydrated to ethylene by alumina when heated to 275° to 300°. Whether these reactions are successive or simultaneous was not determined. They seem to be in complete accord with the theory of Adkins and, further, they state that the size of the pores is the determining factor in the production of ethylene or of ether from ethyl alcohol by alumina. They state that large pores favor the formation of CO_2, while small pores favor

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[1] Sabatier and Mailhe: Compt. rend., **152**, 497, 669 (1911).

[2] Adkins and Kraus: J. Am. Chem. Soc., **44**, 385 (1922).

[3] Briggs: Proc. Roy. Soc. **100A**, 88 (1921).

[4] Adkins: J. Am. Chem. Soc., **44**, 2175 (1922).

[5] Pease and Yung: J. Am. Chem. Soc., **46**, 390 (1924).

the production of ethylene. This explanation does not fully cover the case since in both reactions we have the formation of water.

In the previous discussion two theories of heterogeneous catalysis have been dominant, the intermediate compound theory and the adsorption, or possibly selective adsorption, theory. It would seem that whether the one or the other of these two theories applies to a particular catalytic reaction can be proved directly by experiment. The object of the present research was to make a study of the relative adsorption of the vapors of acetic acid, ethyl alcohol, water and ethyl acetate by the oxides of thorium and aluminum at 100°. From such data it was hoped that we might find some tangible and acceptable theory of heterogeneous catalysis.

Materials

Ethyl Alcohol. Ordinary alcohol was first allowed to stand over fresh quick lime for several weeks, then decanted and distilled; the constant boiling middle portion was refluxed over metallic calcium for six hours, and then distilled through a tall fractionating column. This constant boiling fraction was refluxed for five hours over pure anhydrous silver nitrate to remove aldehydes and again fractionally distilled. In each process the alcohol was carefully protected against moisture by efficient drying trains.

Acetic Acid. The acid was prepared by fractionally freezing glacial acetic acid six times, then fractionally distilled four times. The final product boiled at 118.1° under a pressure of 744.6 mm. (corr).

Ethyl Acetate. The ester was prepared by first washing a high grade sample five times with water to remove acetic acid and alcohol. It was then carefully separated, dried over calcium chloride, and finally fractionally distilled, only the constant boiling middle portion, boiling at 76.8° and 743.2 mm (corr) being retained.

Water. The water used was regular conductivity water distilled from an alkaline solution of potassium permanganate and collected hot to avoid the presence of dissolved gases.

Preparations of Metallic Oxides

The oxides of aluminum and thorium[1] were prepared by precipitation with ammonium hydroxide from dilute solutions of the nitrates; the solutions were boiled to expel the excess of ammonia, the precipitates were allowed to settle and the clear supernatant liquid decanted. The precipitate was washed eight times by decantation with conductivity water and then filtered through a smooth hardened filter. The final precipitate was dried for 18 hours at 120° and then pulverized so as to pass through a 200-mesh sieve. This fine powder was again heated for 24 hours at 240° to 250° and again pulverized to pass through 200-mesh. This product was again heated at the same temperature for 10 hours and then transferred to paraffin sealed bottles.

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[1] We wish at this time to express our appreciation for samples of rare earth salts presented to us by the Du Pont Company, Wilmington, Del.

The density of the two hydrated oxides was accurately determined by evacuating a sample of the oxide in a bulb provided with a drawn out capillary at 236° until the pressure of the vapor remained constant at 0.001 mm, or less, for several hours. The tube was then sealed, allowed to cool and weighed again. The capillary tube was broken under a specially purified sample of benzene; the bulb thus filled was placed in a thermostat at 25°, the level of the benzene brought to a given mark on the capillary and weighed again. The bulb was then cleaned, weighed and refilled with benzene at 25° and weighed. The mean of five different closely agreeing density determinations for each oxide were: Al_2O_3, 2.857; ThO_2, 8.824. These values were used in calculating the "dead space" in the bulb. Obviously, such density values will depend upon the method of preparation of the oxide.

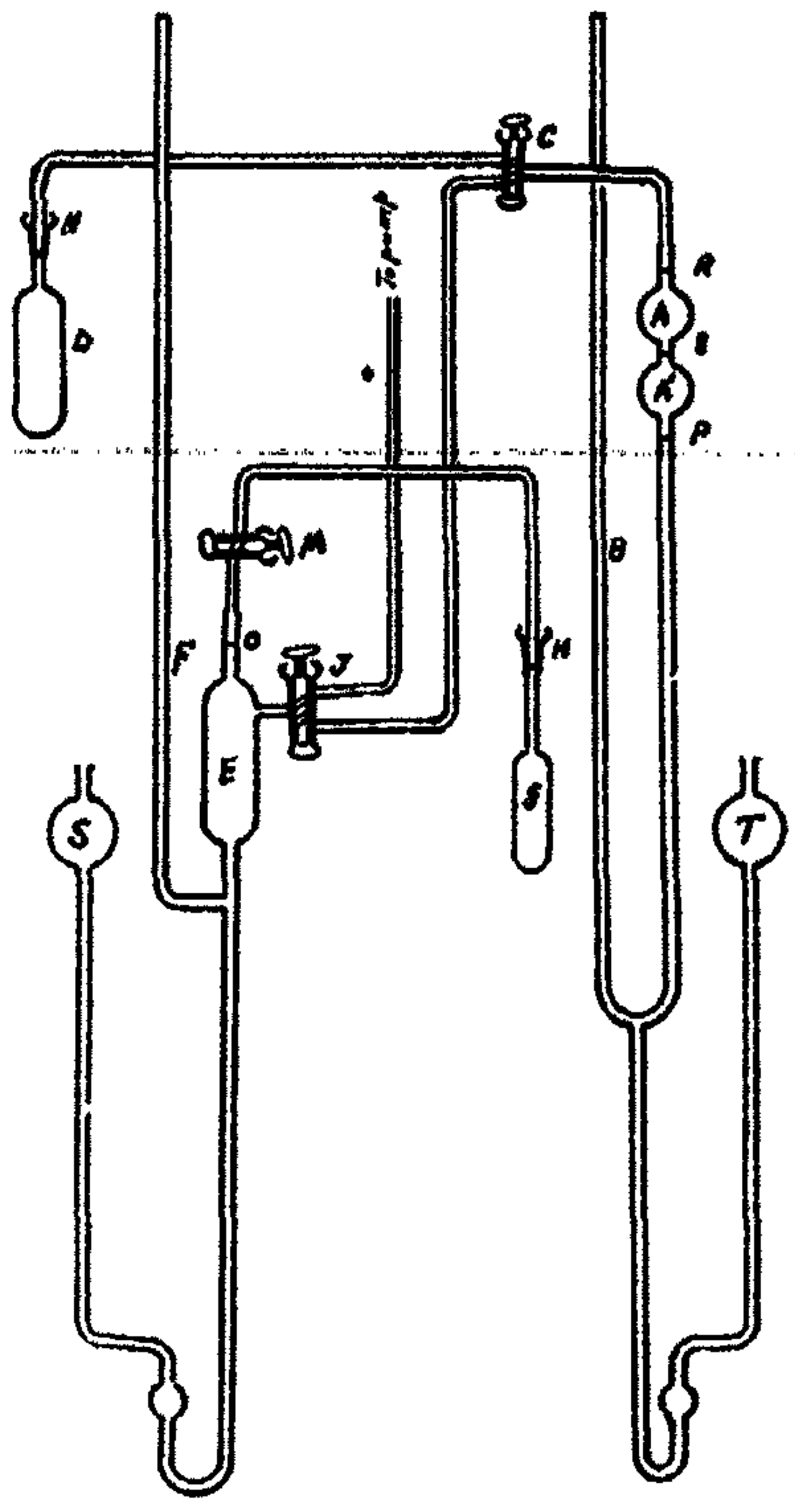

FIG. 1

Apparatus

A sketch of the apparatus is shown in Fig. I. It may suffice to say that the apparatus consists essentially of a pair of vapor measuring bulbs, A A', an expansion bulb E, a reservoir for the pure liquid D, and the pyrex adsorption bulb G. The manometer tubes, F and B, as well as the tubes at the points O, R and P were of heavy wall barometer tubing (I. D. = 4 mm); the ground glass joints N and H, and the stop cocks C, M and J were mercury sealed. The volumes of the capillary tubes from O to H and from C to J, and of the bulbs A, A' and G were determined by direct weighing with mercury before assembling; the volume of the small tube from R to C was accurately calculated from pressure data obtained when small amounts of dry air were first measured at P and then at S. The bulb G containing the oxide was immersed to its whole length in a test tube of mercury which in turn was completely immersed in the vapor of pure boiling water. In this way the temperature of the oxide was maintained constant, subject only to fluctuations in the barometric pressure. No extra effort was made to regulate the temperature of the boiling flask, but if the boiling point of water varied during a series of adsorptions by more than ±0.02°, that series was rejected. All of the glass parts of the apparatus were mounted in a large double-walled wooden air bath, the air space between the walls being packed with magnesite to prevent radiation. This was electrically heated and electrically controlled throughout the work at 51.0 ±0.05°; an electric fan at the bottom kept the air within the bath in rapid circulation. The temperatures of the bath and the boiling vapor were read on standard certified thermometers. The pressure readings were made by means of a precision cathetometer and are accurate to 0.05 mm. The pumps used for evacuation consisted of a Cenco rotary oil pump in series with two Krause mercury condensation pumps.

In manipulating the apparatus the container D was first filled with the liquid whose vapor was to be studied and the air completely removed by the repeated and successive use of the bulbs AA′ and E as Toepler pumps. A known weight of the oxide was then placed in the adsorption bulb G and the system evacuated at the temperature of the bath until the pressure was reduced to 0.001 mm., or less. The heating flask was then put in place and the evacuation continued at the temperature of boiling water until the pressure was reduced to 0.0001 mm. (McLeod gauge). The system was then closed with a mercury valve and allowed to stand over night with the adsorption bulb at the temperature of boiling water. If on opening the valve the pressure throughout the system was less than 0.0008 mm., the initial pressure conditions for beginning a series of adsorptions were considered satisfactory.

The transfer of vapor to the adsorption bulb and the determination of equilibrium pressures were carried out in the usual manner. All volumes were reduced to 0°, latitude 45° and sea level. The volume of vapor adsorbed was calculated by subtracting the corrected volume of the vapor in the "dead" space from the total corrected volume transferred. The time required for attaining adsorption equilibrium varies widely for different vapors. Equilibrium was finally assumed to exist when two successive pressure readings taken at intervals of one hour did not differ by more than 0.05 mm. Successive portions of the vapor were admitted until the equilibrium pressure of the vapor above the oxide became equal to the vapor pressure of the pure liquid at the temperature of the bath, as indicated by the appearance of liquid in the tube at C.

Experimental Results and Discussion

The adsorption data collected for each vapor on either oxide represent at least duplicate series of adsorption measurements. In no case was the study of a vapor discontinued, unless the data obtained in two or more series fell upon the same adsorption isotherm. Except for acetic acid vapor, the isotherms for the vapors studied are easily reproducible on the same sample of aluminum oxide. To obtain data which will fit into the same isotherm for thorium oxide, a new sample of the oxide must be taken for each series of measurements with any given vapor.

The exact position of the isotherm for acetic acid is difficult to place. In a triple series of adsorptions of acetic acid by the same sample of aluminum oxide the first series gave relatively high adsorption values. Upon repeating the measurements after the evacuation of the adsorbed acid vapor the magnitude of the adsorption for corresponding pressures became very much less; after a second evacuation the amounts adsorbed became still less. It would seem, therefore, that the adsorption capacity of hydrated aluminum oxide for the vapor of glacial acetic acid is intimately connected with the amount of water present in the partially dehydrated oxide adsorbent. Evacuation after adsorption not only removes the acetic acid vapor, but with it also some of the water initially present in the oxide. With this loss of water there is a change in the physical state of the oxide,—in its composition, its extent of surface and in its capillary properties, and with these changes there is a change in its capacity to adsorb acetic acid vapor. The fact that the same sample of the oxide may be used repeatedly with the vapors of water, ethyl alcohol and ethyl acetate would indicate that these vapors, when adsorbed, may be removed by evacuation without changing materially the nature of the adsorbent. In a similar manner we may explain the loss of adsorption power of thorium oxide for all four vapors. Here, obviously, the adsorbed or hydrate water initially present in the oxide is not held firmly as it is by aluminum oxide, and some of it is removed along with all of these vapors when evacuated. Patrick and McGavack[1] have applied a similar explanation for the decrease in the adsorption power of silica gel for sulphur dioxide. They found that when the same sample of the gel was used for a second series of adsorptions the amount of sulphur dioxide adsorbed was distinctly less than that adsorbed originally. They attribute this effect to the partial dehydration of the gel during the removal of the gas after the first series of adsorptions. They also claim that this partial dehydration results in making the pores of the gel so large that the capillary forces acting through the second series of adsorptions are enormously decreased. This in their opinion would account for the low adsorption values. On the other hand, if the gel is too highly hydrated, the smaller capillaries are partially filled and hence the available space for the gas is diminished. This should also account for low adsorption power.

If we consider first the adsorption of vapor by a unit mass of adsorbent, x/m, the data and the curves obtained show that aluminum oxide is a better adsorbent for water vapor, ethyl alcohol and ethyl acetate than is thorium oxide. Whereas on the basis of volume of vapor adsorbed by 1 c. c. of the oxide, x/v, thorium appears to be the better adsorbent for water vapor at all pressures, and for ethyl alcohol at low pressures than is aluminum oxide. The order of adsorption of alcohol vapor by the two oxides appears to be exactly reversed at pressures above 75 mm. At all pressures the acetic acid and ethyl acetate vapors are more highly adsorbed by the aluminum oxide.

The densities of aluminum and thorium oxides used are 2.85 and 6.82, respectively. It is evident, therefore, that the volumes occupied by equal weights of these oxides will be inversely proportional to their densities. Consequently the surface, and likewise the adsorbing power, of the aluminum oxide must be greater than that of an equal weight of thorium oxide. On the other hand, for equal volumes of the two oxides, prepared in the manner used in these experiments, the total surface, and hence the adsorbing power, must be greater in the case of the thorium oxide.

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[1] Patrick and McGavack: J. Am. Chem. Soc., 42, 946 (1920).

The values obtained for x/m and for x/v have been plotted on a large scale against the corresponding pressure values, p. From these isotherms we have read the values of x/m and of x/v for round values of *p*, given in Tables I-IV. It was found to be practically impossible to plot the isotherms for the four vapors on a single oxide on one sheet. Hence to save the space which would necessarily be filled by a large number of tables and curves, these Tables only will be submitted. The corresponding magnitudes for the two oxides are placed side by side for comparison; the Tables are self-explanatory.

TABLE I

The Adsorption of Water Vapor by Al_2O_3 and ThO_2 at 99.4°.

P mm.	Al_2O_3 x/m	ThO_2 x/m	Al_2O_3 x/v	ThO_2 x/v
5	2.95	3.75	9.30	25.00
10	5.48	5.80	17.65	38.95
20	7.78	8.17	30.25	56.50
30	13.75	9.80	40.75	69.25
40	15.60	11.45	50.60	80.00
50	18.75	13.10	60.35	90.25
60	24.14	14.68	70.10	100.00
80	31.20	17.53	89.45	119.20
100	36.25	20.30	108.40	137.85

TABLE II

The Adsorption of Ethyl Alcohol Vapor by Al_2O_3 and ThO_2 at 99.4°.

P mm.	Al_2O_3 x/m	ThO_2 x/m	Al_2O_3 x/v	ThO_2 x/v
10	— — —	5.10	— — —	33.75
20	6.38	6.25	15.25	41.25
30	9.35	6.70	26.20	45.60
50	14.62	7.30	42.20	50.40
70	18.20	7.60	51.75	52.70
90	20.40	7.88	58.25	54.00
110	21.95	8.05	63.00	55.25
130	23.15	8.25	66.50	56.25
150	24.10	8.42	69.40	57.20
170	25.00	8.65	71.75	58.25
190	25.70	8.80	73.50	59.30
210	26.40	8.95	75.00	60.40

TABLE III

The Adsorption of Ethyl Acetate Vapor by Al_2O_3 and ThO_2 at 99.4°.

P mm.	Al_2O_3 x/m	ThO_2 x/m	Al_2O_3 x/v	ThO_2 x/v
10	5.60	2.98	16.25	22.75
20	8.00	3.50	23.60	26.40
30	9.60	3.64	28.55	27.00
50	11.50	3.90	35.10	28.60
70	13.25	4.12	39.00	29.60
90	13.98	4.30	41.40	30.25
110	14.70	4.50	43.25	30.75
130	15.26	4.60	44.75	31.25
150	15.72	4.70	45.85	31.80
170	16.10	4.80	46.60	32.50
190	16.45	4.83	47.30	33.00
210	16.76	4.90	48.00	33.40
230	17.10	4.97	48.75	33.85

TABLE IV

The Adsorption of Acetic Acid Vapor by Al_2O_3 and ThO_2 at 99.4°.

P mm.	Al_2O_3 x/m	ThO_2 x/m	Al_2O_3 x/v	ThO_2 x/v
5	4.58	2.27	8.75	15.60
10	6.12	2.89	17.30	20.45
20	11.34	3.68	31.75	24.80
30	14.84	3.95	40.60	27.00
40	17.22	4.20	47.45	28.50
50	19.32	4.36	53.70	29.55

In considering the equilibrium pressures given in these Tables we must remember the existence of the ever present water vapor from the hydrated oxides. The amount of water in the vapor phase may increase by displacement as the volume of the other vapors adsorbed increases. Furthermore, in such a study we cannot hope to attain the same high degree of precision as that which may be attained in the study of the adsorption of gases by crystalline solids. Nevertheless, these Tables show certain definite characteristic differences in the adsorption capacities of aluminum and thorium oxides. While for each oxide the volume of each vapor adsorbed increases with the pressure, the rate of increase is in all cases much greater when aluminum oxide is the adsorbent. This difference in rate is more noticeable in the case of the vapors of ethyl alcohol, acetic acid and ethyl acetate. For the permissible pressure range the volume of water vapor adsorbed by 1 gram of alumina increases by about 12-fold; the corresponding increase in the volume adsorbed by 1 gram of thoria lies between 5 and 6-fold. For the other vapors the volume adsorbed increases by 3 to 4-fold on alumina and only by 1 to 1.5 fold on thoria.

This relatively greater increase in the adsorption capacity of alumina with increase in pressure must be due in part to the greater porosity of the alumina, and consequently to the existence of greater capillary influences.

In his arrangement of the metallic oxides in the order of decreasing power for dehydrating ethyl alcohol, Sabatier found that thorium oxide has a greater capacity in this respect than has aluminum oxide. Exactly the same relation holds for the adsorption of water vapor, and also for ethyl alcohol at low pressures, if we calculate adsorption magnitudes on the basis of equal volumes of the oxide adsorbents.

Freundlich has expressed the relation between the volume of vapor adsorbed by 1 gram of adsorbent and the equilibrium pressure by the empirical equation: $x/m = \alpha p^{1/n}$. This equation may be transformed to read,

$$\log x/m = \log \alpha + 1/n \log p.$$

If the Freundlich equation applies to the adsorption of these vapors by the oxides of aluminum and thorium, then the plot of the logarithms of the equilibrium pressures against the logarithms of the corresponding values of x/m should be a straight line. These plots have been made for each of the four vapors on each oxide. Only in the case of water vapor for both oxides does the logarithmic curve approximate a straight line; only for this vapor does the Freundlich equation apply. The curves for each of the other vapors on both oxides are concave toward the pressure axis. At no pressures do they even approximate straight lines. However, experience teaches us that no one equation now known will express accurately the adsorption relations for all gases. It is perhaps sufficient to state that, in so far as the vapors which we have studied are concerned, we are here dealing with adsorption phenomena.

The magnitude of the adsorption of the vapors has been found to vary with the nature of the vapor; it is greatest for water vapor and least for ethyl acetate, with ethyl alcohol occupying an intermediate position. This is the inverse order of the molecular volumes of the liquids. The adsorption of acetic acid vapor by both oxides seems to vary more specifically with the magnitude of hydration of the oxides.

Both thoria and alumina are good adsorbents for water vapor and ethyl alcohol; these are the two oxides which have the greatest dehydrating power toward ethyl alcohol. In the consideration of esterification equilibria, as represented by the reaction equation: $C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O$, it has been customary with some to invoke the law of mass action and to assume that anything which tends to increase the active concentration of either or both reactants, or to remove from the sphere of chemical action one of the products will cause such reactions to proceed farther from left to right. On the basis of the mass law we might assume that the catalytic effect of these oxides is due to their capacity to remove, by adsorption, active water from the reaction products. We might also assume that by the adsorption of alcohol vapor, and possibly also acetic acid vapor, the active concentrations of one or both of these vapors is effectively increased. In either case the result should be an increase in the rate of ester formation.

The effect of thoria and alumina at 300° to 400° upon alcohols, acids and esters has been found to be primarily one of dehydration. As a rule, one product is water and in most cases ethylene is present. The decomposition of alcohol to ethylene and water may be considered as taking place in one or in two steps: (1) $C_2H_5OH \longrightarrow C_2H_4+H_2O$, or (2) $2C_2H_5OH \longrightarrow (C_2H_5)_2O+H_2O$, followed by a dehydration of the ether: $(C_2H_5)_2O \longrightarrow 2C_2H_4+H_2O$. From the results of their work Pease and Yung[1] conclude that it is unnecessary to assume direct decomposition of the alcohol to ethylene and water, since all of their results were found to be explicable on the assumption that the alcohol gives first, ether, which then decomposes to give ethylene.

The exact mechanism of the reaction is still an open question. Is the unsaturated hydrocarbon when first formed in the decomposition of an alcohol or ether molecule ethylene ($H_2C=CH_2$), or is it the ethylidene group $(CH_3-\overset{\diagup}{\underset{\diagdown}{C}}H)$? Nef[2] was inclined to assume that in the dehydration of alcohol and ether the ethylidene group is first formed and that this then rearranges to form ethylene. In view of the greater reactivity of the ethylidene group over that of the ethylene molecule and in view of the fact that the rate of ester formation in the vapor phase is so greatly increased by the presence of dehydrating catalysts, we are inclined to the opinion that the ethylidene group is first formed and that it then reacts with the acetic acid molecule to form the ester. This idea is in harmony with one of the two possible alternative mechanisms of the formation of ether from alcohol suggested by Senderens.[3] Furthermore, in the adsorption of the alcohol molecule it is the hydroxyl group which is most strongly attracted by the adsorbing surface. We may picture the hydrocarbon radicle as standing out away from the surface. In the cleavage of the alcohol molecule to give water it seems most plausible, therefore, to consider that the hydrogen atom which first combines with the hydroxyl group should be one which is in closest proximity to the hydroxyl group, rather than one attached to an adjacent carbon atom.

Unquestionably, we must assume for oxide catalysts, prepared by partial dehydration, a porosity not so extensive perhaps as, but similar to that in charcoal. These pores or cavities are of all possible sizes and shapes. The smaller water molecules, and the larger alcohol molecules to somewhat lesser extent, will be adsorbed upon the surface of the larger cavities. With decrease in the size of the cavities the adsorption of the alcohol molecules will be relatively more strongly opposed by 'steric hindrance', the effect of which will become more strongly pronounced as the capillaries become smaller and the molecules of the vapor become larger. It is possible that the stress produced by the strong specific attraction of the water constituents of the alcohol molecule opposed by forces resulting from 'steric hindrance' may account, at least in part, for the cleavage of the alcohol molecule. Obviously, as the

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[1] Pease and Yung: J. Am. Chem. Soc., 46, 390 (1924).

[2] Nef: Ann., 218, 198 (1901).

[3] Senderens: Ann. Chim. Phys., (8) 25, 505 (1912).

vapors over the catalyst become saturated the capillaries will become filled with the liquids, if their molecules are small enough to enter the capillaries. This must be classed as a capillary phenomenon and not as adsorption. At the high temperatures at which these oxides are used as catalysts the condensation of liquid in the capillaries will be relatively small.

In view of these considerations the most plausible representation of the mechanism of esterification in the presence of oxide catalysts seems to be the following. In the passage of the vapors of ethyl alcohol and acetic acid over alumina or thoria the alcohol molecule is strongly adsorbed, primarily through the residual valences of the hydroxyl group. Under the prevailing conditions of stress the less highly attracted ethylidene group splits off from the alcohol molecule and then combines with the acid molecule to form the ester. The adsorbed water vapor then evaporates under the existing conditions and is carried away by the effluent vapors. If the vapor pressure of the water in contact with the catalyst should become so great that the rate of condensation exceeds that of evaporation, we can conceive of the catalyst surface becoming so completely covered with water molecules that no alcohol molecules are adsorbed. In such cases no dehydration of the alcohol will occur. To facilitate the regulation of temperature in large scale processes water vapor is sometimes admitted along with the alcohol. In this case the undoubted decrease in the rate of decomposition of the alcohol must be counterbalanced entirely or in part by working at higher temperatures.

A second possible mechanism of the process should also be mentioned. Let us assume that in the passage of the alcohol and acetic acid vapors over the heated oxide, the molecules of both are adsorbed on adjacent elementary spaces. Under the conditions of stress prevailing at the given temperature and pressure the hydroxyl group of the alcohol and the hydrogen atom from the carboxyl group of the acid are split off from their respective molecules and are momentarily held as adsorbed water. The liberated C_2H_5- and CH_3-COO-radicles then combine to form the ester molecule which passes on with the vaporized water. While this explanation may account for the formation of the ester, it does not allow for the possible formation of ethylene.

Summary

1. The adsorption of the vapors of water, ethyl alcohol, acetic acid and ethyl acetate by the oxides of thorium and aluminum has been studied at 99.4°.

2. The adsorption isotherms have been plotted and the curves obtained are similar to those typical of true adsorption. Only in the case of water vapor does the Freundlich relation, $x/m = \alpha p^{1/n}$ apply.

3. The adsorption capacity of aluminum oxide for water, ethyl alcohol, and ethyl acetate vapors remains unaltered by successive adsorptions and evacuations. With acetic acid the adsorptive power of this oxide decreases with continued use. The adsorption capacity of thorium oxide for all four

vapors decreases with successive adsorptions and evacuations. There seems to be an intimate relation between the hydration of this oxide and its adsorbing power.

4. For a unit mass of adsorbent the adsorption capacity of aluminum oxide is greater than that of thorium oxide. For unit volume of oxide the adsorption of thorium oxide is greater than that of alumina. This is the order of their dehydrating power toward ethyl alcohol.

5. Two possible theories based on adsorption have been suggested to explain the catalytic influence of these oxides in ester formation.

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THE SURFACE CONCENTRATION OF GELATINE AT A LIQUID-GAS INTERFACE AS INDICATED BY THE CHANGE IN SURFACE TENSION

BY J. M. JOHLIN

There are so many factors to be considered in measuring the surface tension of gelatine solutions that, although much careful work has been carried out, there is little accurate information to be found on this subject. Quincke[1] and Zlobicki[2] made some of the earliest measurements of the surface tension of gelatine solutions, at a time, however, when the purification of gelatine and its hydrogen-ion concentration received little consideration. More recently Holmes and Childs[3] measured the interfacial tension between emulsions of finely divided gelatine gel and oil, and concluded that "no concentration by adsorption" takes place at the interface. They employed the drop number method. Sheppard and Sweet[4], by a similar method, measured the interfacial tension between toluene and solutions of gelatine. They used very pure gelatine, and noted especially the effect of varying the hydrogen-ion concentration of their solutions but record no change of surface tension as the time of drop-formation varied. Reynolds[5] had noted a change of surface concentration with time at the interface between benzene and solutions of gelatine. He noted a considerable change fifteen minutes after a fresh interface had been formed, after which there was a slow change for a long time. Nugent[6] had also noted that emulsions of benzene and gelatine solutions were more slowly broken up by caustic soda as they grew older. He ascribed this changing inhibition to the gradual adsorption of gelatine at the interface bounding the benzene particles. Although this afforded an apparently accurate means of measuring the rate of change of inhibition under the conditions of his experiments, it does not give any indication of the corresponding surface tension. Strangely there appears to be no inhibition when emulsions are formed with gelatine solutions of 0.1 percent concentration or less. The grade of gelatine used and its hydrogen-ion concentration are not noted. Since the present investigation was begun Davis, Salisbury and Harvey[7] have published data to show the change in drop weight of gelatine solutions with the variation of temperature, concentration, hydrogen-ion concentration, and age of solutions. They employed the drop weight method as described by Morgan, a method which involves the formation of 15 to 20 drops in fifteen minutes. The interpretation of results is left to their critics. A proper interpretation is, however, made difficult by the fact that they did not take into account the exact

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[1] Ann. Physik, 10, 507 (1903).

[2] Bull. Acad. Sci. Cracovie, 1906, 488.

[3] J. Am. Chem. Soc. 42, 2049 (1920).

[4] J. Am. Chem. Soc. 44, 2787 (1922).

[5] J. Chem. Soc. 119, 473 (1921).

[6] Trans. Faraday Soc. 17, 703 (1921).

[7] Ind. Eng. Chem. 16, 161 (1924).

time required for the formation of each drop. In a recent paper Lasnitzky and Loeb[1] employed the drop number method to determine the relative surface tension of water, gelatine solutions and solutions of organic acids to which purified gelatine had been added. Their results indicate that gelatine solutions having a concentration of 1.0, 0.5, and 0.3 percent have the same surface tension, and that there is but a very slightly difference between these and concentrations of 0.2, 0.1, and 0.05 percent solutions. Criticism and data regarding the recent use of the drop number method for measurements such as these will be reserved for another report.

In the present investigation the surface tension of ash-free iso-electric gelatine was determined at 40 degrees Centigrade, at the interface between air and solutions of varying concentration, and the change in surface tension, noted as the age of the interface increased. Both the drop weight and the capillary rise methods were employed.

Experiments with the Drop Weight Method

The difficulty of making a satisfactory tip for use in the drop weight method is so strongly emphasized by both Morgan and Harkins[2] that the rather simple modification which the writer devised to remedy the chief difficulty is given in some detail. The writer observed that scaling of the edge of the tip during the perpendicular grinding is due to the scratches on its horizontal surface received when the tip was ground round. No amount of horizontal polishing with an abrasive seemed to be sufficient to prevent this scaling entirely. If, however, a well polished tip of resistance glass is further carefully polished in a small gas flame, scaling of the edge during the perpendicular grinding is entirely eliminated. After many failures due to lack of polishing by heat the tip used in this investigation was prepared in about three hours. The method has been used with equal success by others since.

A short, nearly round, piece of resistance-glass capillary tubing was accurately centered in a brass tube by means of Wood's metal; one of the protruding ends was then ground round in a precision lathe by means of fine emery powder against a brass shoulder containing a semi-circular depression about the size of the glass tube; it was then polished with 0 to 0000 emery paper until to the naked eye it appeared quite smooth after which it was carefully polished in a small gas flame; a short piece of tightly-fitting brass tubing was then placed over the end of the tube in which the tip was centered and the space between the tip and the outer tube filled in with more metal so as to prevent chipping during the perpendicular grinding. After grinding, this tip had no flaws that could be seen under a magnification of forty diameters. The maximum deviation from its diameter of 0.59345 cm., as measured by a travelling microscope, was 0.00015 cm. The surface tension of water at 20 degrees as measured with this tip was found to be 72.65 dynes per cm. when calculated according to the method recently outlined by Iredale[3].

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[1] Biochem. Z. 146, 96 (1924).
[2] J. Am. Chem. Soc. 41, 499 (1919).
[3] Phil. Mag. (6) 45, 1088 (1923).

The tip was mounted on an apparatus similar to that used by various other investigators. In Fig. 1, A is an air-tight compartment in which the air pressure can be varied through a tube *a* which leads through a three-way stop-cock to an aspirator automatically kept at 30 cm. of water pressure, or to the atmosphere of the room. By means of a screw *b* the vessel C containing the solution to be measured can be raised or lowered to any desired level. The lower part is fitted on by a ground joint. The compartment B is also air-tight except for a small hole at *d* which allows this compartment to remain at atmospheric pressure. The lower part, which holds the weighing bottle accurately centered beneath the tip, is also attached by a ground joint.

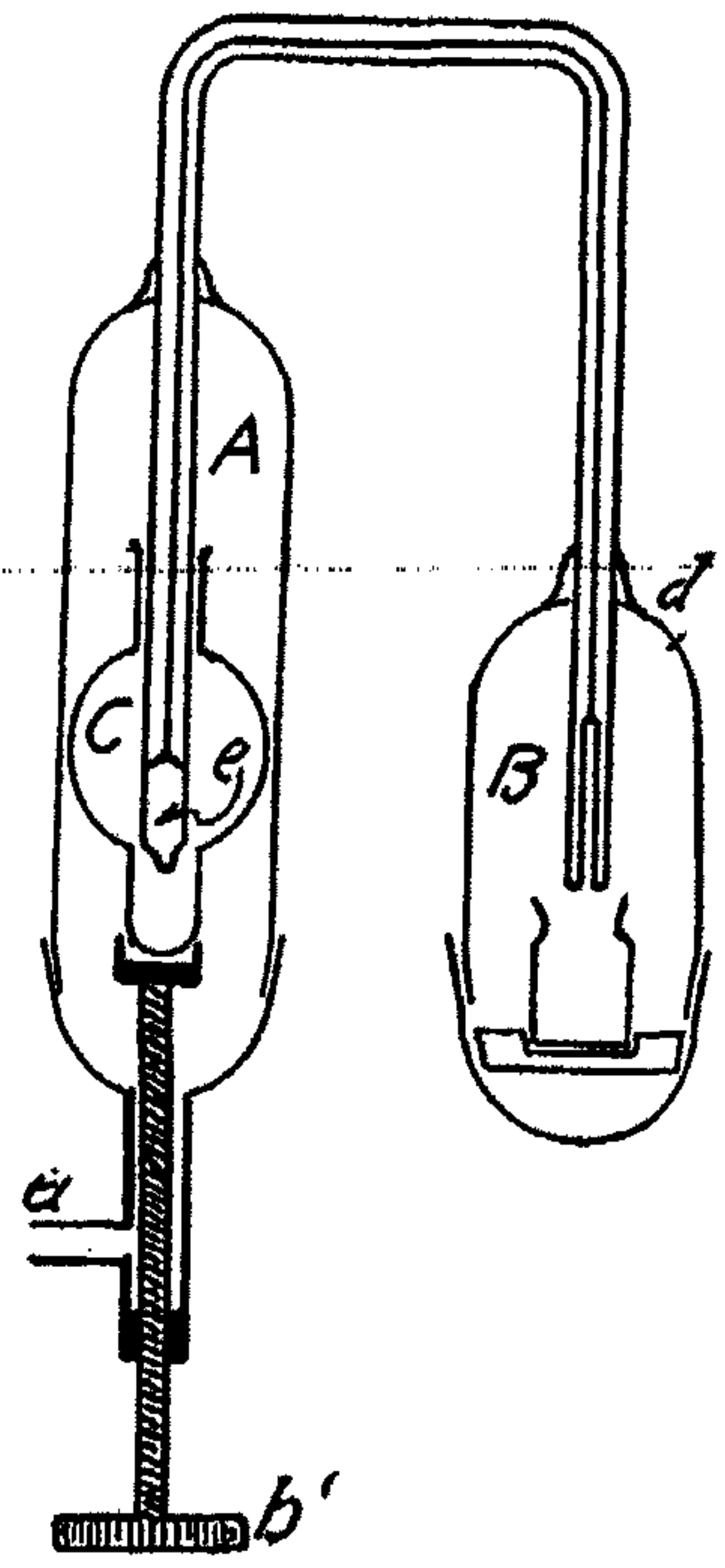

Fig. 1
Illustrating the Drop Weight Apparatus

During any determination the vessel C was never raised above a level which would permit a drop to form under force of gravity and detach in less than four minutes. For the formation of a drop, pressure was applied from the aspirator until the drop had reached 75 percent of its full size, when the pressure was instantaneously released and the drop allowed to complete itself under force of gravity in one to four minutes as desired. This latter period could be varied by raising or lowering the vessel C. Although drops could be quite rapidly formed by means of this contrivance, the maximum kinetic effect at the moment of detachment was never greater than that of a four-minute drop and nearly always much less than this. The time of forcing a drop and the time subsequently allowed for its completion were accurately measured by a stop-watch. When very slow drops were desired, the lower stem of the vessel C was filled with very pure, triply distilled, mercury and the vessel raised until the opening of the small pipette *e* was sealed. By additional raising of C a drop could be rapidly formed and then left suspended at nearly its full value for a long time. Care had to be exercised not to force the drop too far, for too large a drop would detach prematurely due to the fact alone that increasing surface concentration lowered the surface tension sufficiently for detachment.

When rapidly formed drops were collected, ten were usually weighed. In the case of slowly formed drops, a smaller number was weighed at a single determination. They were collected in wide-mouth, glass-stoppered, bottles of one ccm. capacity. To prevent evaporation from the solution in the vessel C, the narrow neck of this was wound with strips of wet filter paper so as to keep the atmosphere of compartment A well saturated with moisture from this source. To prevent evaporation from the drops forming in compartment B, the weighing bottle was surrounded by a cylinder of wet filter paper. The apparatus was mounted in an air thermostat which was regulated at forty degrees to ±0.1°. Two large beakers of water within the thermostat kept the atmosphere of this well saturated with moisture. The perpendicular position of the tip was determined by a plumb-line. Previous to use, the weighing bottles were heated to 105° in a drying oven and allowed to cool within the thermostat, in order that their introduction into the thermostat would not cause moisture to condense on them. Considering their small capacity, this procedure was considered sufficiently careful to eliminate the necessity for any weighing correction. To avoid sudden changes in temperature and humidity, minor operations, such as the introduction of weighing bottles, were made through an arm-hole in the side of the thermostat.

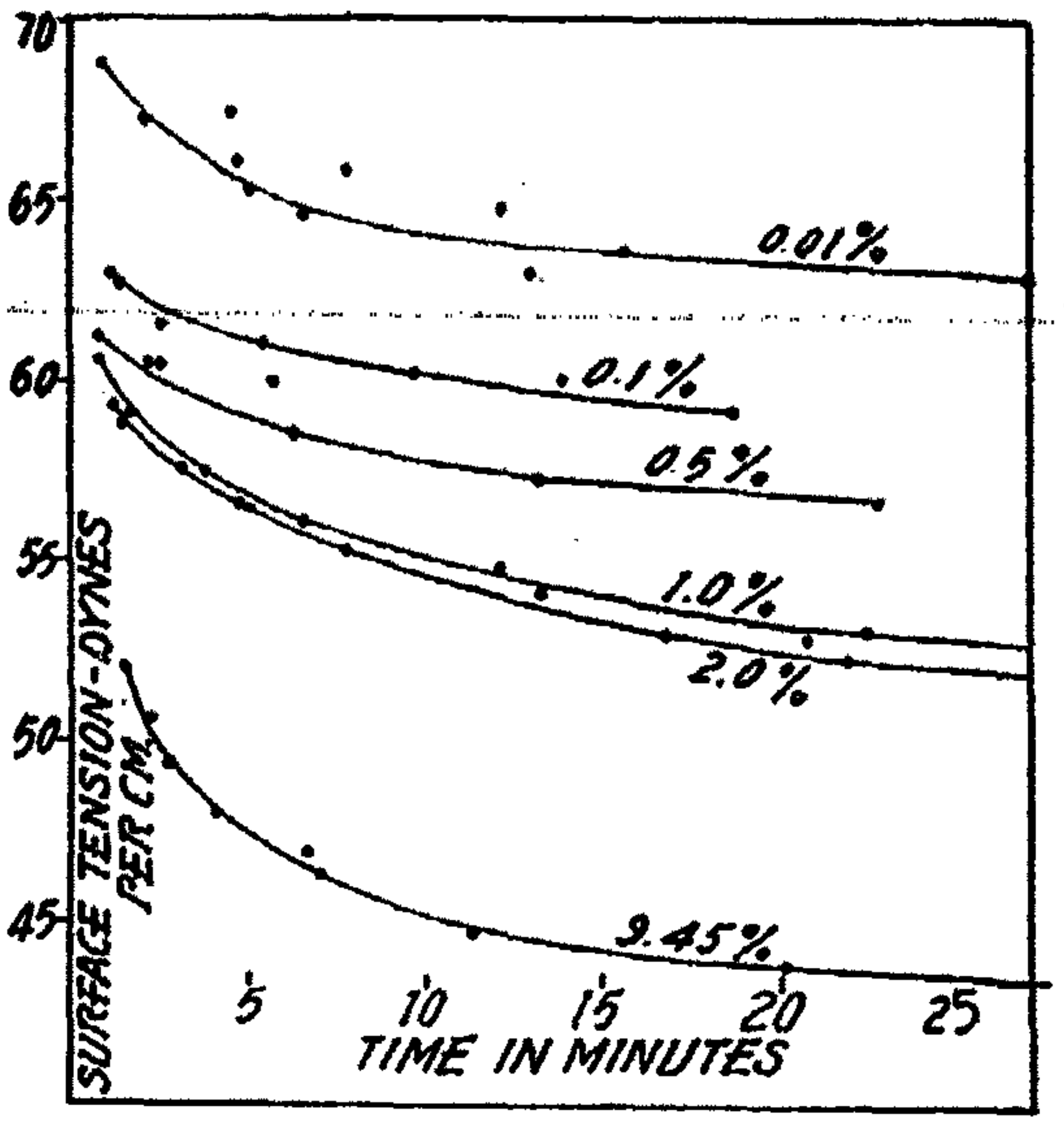

Fig. 2
Illustrating Change of Surface Tension with Time by the Drop Weight Method.

In the case of drops formed in less than three minutes, the time of drop formation could be regulated so as to vary but a few seconds. In the case of longer periods of formation the fluctuations were greater. Unless the fluctuations are very great, however, the error of taking the average of the period of formation of several drops should not be great. As will be noted later, dilute solutions caused the greatest fluctuations in weight for the same period of drop formation.

The gelatine used in these experiments was rendered ash-free electrolytically by means of an apparatus not unlike that described by Knaggs, Manning and Schryver.[1] It was, however, made of quartz and platium entirely. Dilute gelatine solutions at least, were found to become slightly more alkaline after being in contact with even resistance glass for a time. In the process of de-ashing, the gelatine (Nelson's powdered gelatine) was not previously dialysed but a ten percent gel was electrolysed directly. At the beginning it was necessary to cool the apparatus with ice and to change the water around the platium electrodes frequently. When the gel was found to crack or disintegrate it was remelted and allowed to set again before proceeding further. The maximum current density, controlled by an outside resistance, was ten milliamps per sq. cm., at 220 volts. The acid was found to concentrate in the water at the anode but the bases were found to remain chiefly in the gel nearest the cathode where they formed an intensely turbid, opalescent zone. After a considerable time this layer peeled away from the remainder of the gel. Though the crude gelatine contained but one and a half percent ash this layer contained as much as eighteen percent. It was never found possible even after weeks of electrolysing to remove all the iron, traces of which were always found. The ash-free gelatine was precipitaded by pure acetone as recommended by Sheppard and Sweet.[2] The hydrogen-ion concentration was determined by the Michaelis indicators. The pH of the pure gelatine was found to be 4.8 in one percent solutions. It was found repeatedly that when known amounts of acid are added to a one percent solution of gelatine purified either electrolytically or by dialysis the hydrogen-ion concentration does not increase nearly as rapidly when measured by Michaelis indicators as is indicated by Loeb's measurements[3]. The difficulty of obtaining consistent results by means of a hyrogen electrode when measuring the pH of gelatine solutions is well known.

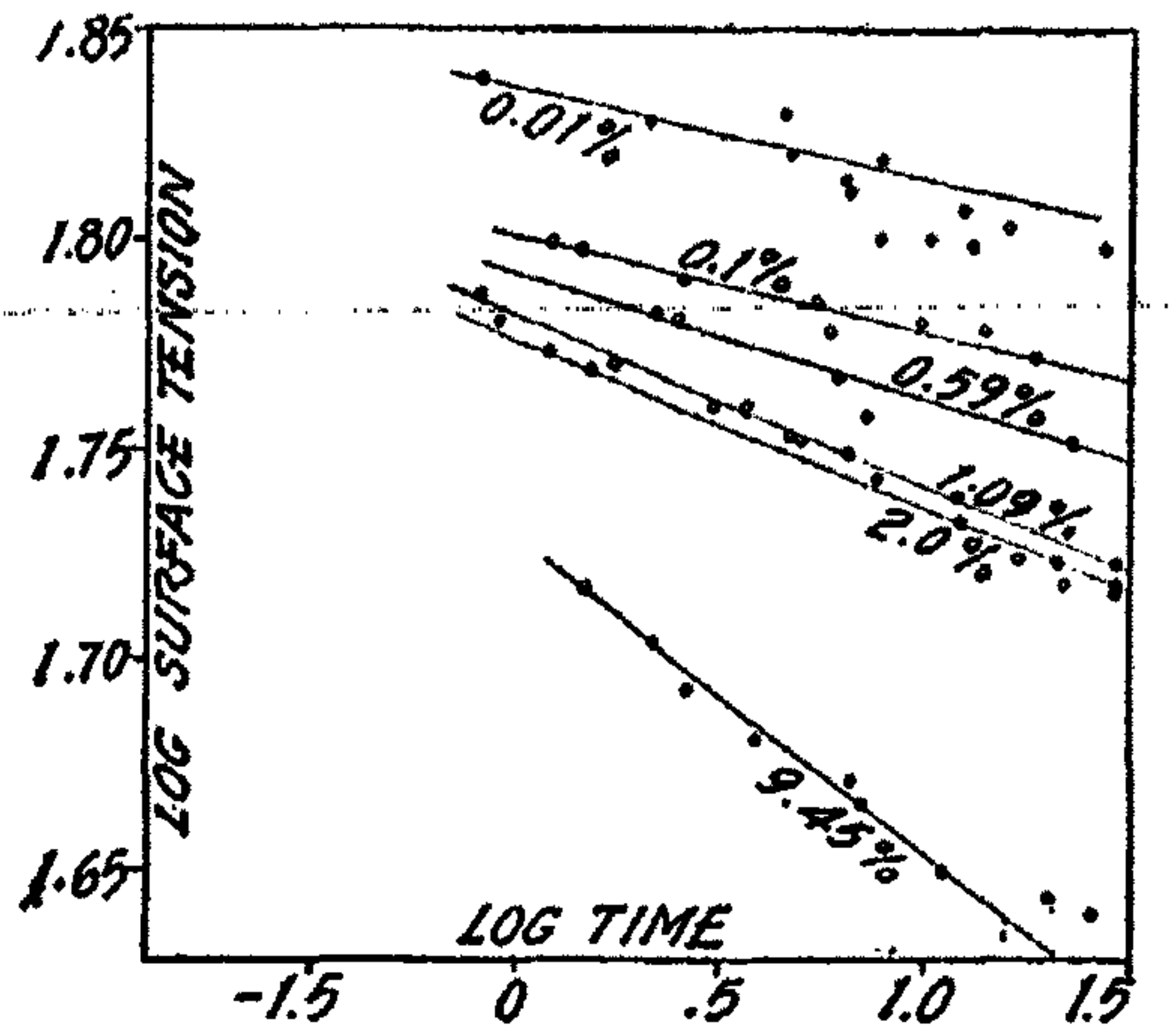

Fig. 3
Logarithms of Surface Tension and Time illustrated in Fig. 2.

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[1] Biochem. J. 17, 483 (1923).

[2] J. Am. Chem. Soc. 41, 499 (1919).

[3] Loeb: "Proteins and the Theory of Colloidal Behavior."

Dilute solutions were freshly prepared from a stock solution. The solutions were heated to 55° for about one hour before they were transferred to the apparatus where they were left another hour before measurements were made. After this slight preheating the temperature of the solutions was not permitted to drop below that at which measurements were made. Although the concentrated stock solution was preserved by keeping a tube of toluene within the flask containing the gel, it was shown experimentally that after subsequent preheating and dilution there was not sufficient toluene present to have any noticeable effect upon the results. Solutions of 0.01, 0.1, 0.5, 1.0, 2.0, and 9.45 percent concentration were measured. The change of surface tension with the change of time of drop formation, and the rate at which the surface tension changed with time, are shown by the following table and by Figs. 2 and 3. The time is given in minutes and the surface tension in dynes per cm. The data are given in Table I.

TABLE I

0.01%		0.1%		0.5%	
Time	Dynes	Time	Dynes	Time	Dynes
0.9	68.84	1.2	62.94	0.8	61.14
2.1	67.28	1.4	62.66	0.8	61.22
4.5	67.54	2.6	61.62	2.2	60.50
4.7	66.97	5.4	60.97	2.5	60.47
5.0	65.27	9.8	60.19	5.7	59.95
6.5	64.73	13.9	60.00	6.2	58.54
7.8	65.90	18.7	59.13	12.2	57.25
7.8	63.19			22.8	56.51
10.2	62.88				
12.2	64.08				
13.0	62.96				
15.7	63.59				
27.0	62.91				

1.0%		2.0%		9.45%	
Time	Dynes	Time	Dynes	Time	Dynes
0.9	60.59	1.2	59.24	1.5	52.04
1.7	59.09	1.5	58.81	2.2	50.60
3.7	57.50	3.1	57.59	2.2	50.60
4.7	56.62	5.0	56.43	2.6	49.36
6.5	56.13	7.8	55.34	2.8	49.30
12.1	54.78	12.3	54.09	2.8	49.41
20.8	52.90	16.9	53.01	4.0	48.00
29.1	52.24	22.0	52.29	6.6	46.88
29.1	52.84	22.5	53.07	7.0	46.33
		28.7	52.02	11.3	44.68
				20.1	43.90
				25.8	43.58

The irregularity of results obtained with very dilute solutions can not be explained with certainty. It is barely possible that it may be due to evaporation from the surface of the hanging drops. In plotting the log curves, preference in deciding the slope of these curves was given to the earlier points where the time of formation was shorter and results were more readily reproducible. At least some of the curves of Fig. 3 show that the change in surface tension, as indicated by the curves of Fig. 2, took place for a period according to the formula $\sigma = \frac{a}{t^n}$, where σ is the surface tension, t the time of drop formation, and a and n are constants. Values for a would naturally be represented by the surface tension of a one minute drop.

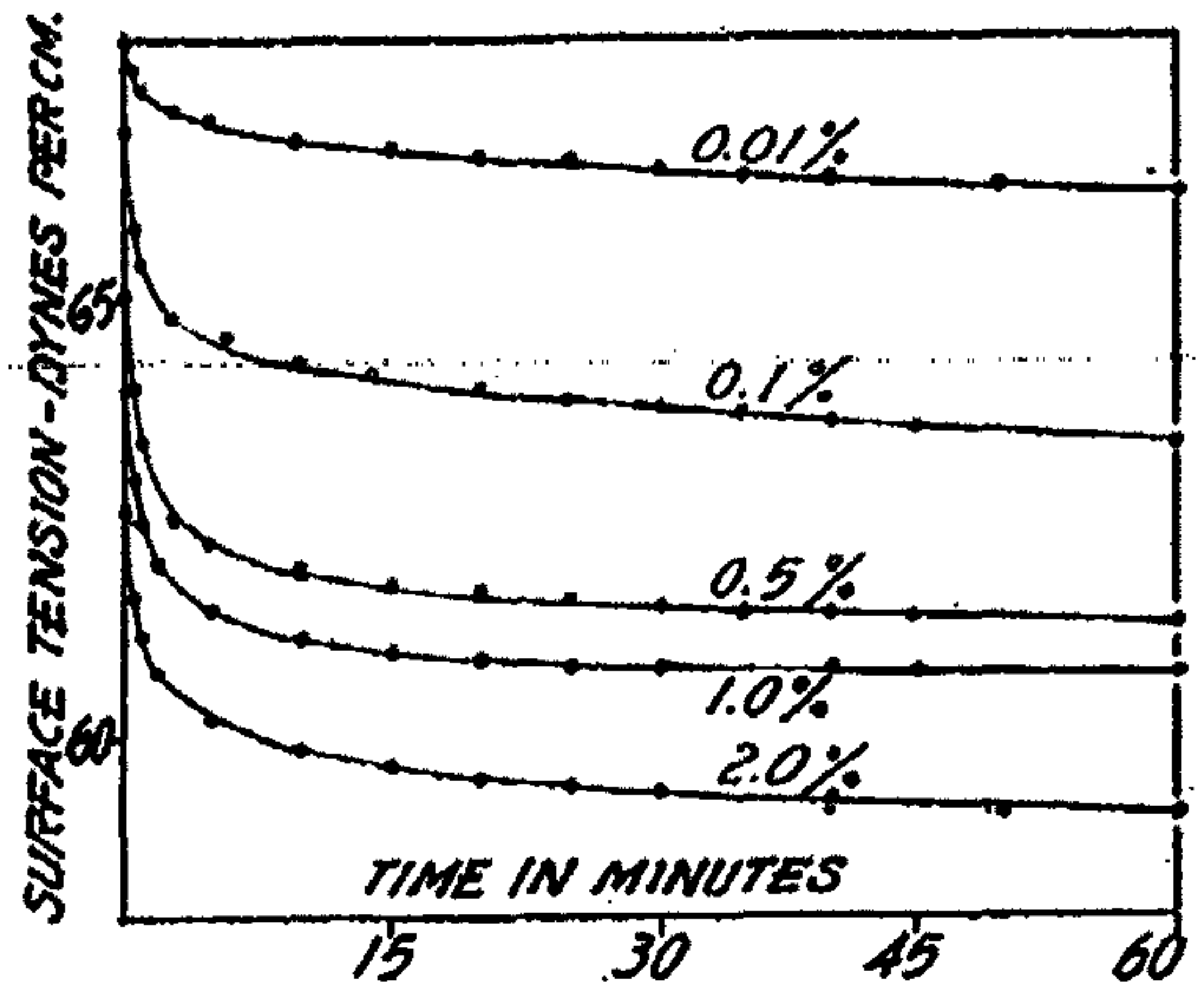

FIG. 4
Illustrating Change of Surface Tension with Time by the Capillary Rise Method.

These experiments would indicate that the determination of the surface tension of iso-electric gelatine is not a simple matter, and that it is practically impossible to secure, by this method, any absolute values for the surface tension of solutions whose surface tension can only be expressed in relation to the age of the interface. Although the change in surface tension with time seemingly takes place in accordance with the equation given above, this approximate relation does not appear to hold under all conditions. This will be shown more clearly in the second part of this report where experiments with another method are described. There is, therefore, no means of calculating what might be the ultimate value of the interfacial tension after the interface had been left undisturbed for a very long time. In any experimental procedure it must be kept in mind that even ash-free iso-electric gelatine will finally be acted upon by bacteria although this decomposition takes place far less readily than in the case of ordinary gelatine.

Experiments with the Capillary Rise Method

The apparatus used in these measurements was similar to that described by Richards and Coombs[1]. The capillary tube was standardized according

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[1] J. Am. Chem. Soc. 37, 1656 (1915).

to the method described by Harkins and Brown[1]. A mercury column measured in different parts of the tube by means of a travelling microscope was found to have the following lengths: 1.7682 cm., 1.7672 cm., 1.7676 cm., 1.7659 cm. The average radius, determined by measuring columns of mercury of different lengths, was 0.02164 cm. The surface tension of water was found to be 70.00 at 40°. The thermostat of the previous experiments, at 40°, was used. Readings were made with a Cambridge and Paul cathetometer, which was graduated to 0.01 mm.

The same precautions of preheating the solutions as in the previous experiments were observed and care was taken that the temperature of the solutions should not drop below that of the thermostat. Before any readings were made, the solution to be measured was forced up and down the capillary tube for several minutes so as to insure thorough wettings of the tube. Just before the first reading was taken the liquid was forced up the tube to a certain point and then instantaneously released. Ten seconds later the first reading was taken. This procedure was continued until successive readings were constant. It was naturally of importance to note the change in surface tension as soon as possible after the formation of a fresh surface. That the large changes which at first are noted are to be attributed to an actual change in surface tension and not to any lag can be deduced from the fact that water changes its level very little after the first few moments and some of the solutions measured differed little in viscosity from water. The results of measuring the surface tension of solutions of iso-electric gelatine of various concentrations and of one percent solutions of varying hydrogen-ion concentration are given in Tables II and III and in Figs. 4-12. According to Fig. 5 it would appear that the change of surface tension with time takes place according to the equation given, $\sigma = \frac{a}{t^n}$. This relation appears to hold quite well for dilute solutions over a considerable period of time. Readings taken at ten seconds, however, do not conform to this equation and earlier values should still less

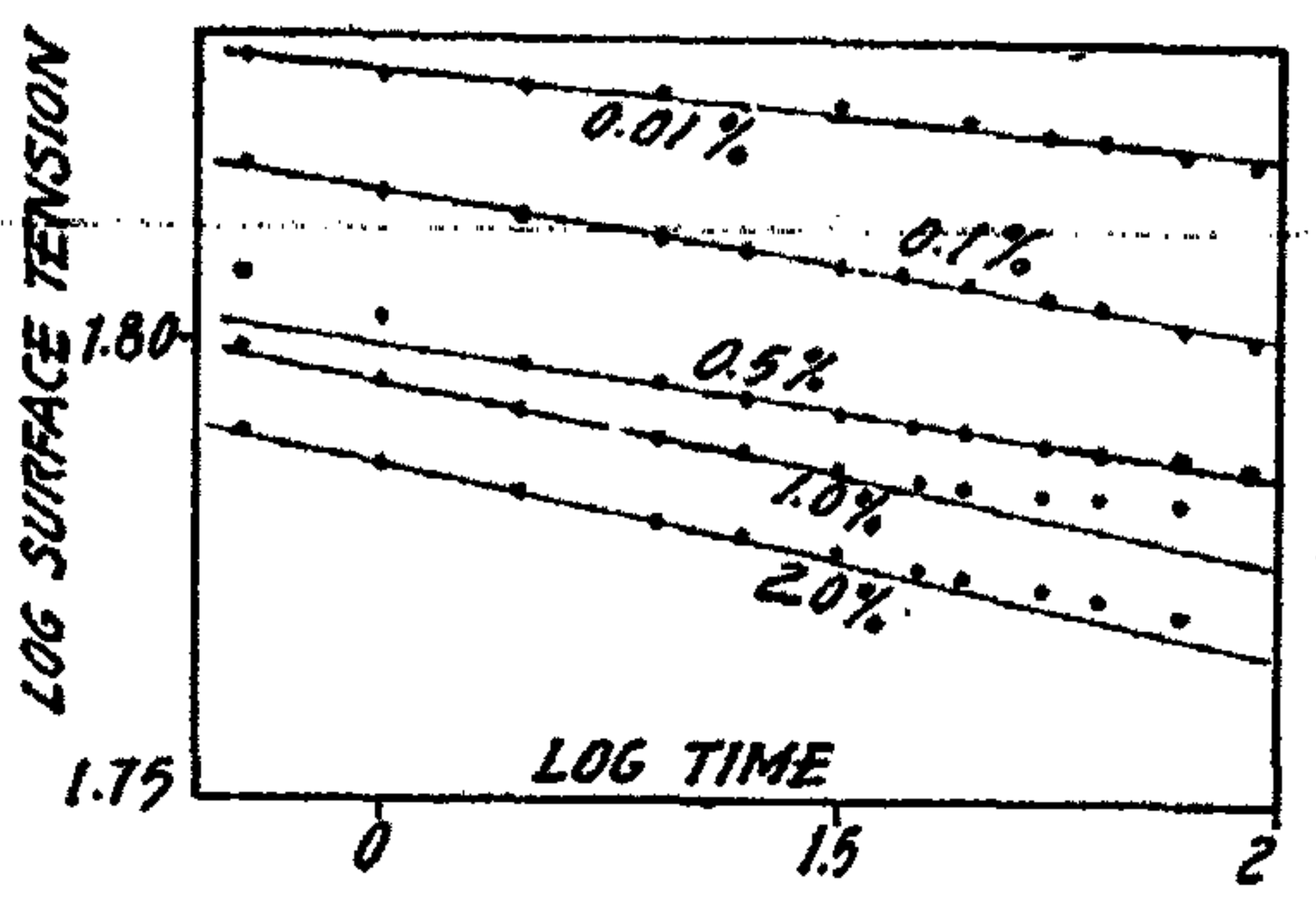

Fig. 5

Logarithms of Surface Tension and Time illustrated by Fig. 4.

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[1] J. Am. Chem. Soc. 41, 499 (1919).

be found to have changed with time according to this relation. If this were not true, values for σ as t approaches zero would be quite impossible ones. In the case of more concentrated solutions changes in values of σ conform to the equation for a brief period after the formation of a fresh surface and soon deviate quite largely. The gradual but regular deviation which takes place even in the case of a 0.01 percent solution is shown by Figs. 6 and 7. The time of the measurements represented by these curves extended over a period of 71 hours. The inflection shown in the curve of Fig. 6 will be referred to again later. That the changes noted were not due to any chemical change in the gelatine solution was shown by repeating the early measurements three times, using the same solution that had stood 71 hours. The results obtained were identical with the original.

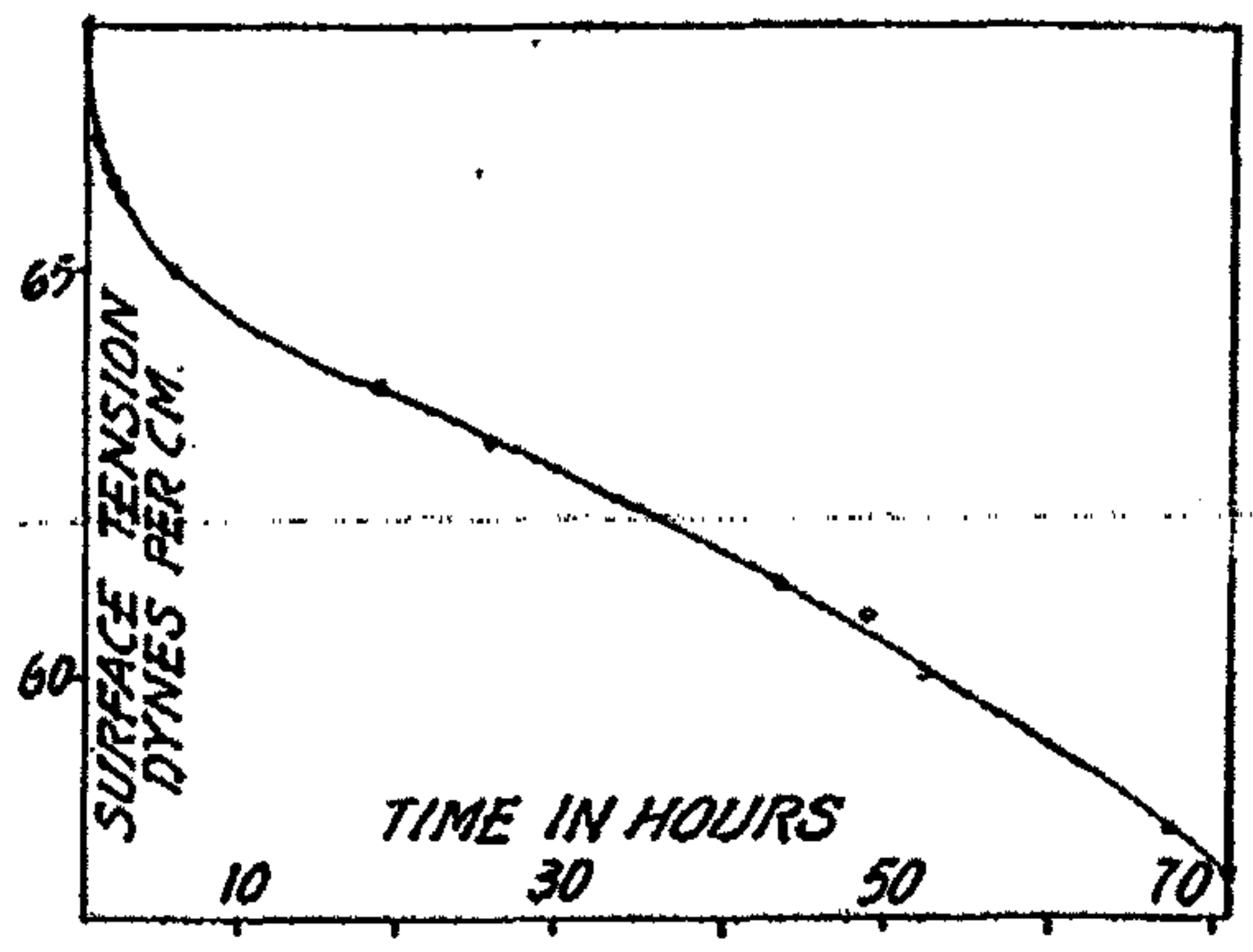

Fig. 6

Illustrating Change of Surface Tension with Time of .01 per cent solution by the Capillary Rise Method.

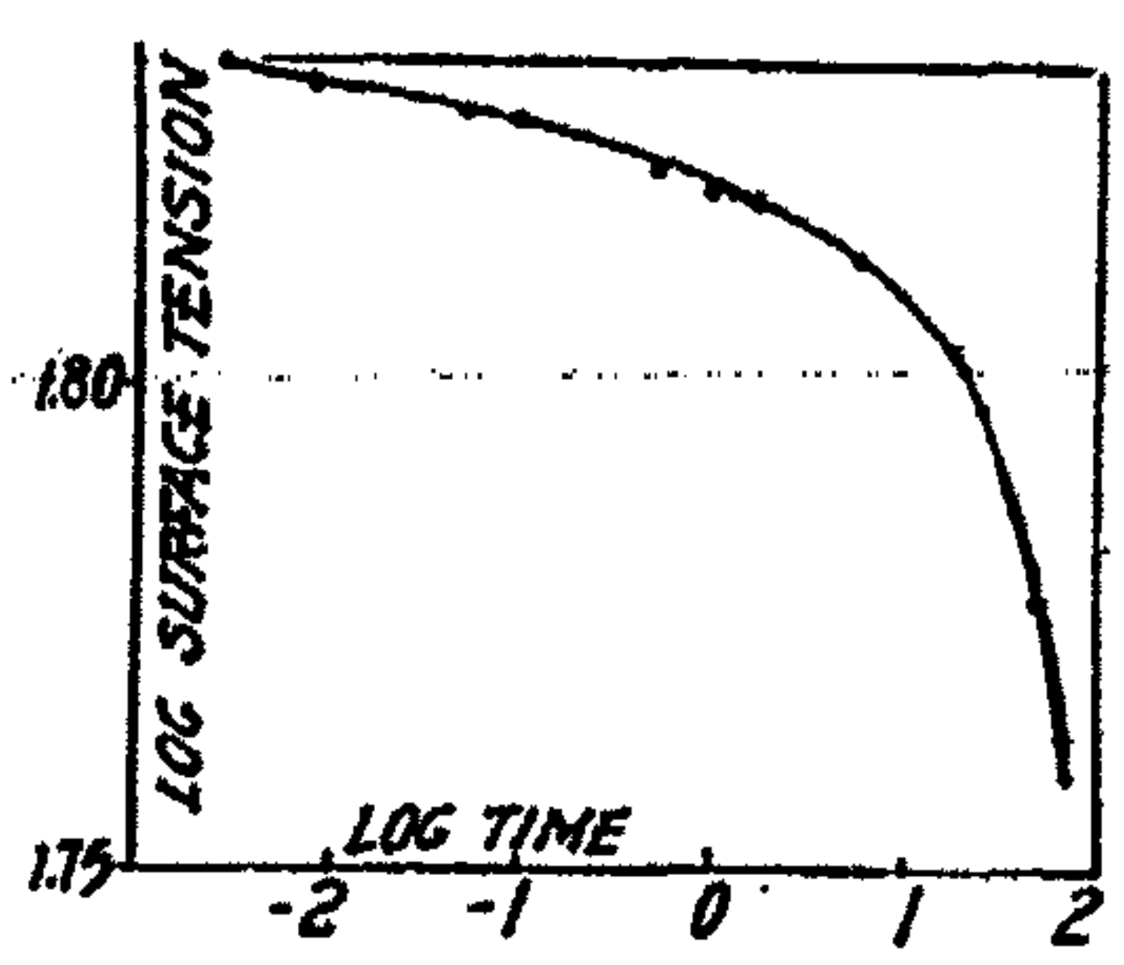

Fig. 7

Logarithm of Surface Tension and Time illustrated by Fig. 6.

It will be noted in Fig. 4 that in the case of more concentrated solutions the curves flatten out more as time progresses than they do in the case of more dilute solutions. In a large number of cases there was noted a reverse, i. e. a rise, in the values for σ. An example of this is given in the lower curve of Fig. 8. This curve represents a series of measurements made with a two percent solution of iso-electric gelatine and the other curve a similar series made with the same solution after acidification. The upper curve conforms to the given equation remarkably well and the lower one also, up to the point where a minimum is shown. This fact is illustrated by the log curves given in the same figure. Such phenomena as are illustrated by the lower curve of this figure are quite regularly to be obtained with more concentrated solutions and with more dilute ones in the case of wider capillary tubes. In Fig. 9 there is given a serious of results representative of many obtained with a wider capillary (dia. 0.0378 cm.). The initial readings in the case of a one percent solution of iso-electric gelatine were the same as those obtained with the smaller capillary tube. The reverse changes are not always so great as those

TABLE II

Illustrating change of surface tension with time for one percent solutions of ash-free gelatine of variable hydrogen-ion concentration at 40°.

Time	pH 3.1	pH 3.9	pH 4.4	pH 4.6	pH 4.8
10″	67.73	67.18	65.93	65.41	63.95
30″	67.10	66.43	64.97	63.31	62.92
1′	66.86	66.02	64.41	62.77	62.47
2′	66.72	65.77	63.78	62.45	62.11
5′	66.40	65.47	63.25	61.89	61.68
10′	66.20	65.40	62.91	61.53	61.40
15′	66.15	65.33	62.70	61.26	61.33
20′	66.04	65.34	62.52	61.13	61.26
25′	66.01	65.21	62.36	61.02	61.25
30′	65.97	65.11	62.24	60.86	61.25
40′	65.95	64.99	62.01	60.74	61.24
50′	65.79	64.79	61.89	60.60	61.23
60′	65.56	64.62	61.73	60.48	61.23

Time	pH 5.3	pH 6.9	pH 7.6	pH 4.8 heated
10″	64.60	66.25	66.90	63.49
30″	63.49	65.34	65.81	62.32
1′	62.98	64.82	65.33	61.60
2′	62.59	64.54	64.86	60.99
5′	62.26	64.28	64.50	60.29
10′	62.12	64.12	64.40	59.52
15′	62.04	64.05	64.31	59.16
20′	61.99	64.03	64.25	58.85
25′	61.95	64.02	64.13	58.60
30′	61.89	63.99	64.08	58.38
40′	61.89	63.99	63.89	58.08
50′	61.89	63.95	63.82	57.84
60′	61.89	63.91	63.67	57.60

shown in this figure but practically in all cases of results obtained with this wider capillary the plotted curves have two points of inflection. If the rate of change $\frac{d\sigma}{dt}$ is plotted with respect to time this curve will have a maximum and a minimum point in all cases where the surface tension curve had two points of inflection whether there was an actual reversal in surface tension or whether the curve merely flattened out and then fell again more rapidly in a positive direction. In the latter case $\frac{d\sigma}{dt}$ would naturally never have a negative value. In the case of the results shown in Fig. 6 the first point of inflection had been passed and the second point evidently not yet reached. With-

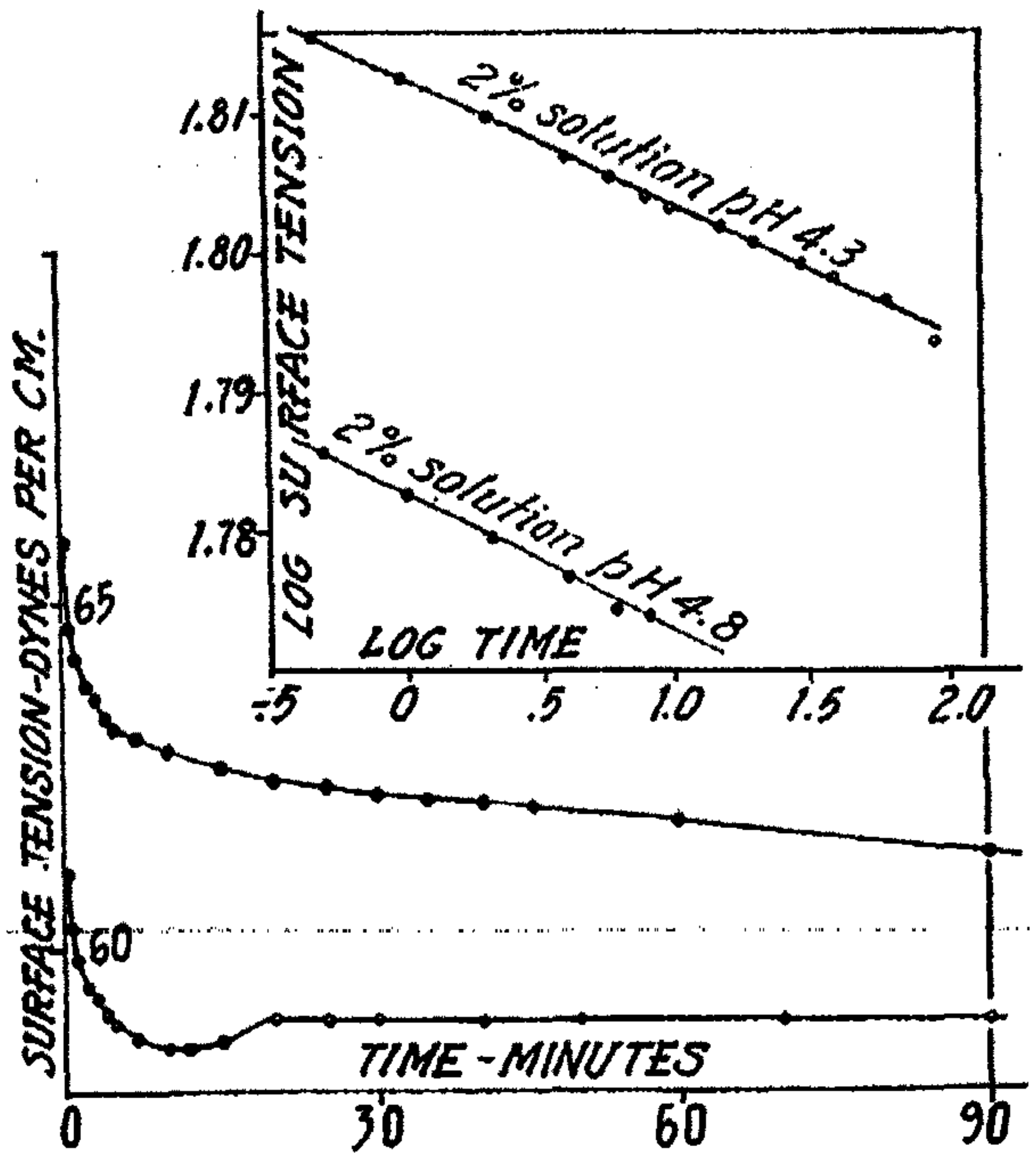

FIG. 8

Illustrating Change in Surface Tension with Time of 2% Solution before and after Acidification by Drop Weight Method.

TABLE III

Illustrating change of surface tension with time for one percent solutions of ash-free gelatine of variable hydrogen-ion concentration at 30°.

Time	pH 3.1	pH 3.6	pH 4.5	pH 4.8	pH 6.5	pH 7.2	pH 7.8
10″	68.94	69.13	65.36	65.36	67.06	67.87	68.48
30″	68.06	68.22	64.18	61.11	65.90	66.78	67.54
1′	67.72	67.88	63.54	63.67	65.36	66.36	67.10
2′	67.38	67.55	62.99	63.29	64.87	65.95	66.69
5′	67.01	67.22	62.48	62.85	64.44	65.58	66.21
10′	66.86	66.97	62.10	62.56	64.20	65.43	65.97
15′	66.82	66.96	61.89	62.36	64.10	65.37	65.90
20′	66.80	66.83	61.73	62.26	64.03	65.29	65.88
25′	66.77	66.70	61.61	62.15	63.98	65.22	65.86
30′	66.75	66.58	61.50	62.09	63.91	65.22	65.84
40′	66.74	66.36	61.36	61.94	63.85	65.15	65.81
50′	66.73	66.14	61.23	61.83	63.83	65.13	65.76
60′	66.67	65.86	61.13	61.73	63.76	65.12	65.67

out a second point of inflection the value of σ would rapidly have approached zero. A curve much like the lower one of Fig. 9 was quite recently shown by Lascaray[1] who determined the surface tension of sodium caprylate at various concentrations. Although in that case surface tension which is dependent on concentration and surface excess is plotted against concentration, the present

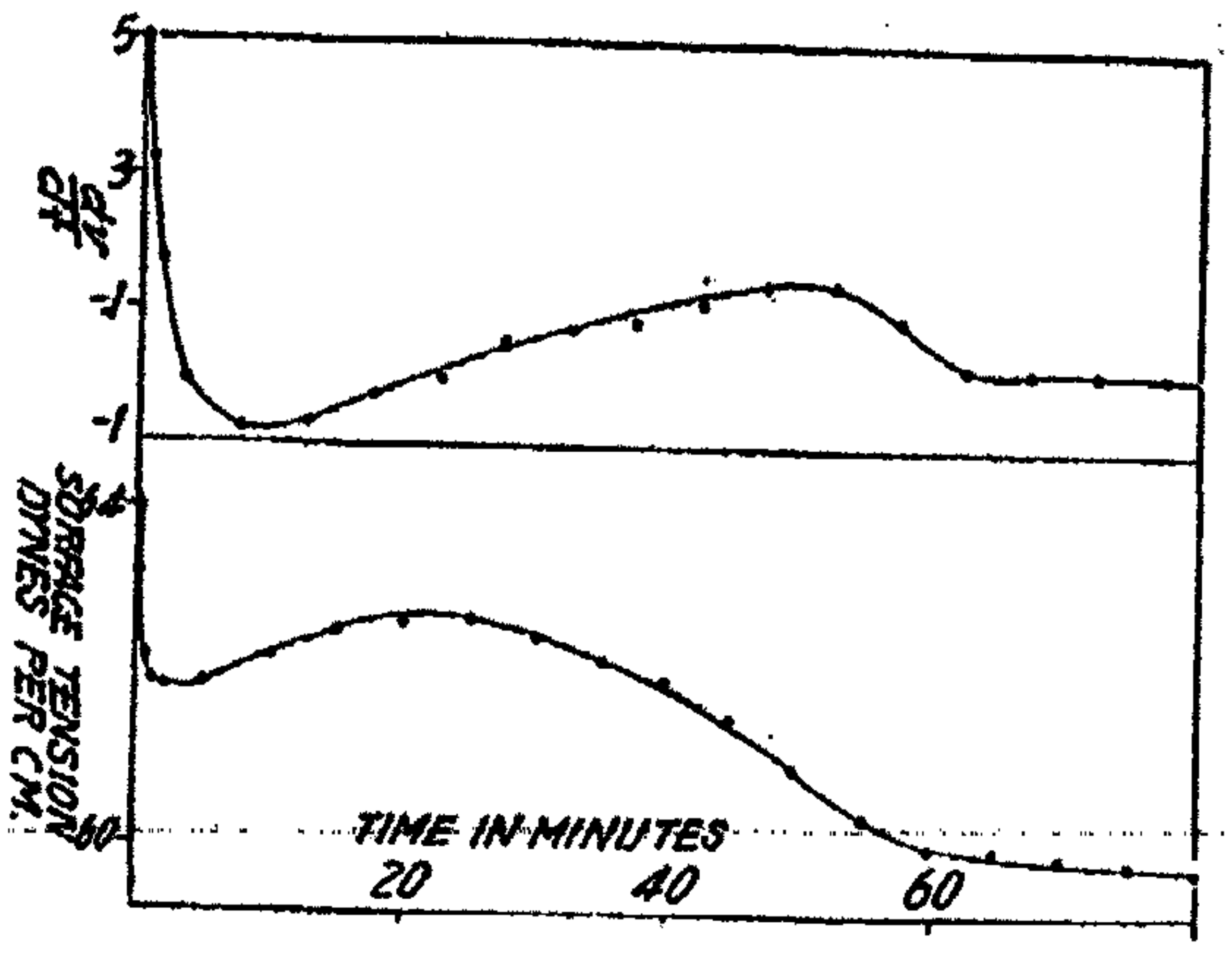

Fig. 9

Lower Curve illustrating Change of Surface Tension of 1% Solution of Iso-electric Gelatine at 40°C by means of Wider Capillary Tube. Upper Curve gives Rate of Change.

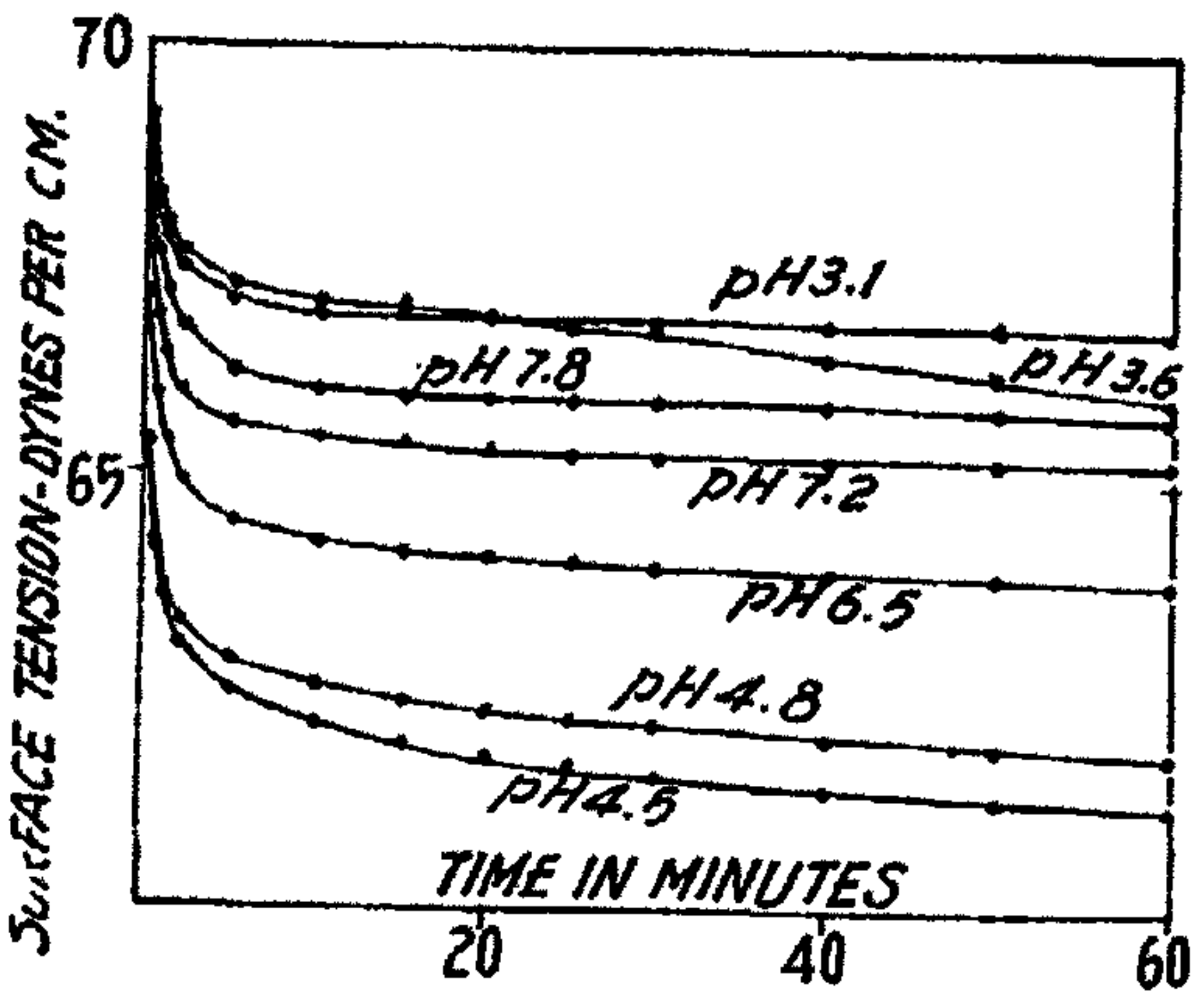

Fig. 10

Illustrating Change in Surface Tension with Change in pH for Ash-free Gelatine at 30° C(1% solution).

results may be considered comparable to the extent that excess surface concentration increases with time resulting in an attendant lowering of surface tension.

Any change in the preheating, or any change with respect to any other controllable variable could not be given as the cause for the somewhat varied results that were sometimes obtained. Evidence of rearrangements at the surface is indicated by the frequent throbbing or pulsating of the meniscus,

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[1] Kolloid-Z. 34, 75 (1924).

without necessarily resulting in any immediate change in surface tension—a fact invariably observed in all experiments with a wider capillary tube.

The effect which changing the hydrogen-ion concentration has upon the surface tension of one percent solutions, at 30 and at 40°, is shown by Figs. 10, 11, and 12. There is included in Fig. 11 a curve showing the effect of heating a one percent solution of pure iso-electric gelatine for 48 hours at 105° in a sealed tube without any other reagent present. As compared with the curve immediately above it, representing the same solution before it was heated, the initial readings are practically the same, but the surface tension of the heated gelatine decreases about twice as fast as the other in successive periods of time. In the case of the heated gelatine the change follows the given equation for a much longer period (four times as long) as can be seen from the log curve. Similar facts were noted when the gelatine was purified by dialysis only, though the difference was not quite so pronounced. Freundlich[1] cited cases of mixtures of amino acids and polypeptides where substances of small molecular weight greatly influence the rate of adsorption of those of greater molecular weight upon charcoal when the substances are of a similar nature and thus cause much greater adsorption of the larger molecule than would be the case if it were present in solution along, whereas substances of a dissimilar nature do not have any such influence. It would seem possible then that the presence of hydrolysis products, even though these might not tend to have any great effect upon the surface tension themselves, might greatly hasten the rate at which the non-hydrolysed gelatine is adsorbed at the surface. Conditions in the two cases are naturally quite different.

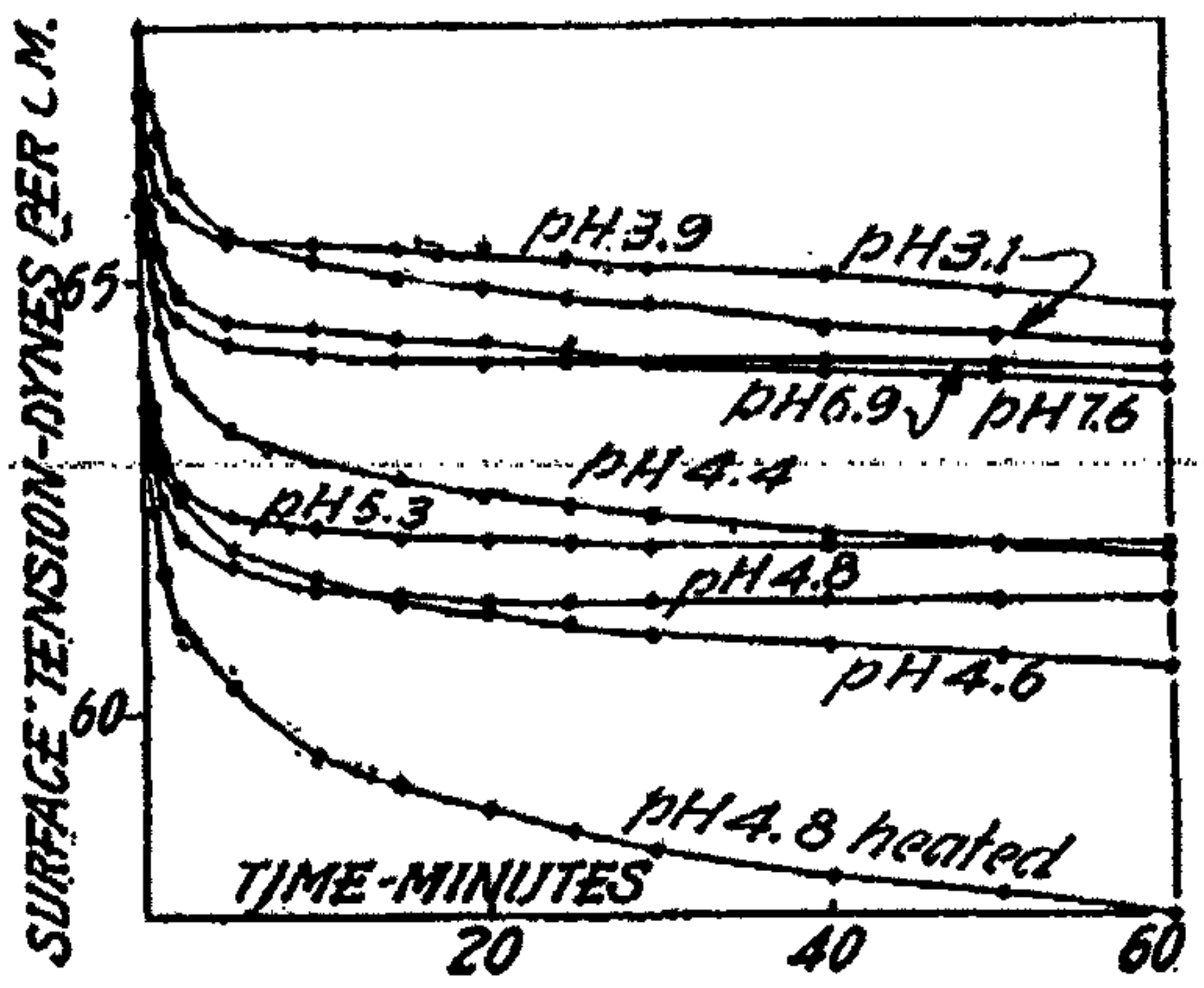

FIG. 11
Illustrating Change in Surface Tension at 40°C with Change of pH for Ash-free Gelatine (1% solution).
Also illustrating effect of heating gelatine to 105°

Ramsden[2] in a preliminary paper, showed that proteins of all kinds, including gelatine, as well as many other substances, are concentrated at the interface of solutions bounding a gas phase. It would be of interest to note what would be the behavior of some of these substances besides gelatine, and

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[1] "Kapillarchemie", 882 (1922).
[2] Proc. Roy. Soc. 72, 156 (1914).

of others of a similar nature, when observed under similar conditions over definite periods of time and at varied concentrations and temperatures. As regards the surface concentration of gelatine at the interface between its solutions and air and the effect upon the surface tension, it is evident that it is by no means a simple phenomenon and that the value of the surface tension of gelatine solutions can at best be only a relative one.

Although the writer is for the present limiting this investigation to a more exhaustive study of the behavior of the various proteins, a preliminary investigation on several types of colloids has shown that it may well be applied with success to colloids in general. The behavior shown by gelatine as illustrated by the above investigation is not unlike that shown by dilute silica gel, by solutions of night-blue and of potassium oleate, and to a much lesser extent by sols such as those of ferric hydrate and of sulphur and by emulsoids such as those of starch. Solutions of soluble starch, on the other hand, do not show any unusual behavior except to a questionable degree; neither does a sodium silicate solution until a certain amount of acid has been added. Solutions of soaps containing fifty percent alcohol show a behavior which is quite different from that of aqueous solutions. A considerable series of data, tables and curves might be introduced to illustrate these facts but in view of the many variables that should be introduced into a study of these substances, details will be reserved until a more thorough investigation has been made. To what extent the method might be used to differentiate between true solutions and colloidal solutions can not be stated with safety until a much larger number of such solutions has been studied.

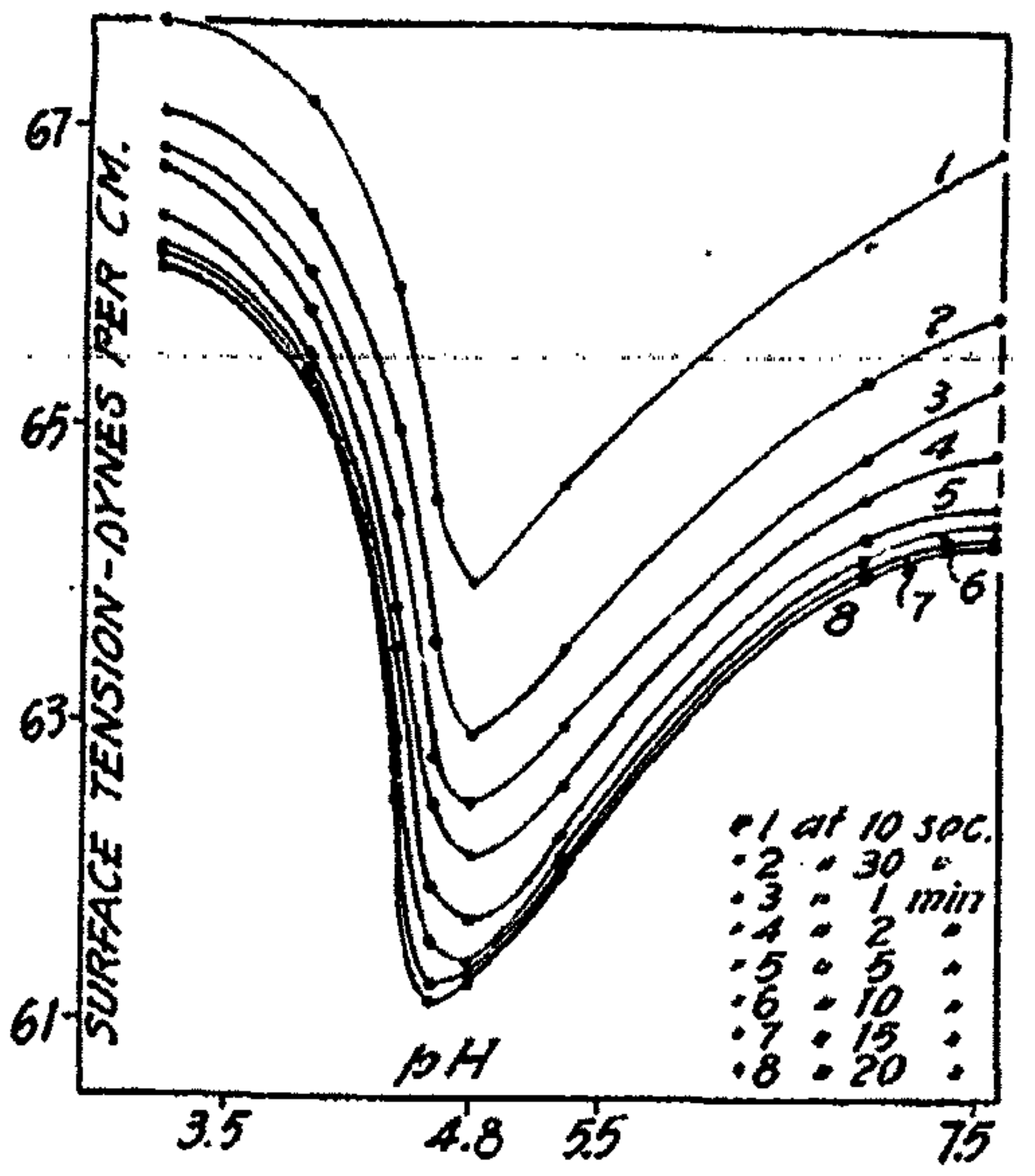

Fig. 12
Illustrating Change of Surface Tension with Change in Hydrogen Ion Concentration at 40°C, for a 1% Solution of Ash-free Gelatine.

William Ramsay Laboratories of Physical and Inorganic Chemistry,
University College, London.
June 6, 1924.

THE DISTRIBUTION OF HYDROGEN IONS BETWEEN GELATINE AND WATER

BY I. I. SHUKOFF AND S. A. STSCHOUKAREFF

The present paper contains the results of a series of electrometric titrations of hydrochloric acid in presence of different quantities of gelatine. These experiments were undertaken in order to clear some points connected with the question of the interaction between gelatine and acids and gelatine and bases.

The experiments were made as follows. For each titration we used to take 25 ccm of N/HCl mixed with 50 ccm of a solution of gelatine. The gelatine used by us was "Simeons Photographic Gelatine for Emulsion." The solutions of gelatine were prepared by allowing a weighed quantity of gelatine to swell in distilled water for some time, and raising the temperature of the latter not higher than 70° on a water bath. The acid was added after the complete dispersion of gelatine to a somewhat cooled solution. The resulting mixture was placed in the thermostat and titrated.

The amount of gelatine in 75 ccm in our experiments was as follows:

1) 0.075 gr.......0.1%
2) 0.375 gr.......0.5%
3) 0.75 gr........1.0%
4) 1.5 gr.........2.0%
5) 2.25 gr........3.0%
6) 3.0 gr.........4.0%
7) 3.75 gr........5.0%

The titration was made with NaOH. The solution of NaOH was not exactly N/10, 25 ccm of N/10 HCl being equivalent to 24.4 ccm of NaOH. The titration was made in a closed vessel, through the tight-fitting cork of which were introduced an electrode of the Hildebrand type, the end of the burette, the connecting tube of the calomel electrode (N/1,KCl) and a capillary tube for the escaping hydrogen. The experiments were made at 30° in an electrically-heated water thermostat. The hydrogen electrode was made of gold covered with platinum black.

Besides preventing the possible diffusion of oxygen into the solution, the titration in the atmosphere of hydrogen has the great advantage that under these conditions the solution of gelatine does not foam under the action of the bubbles of hydrogen. The stirring of the solution was accomplished by the passing bubbles of hydrogen.

In the presence of gelatine up to 5% the electrode behaved normally, coming up in the acid and alkaline region to a definite potential after 10-15 minutes, but in the region near the neutral point we had to wait a considerably longer time before the constant value was reached.

The measurements were made after the compensation method with a mirror galvanometer. The accuracy with which we were able to reproduce our experiments was such, that the difference for the values of pH obtained in several independent experiments did not exceed 0.05, but usually was much less. The measurements of pH in the same solution were reproducible with an accuracy of more than half a millivolt. In Table I are given the values of pH for different concentrations of gelatine.

TABLE I

HCl		HCl+0.1% gelatine.		HCl+0.5% gelatine.		HCl+1.0% gelatine.	
ccm of added NaOH	pH	ccm of added NaOH	pH	ccm of added NaOH	pH	ccm of added NaOH	pH
0.00	1.57	0.00	1.60	0.00	1.60	0.00	1.65
10.00	1.83	10.00	1.84	5.00	1.74	3.00	1.75
15.00	2.02	15.00	2.05	10.00	1.87	5.00	1.82
20.00	2.30	20.00	2.41	15.00	2.06	8.00	1.94
22.00	2.62	22.00	2.74	20.00	2.81	10.00	2.02
23.00	2.83	23.00	3.09	21.00	3.18	12.00	2.17
23.50	3.00	24.00	4.08	22.00	3.68	15.00	2.49
23.80	3.18	24.30	5.03	22.50	3.99	18.00	3.09
24.00	3.32	24.40	5.72	23.00	4.26	20.00	3.70
24.30	4.17	24.70	9.13	23.50	4.62	21.00	4.00
24.40	8.27	25.00	9.91	24.00	5.07	22.00	4.38
24.50	9.26	25.30	10.29	24.40	5.72	23.00	4.71
24.60	9.72	26.00	10.70	24.70	7.59	23.50	4.94
24.80	10.03	28.00	11.15	24.80	8.73	24.00	5.23
25.10	10.44	32.00	11.48	25.00	9.22	24.40	5.61
25.60	10.72	40.00	11.73	25.50	9.95	24.50	5.72
26.60	10.99	50.00	11.89	26.00	10.32	24.70	6.20
31.60	11.52			27.00	10.76	25.00	7.18
40.00	11.79			30.00	11.27	25.20	8.19
50.00	11.92			40.00	11.69	25.50	9.08
				50.00	11.86	26.00	9.65
						27.00	10.31
						28.00	10.64
						30.00	11.05
						32.00	11.27
						40.00	11.65
						50.00	11.82

(*Table I continued*)

HCl+2.0% gel.		HCl+3% gel.		HCl+4% gel.		HCl+5% gel.	
ccm of added NaOH	pH	ccm of added NaOH	pH	ccm of added NaOH	pH	ccm of added NaOH	pH
0.00	1.86	0.00	2.18	0.00	2.91	0.00	3.31
5.00	2.10	3.00	2.48	12.30	4.03	10.00	4.07
10.00	2.58	5.00	2.79	17.41	4.49	15.00	4.27
12.00	2.97	8.00	3.19	18.90	4.65	20.00	4.95
15.00	3.50	12.00	3.70	21.50	4.98	21.00	5.02
18.00	4.02	15.00	4.07	23.30	5.24	22.00	5.11
20.00	4.37	20.00	4.64	24.35	5.49	23.00	5.27
21.00	4.55	23.00	5.13	25.00	5.71	24.00	5.47
22.00	4.78	24.40	5.56	26.00	6.22	24.00	5.55
23.00	5.05	25.00	5.82	27.40	7.66	25.00	5.73
23.50	5.22	25.50	6.18	27.50	7.82	26.00	6.15
24.00	5.38	26.50	7.40	29.70	9.33	27.00	6.83
24.40	5.64	27.50	8.86	34.00	10.34	28.00	7.90
25.00	6.07	28.50	9.44	38.00	10.89	32.00	9.71
25.20	6.42	30.00	10.00	50.00	11.62	40.00	10.90
25.50	6.95	33.00	10.63			50.00	11.53
25.70	7.58	40.00	11.41				
26.00	8.32	50.00	11.76				
27.00	9.20						
28.00	9.81						
29.00	10.19						
31.00	10.63						
33.00	11.04						
40.00	11.52						
42.70	11.59						
50.00	11.75						

If we plot the values of pH as ordinates and the number of added ccm of NaOH as abscissae, we obtain the curves represented in Fig. 1.

These curves correspond:

Curve 1 to pure HCl
" 2 to HCl+0.1% gelatine[1]
" 3 " " " 0.5 " "
" 8 " " " 5.0 " "

Curve 5 to HCl+ 2.0 gelatine
" 6 " " " 3.0 "
" 7 " " " 4.0 "
" 4 " " " 1.0 "

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[1] The percentage of gelatine given in our paper corresponds always to the initial concentration of the solution. During the titration, of course, the concentration of gelatine changes as the result of the dilution with NaOH.

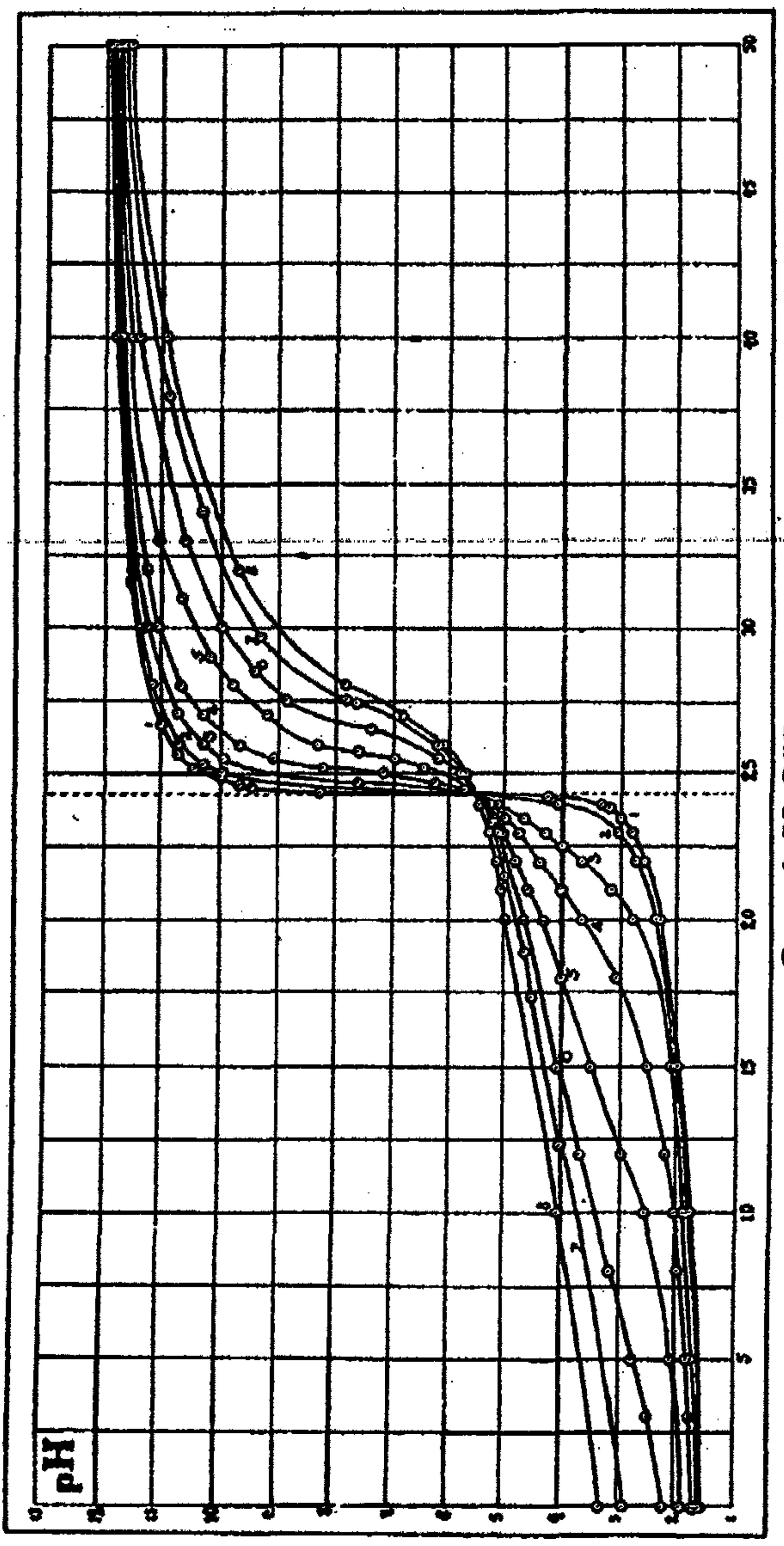

Fig. 1

As the result of absorption of acid by gelatine in the acid region the values for pH are higher, than for the pure acid, and in the alkaline region they are lower as the result of absorption of alkali. All the curves meet in the point corresponding to pH = 5.6. We consider this point as the isoelectric point of gelatine in our case.

For the sols of gelatine without acid, containing 0.5%, 1.0% and 2.0% of gelatine, we obtained values of pH = 5.67-5.75. The interpolation from the curves of Fig. 1 shows, that between pH = 3.0 and pH = 10.5 for a definite pH the quantity of the unneutralised acid, as well as the quantity of the alkali in excess are proportional to the quantity of gelatine in solution.

TABLE II

pH	ccm of unneutralised 1/10 HCl						
2.25	3.7	5.95	9.4	14.9	21.4		
3.0	1.6	3.75	6.7	12.3	17.7	23.4	
3.5	0.8	2.75	5.0	9.3	13.9	17.8	21.9
4.0	0.45	1.9	3.4	6.5	10.0	12.4	15.2
4.5	0.25	1.05	2.0	3.7	5.65	7.1	9.4
4.70	0.2	0.8	1.45	2.8	4.05	5.05	7.1
5.0	0.1	0.45	0.8	1.55	2.2	2.9	3.7
5.25	0.075	0.25	0.4	0.8	1.0	1.1	1.45
	ccm of NaOH in excess						
7.0	0.1	0.2	0.55	1.1	1.8	2.45	2.75
8.0	0.2	0.35	0.75	1.45	2.4	3.25	3.7
9.0	0.3	0.55	1.05	2.3	3.4	4.5	5.3
10.0	0.65	1.2	2.1	4.0	5.6	7.6	8.9
10.5	1.2	2.0	3.05	5.7	7.7	10.4	11.7
per cent of gelatine	0.1	0.5	1.0	2.0	3.0	4.0	5.0

Obviously the calculation of the number of ccm of unneutralised acid or alkali in excess must be done from the dotted line (Fig. 1), representing the equivalent amount of acid and alkali in our experiments.

It is clear, that the flatness of a large portion of the curves makes the interpolation for high and low values of pH very difficult.

If we plot as ordinates upwards from zero the ccm unneutralised acid and downwards the ccm of alkali in excess, and as abscissae the percentage of gelatine, we obtain a bundle of straight lines for different values of pH (Fig. 2). From these curves it is possible to calculate the amount of acid, that is necessary to add to a solution containing a given percentage of gelatine in order to obtain the required pH, or to calculate the value of pH in a given mixture of gelatine and hydrochloric acid.

These results do not depend practically on the presence of NaCl formed during the neutralisation. The values of pH obtained by gradual addition of HCl to a 1.5% solution of gelatine, were in good accordance with values of pH obtained by titration of the identical solution, containing 25 ccm of n/10 HCl.

From the data of Table II it is easy to calculate for a definite pH the amount of acid or alkali bound by 1 gramme of gelatine. In this calculation, besides the data of Table II, we have taken in consideration the normality of HCl and NaOH, the change of the volume of the solution during the titration, the obtained pH and the weight of the gelatine in solution.

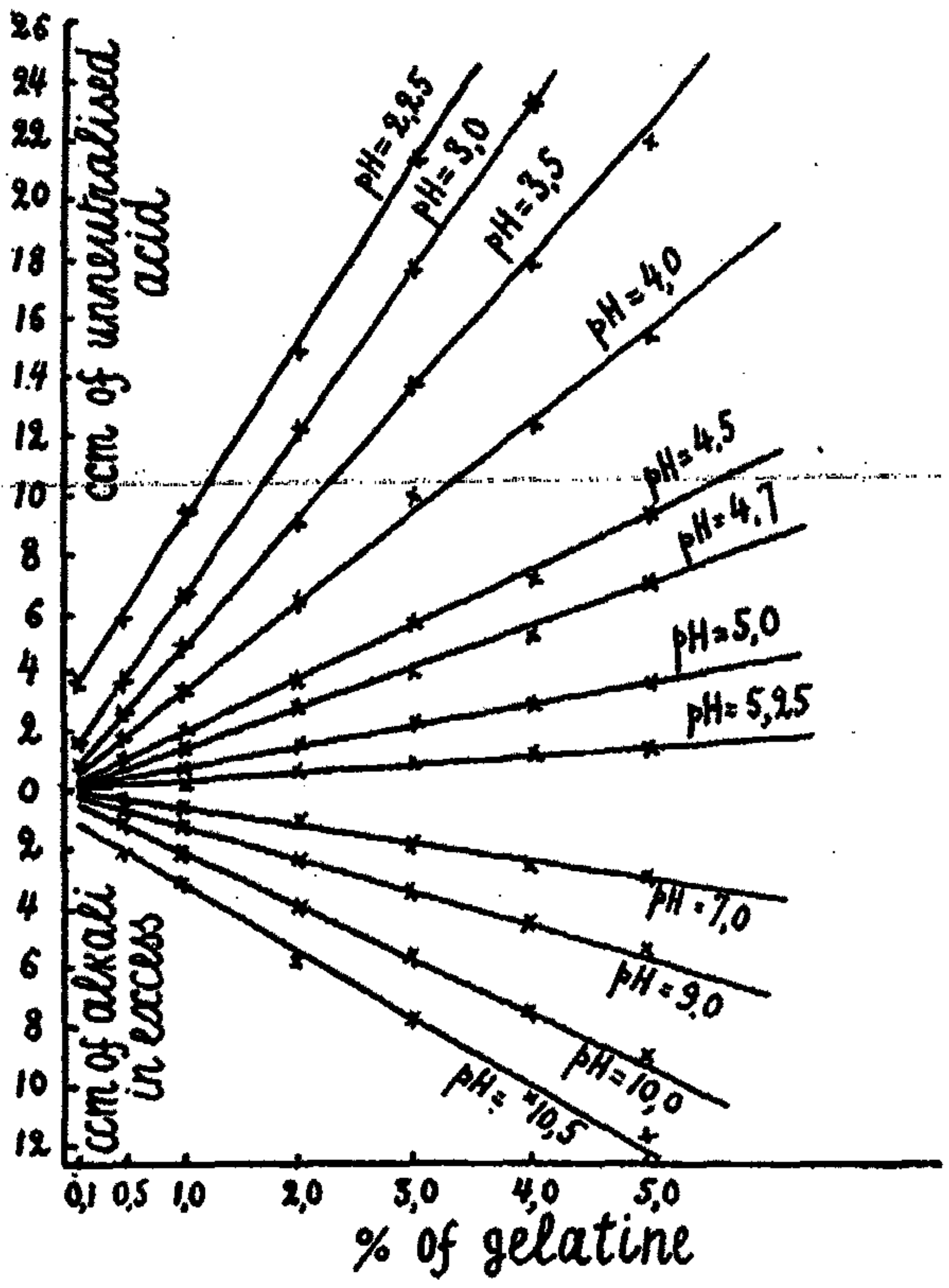

FIG. 2

In Table III are given the results of this calculation.

As one may see the quantities of H and OH bound by one gramme of gelatine for a definite pH are practically constant and do not depend on the concentration of gelatine.[1]

Therefore, if we take for instance 50 ccm of an acid solution of gelatine with pH = 4.7 and if we dilute it 10 times with slightly acid water, having a pH = 4.7 the gelatine will neither absorb nor lose H-ions.

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[1] In all our calculations we did not take in consideration the possible contact potential.

TABLE III

Gramme-ions $H \times 10^4$ bound by one gramme of gelatine

pH / Grammes of gelatine in solution	2.0	2.5	3.0	3.5	4.0	4.5	4.7	5.0	5.25
0.075									
0.375		8.1	7.7	6.6	4.9	2.8	2.1	1.2	0.6
0.75		8.9	7.9	6.4	4.5	2.7	1.9	1.1	0.5
1.5	9.1	8.3	7.8	6.1	4.4	2.5	1.9	1.0	0.5
2.25		8.5	7.7	6.2	4.5	2.5	1.8	1.0	0.4
3.0			7.7	6.0	4.2	2.4	1.7	1.0	0.4
3.75				5.6	4.1	2.5	1.9	1.0	0.4

Gramme-ions $OH' \times 10^4$ bound by one gramme of gelatine.

pH / Grammes of gelatine in solution	6	7	8	9	10	10.5	11
0.075							
0.375				1.5			
0.75		0.7	1.0	1.6	2.7	3.8	5.7
1.5		0.7	1.1	1.6	2.6	3.6	4.9
2.25	0.4	0.8	1.1	1.5	2.5	3.3	4.5
3.0	0.4	0.8	1.1	1.5	2.5	3.4	4.9
3.75	0.4	0.7	1.0	1.4	2.1	3.1	4.3

It is rather difficult, as it seems, to bring this fact in agreement with the view, that gelatine forms easily hydrolysed salts with acids and alkalis. From this fact one may draw rather the more or less definite conclusion, that the micelles of gelatine form with acids and alkalis an absorption complex.

The degree of hydrolysis ought to be greater in more dilute solutions of gelatine, and we might expect to find an increase of free $H^{\cdot}$ and OH' in dilute solutions.

On the contrary, from Table III we may see that, even if there is some inconstancy in the amounts of bound acid or alkali for a definite $pH^{\cdot}$, we observe in solutions with small concentrations of gelatine rather an increased tendency for binding $H^{\cdot}$ and OH'-ions. Perhaps the decrease of the amount of $H^{\cdot}$ and OH' bound by one gramme of gelatine in concentrated sols may be explained by the smaller relative surface of the micelles of gelatine in these sols.

If we consider that amount of bound $H^{\cdot}$ and OH' as constant for a definite pH and if we take the mean value of the data of each column of Table III, we obtain Table IV.

TABLE IV

pH	Gramme-ions $H' \times 10^4$ bound by one gramme of gelatine.
2.0	9.1
2.5	8.4
3.0	7.8
3.5	6.1
4.0	4.3
4.5	2.6
4.7	1.9
5.0	1.0
5.25	0.4

pOH		Gramme-ions $OH' \times 10^4$ bound by one gramme of gelatine.
6.0	8.0	0.4
7.0	7.0	0.8
8.0	6.0	1.0
9.0	5.0	1.5
10.0	4.0	2.5
10.5	3.5	3.1
11.0	3.0	4.9

The data of Table IV are represented graphically in Fig. 3. It follows from the results of J. Loeb[1] that the amount of HCl bound by one gramme of gelatine in the region of $pH = 1\text{-}2$ is 9.2×10^{-4}.

In rather close agreement for $pH = 2$ we find 9.1×10^{-4}.

It is interesting to note that between $pH = 3$ and $pH = 5$ in the acid region the curve forms nearly a straight line.

As one may observe the acid is more easily bound by gelatine, than the alkali: for instance, at $pH = 3$ there are 7.8×10^{-4} gramme-ions of H' bound by one gramme of gelatine, and at $pOH = 3$ there are only 4.9×10^{-4} gramme-ions of OH' bound by one gramme of gelatine.

From the acid nature of gelatine we might expect the contrary.

If we plot as ordinates the amount of bound H. and OH' per liter of solution and one gramme of gelatine in gramme equivalents, and as abscissæ the total amount of acid or alkali per liter in gramme equivalents, we obtain the curves of Fig. 4.

These curves are plotted from the data for the 2% sol of gelatine, but as the amount of H' or OH' bound by one gramme of gelatine does not depend on the percentage of gelatine in solution (for a definite pH), these curves will coincide with the curves for all the concentrations of gelatine between 0.1 and 5%.

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[1] Chem. Central bl. 1921, I, 251; J. Gen. Physiol. 3, 35.

The coincidence of the curves in the region between pH = 3 and pOH = 3.5 with straight lines starting from the isoelectric point and forming with the axis of the abscissæ an angle of 45° explains the curves of Fig. 2.

In fact, the amounts of bound acid or alkali are proportional to the quantity of gelatine in solution and at the same time the free acid or alkali are present in practically negligible quantities.

From here follows the practical proportionality between the total amount of acid or alkali and the amount of gelatine in solution for a definite pH. In the paper by S. O. Rawling and W. Clark[1] we find, that the quantities of sulfuric or acetic acid, necessary to obtain pH = 4.7 in a solution of gelatine are dependent on the concentration of gelatine.

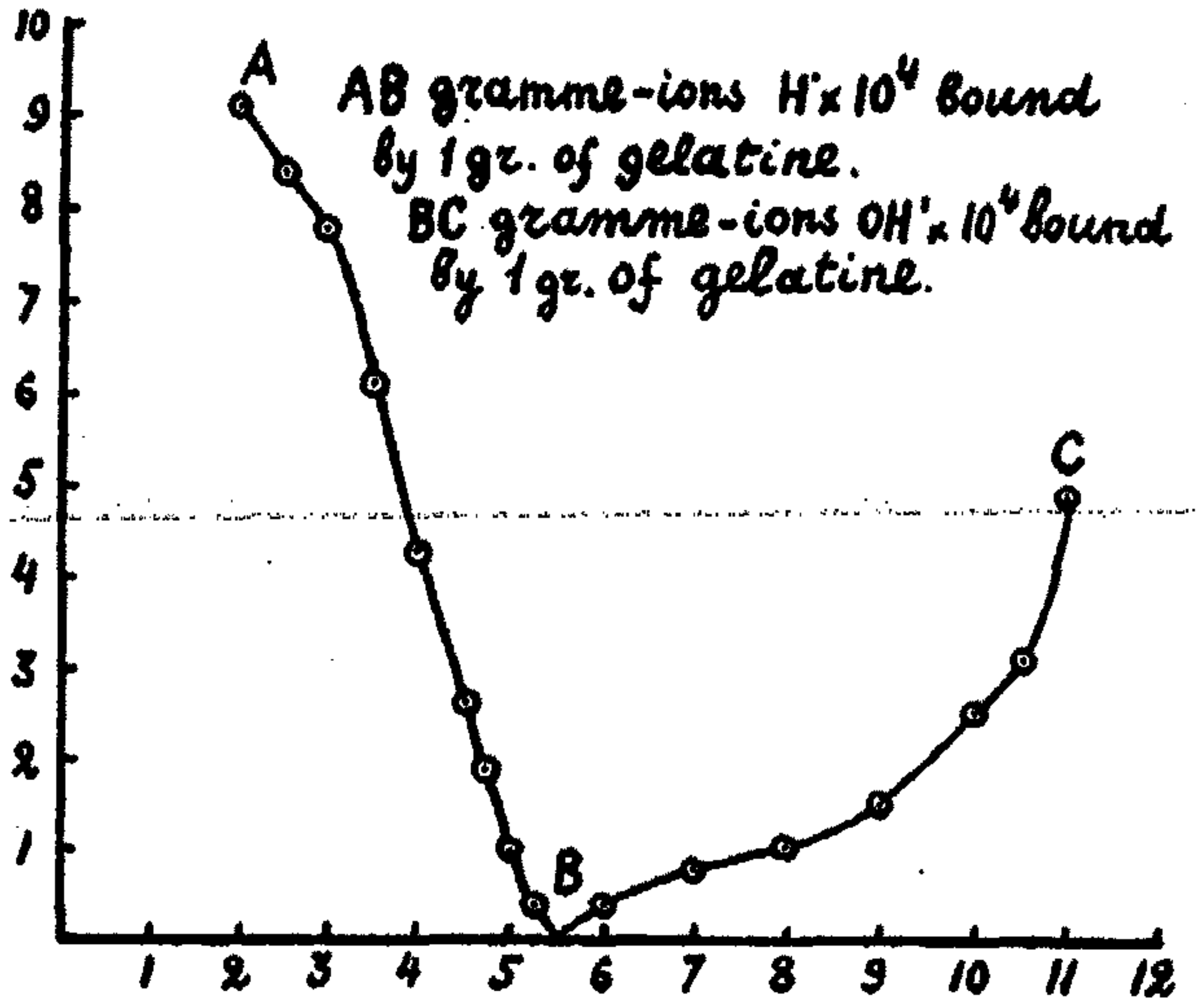

FIG. 3

Their experimental results as well as those of Pauli and Samec's[2] are expressed by a straight line function.

Our experiments are in agreement with these results, but at the same time they show that there exists a proportionality between the quantity of acid and the concentration of gelatine for other values of PH in a much wider region; we find the same proportionality in the alkaline region.

The value of pH = 4.7 for the isoelectric point of gelatine, as observed by a number of other authors, is not in agreement with pH = 5.6 for the same point, resulting from our experiments. It follows from the results of Pauli that in a strong acids the isoelectric point of gelatine, as determined by electrophoresis lies at a pH higher, than 4.7.

The results of S. O. Rawling and W. Clark show us, that at pH = 4.7, where they observed the minimum viscosity, the total amount of acid in solution is not independent of the concentration of gelatine. S. O. Rawling and

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[1] J. Chem. Soc. 121, 2830 (1922).

[2] Pauli: "Kolloidchemie der Eiweisskörper."

W. Clark make the suggestion, that gelatine is a mixture of two substances, one having an isoelectric point at pH = 4.7, and another near pH = 8.

The experiments of Higley and J. H. Mathews[1] on the absorption of light by sols of gelatine show us two characteristic points at pH = 4.69 and pH = 7.65. This fact also confirms, as it seems, the views expressed by S. O. Rawling and W. Clark.

We consider it possible that our value for the isoelectric point pH = 5.6 represents the mean value for the different substances forming gelatine.

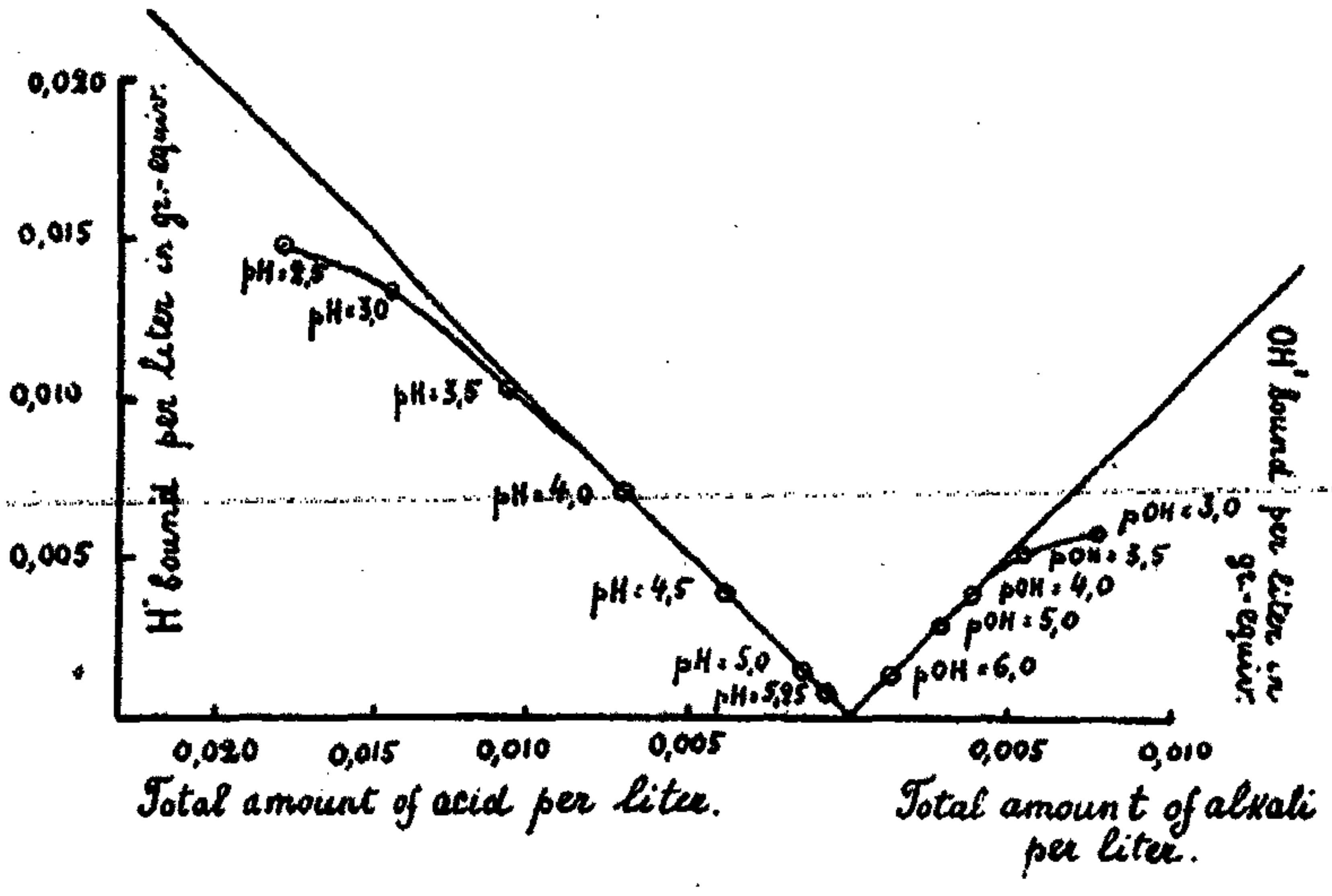

FIG. 4

Summary

1. Electrometric titration curves of HCl in presence of different quantities of gelatine were obtained.
2. The curves for mixtures, containing between 0.1 and 5.0% of gelatine meet at one point, corresponding to pH = 5.6.
3. Between pH = 3 and pH = 10.5 for a definite pH the amount of the unneutralised acid, as well as the amount of the alkali in excess are practically proportional to the quantity of gelatine in solution.
4. For a definite pH the amount of gramme-ions of H′ and the amount of gramme-ions of OH′ bound by one gramme of gelatine are constant and independent on the concentration of gelatine.
5. The obtained results seem to point to a formation of an adsorption complex between acids or alkalis and gelatine.
6. The obtained value pH = 5.6 for the isoelectric point of gelatine may be explained by the assumption, that gelatine is a mixture of two substances with different isoelectric points.

Physico-Chemical Laboratory of
the University of Leningrad.
May, 1924.

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[1] J. Am. Chem. Soc. 46, 825, (1924.)

THE INFLUENCE OF A THIRD SUBSTANCE ON THE CRITICAL SOLUTION TEMPERATURE OF PHENOL AND WATER

JOHN DUCKETT AND WILLIAM HAMILTON PATTERSON

The result of investigation of critical solution temperatures of several pairs of liquid systems especially with small additions of a third component has been published by Timmermans[1] in an extensive paper with bibliography. Since the following work has been in progress, two papers have appeared[2] dealing with the change of mutual miscibility of phenol-water mixtures on the addition of a small quantity of another component. Critical solution temperature[3] has also been made use of as a criterion of purity.

The addition of a third substance may raise or lower the temperature at which two liquid phases become one. In phenol-water mixtures the addition of most electrolytes raises this temperature considerably. The maximum rise is expected when the added substance is soluble in one of the liquid constituents only. If it is soluble in both, the rise may be small, or the critical solution temperature may be much depressed, the maximum lowering occurring when the third substance is equally soluble in both liquids[4].

Critical Solution Temperature

The purpose of this investigation was to ascertain the effect of the nature and concentration of the added substance on the mixture of phenol and water (36.1 phenol and 63.9 water) which gives the maximum temperature for mutual solubility. We have found this to be 66.0° for phenol M.Pt. 41° and pure water in the above ratio. (Other workers have given values 65.3°-70°.—Friedländer[5], 66.06°). Above 66.0° an opalescence is shown (the critical opalescence); at and below 66.0° however the turbidity in a tube 15 mm. diameter becomes such that the stirred mixture is no longer transparent, so this temperature has been selected as the basis. The disappearance of the opalescence is gradual; a range of 2° as a rule suffices to make the liquid quite clear, even when a third substance has been added. The homogeneous solution of a phenol-water mixture was found to give the Tyndall cone effect and examination of the scattered light with crossed Nichols showed it to be plane polarised with a critical change in the angle just before turbidity set in, as distinct from opalesence. This has not been observed hitherto and deserves fuller investigation.

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[1] Z. physik. Chem. 58, 129-213 (1907).

[2] C. R. Bailey: J. Chem. Soc. 123, 2579 (1923); Boutaric and Nabot: Compt. rend. 176, 1618 (1923).

[3] Crismer: Bull. Soc. chim. Belg. 9, 145 (1895) etc.; Orton and Jones: J. Chem. Soc. 115 1055 (1919).

[4] Cf. Roozeboom, "Die heterogenen Gleichgewichte", III Part 2 (1913); Bancroft: J. Phys. Chem. 1, 414 (1897).

[5] Z. physik. Chem. 38, 389 (1901); Scarpa, 65, 8°: J. Chim. phys. 2, 447 (1904).

The following results were obtained on adding a third component to the phenol-water mixture giving a C.S.T. of 66.0°.

(1) Salts which raise the Critical Solution Temperature Soluble in Water

c = grams of salt per 1,000 grams of total solution
Mol. c = molecular concentration i.e., c/Molecular Weight
C.S.T. = Critical Solution Temperature of mixture
e = elevation of C.S.T. produced by addition of salt
E = molecular elevation

NaCl

c	mol. c.	C. S. T.	e	E
1.550	.02649	69.25	3.25	123
2.313	.03954	70.65	4.65	118
4.430	.07571	74.3	8.3	110
4.775	.08162	74.6	8.6	106
8.194	.1401	79.9	13.9	99.2
9.080	.1552	81.3	15.3	98.6
9.642	.1648	82.2	16.2	98.3

KCl

1.772	.02379	68.45	2.45	103
5.130	.06885	72.5	6.5	94.4
7.004	.09401	73.9	7.9	84.0
8.790	.1180	75.9	9.9	83.9
14.60	.1959	82.2	16.2	82.7
15.54	.2085	83.2	17.2	82.5

KBr

4.481	.03766	69.5	3.5	92.9
6.772	.05692	71.1	5.1	89.6
9.200	.07732	72.4	6.4	82.8
15.15	.1274	75.8	9.8	77.0
18.47	.1552	77.5	11.5	74.1
22.51	.1892	79.7	13.7	72.4
27.46	.2308	82.2	16.2	70.2

KI

4.149	.0250	67.85	1.85	74.0
9.740	.05868	69.80	3.8	64.8
20.01	.1205	72.95	6.95	57.7
25.30	.1524	74.4	8.4	55.1
32.09	.1933	76.15	10.15	52.5
37.96	.2288	77.75	11.75	51.4
57.51	.3465	83.1	17.1	49.4

NH_4Cl

c	mol. c.	C. S. T.	c	E
2.230	.04169	69.2	3.2	76.8
5.576	.1042	73.25	7.25	69.6
7.145	.1336	74.9	8.9	66.7
9.543	.1783	77.4	11.4	63.9
12.83	.2400	80.7	14.7	61.3
15.09	.2819	82.7	16.7	59.2

NH_4Br

1.913	.01952	67.45	1.45	74.3
7.230	.07377	70.90	4.90	66.4
13.14	.1341	73.95	7.95	59.3
21.32	.2176	77.8	11.8	54.2
31.17	.3181	82.4	16.4	51.6
39.26	.4006	86.0	20.0	49.9

NH_4NO_3

4.294	.05368	68.5	2.5	46.6
6.688	.0836	69.6	3.6	43.1
11.54	.1442	71.8	5.8	40.2
15.77	.1972	73.5	7.5	38.1
23.52	.2940	76.0	10.0	34.0
35.61	.4451	80.35	14.35	32.2

KNO_3

1.586	.01570	67.25	1.25	79.6
5.732	.05675	69.65	3.65	64.3
6.247	.06186	69.95	3.95	63.9
15.90	.1574	74.75	8.75	55.6
25.66	.2541	78.8	12.8	50.4

$Na_2SO_4 \cdot 10H_2O$

2.147	.00667	68.6	2.6	390
5.023	.0156	75.75	5.75	369
6.689	.0208	73.2	7.2	347
8.861	.0275	75.1	9.1	331
10.07	.0313	76.25	10.25	328

K_2SO_4

2.057	.0118	69.7	3.7	313
4.241	.0244	72.75	6.75	277
9.262	.05323	79.4	13.4	252
10.87	.0625	81.4	15.4	246
12.49	.0718	83.45	17.45	243

d. Na. H. Tartrate

c	Mol. C	C. S. T.	θ	E
6.169	.0325	71.2	5.2	160
9.642	.0508	73.5	7.5	148
15.27	.0804	77.0	11.0	137
15.95	.0800	77.35	11.35	135
21.99	.1157	81.3	15.3	132

Na. H. Racemate

c	Mol. C	C. S. T.	θ	E
7.122	.0375	71.7	5.7	152
10.67	.0562	74.3	8.3	148
13.87	.0730	76.1	10.1	138
21.95	.1154	81.2	15.2	132
23.83	.1254	82.2	16.2	129

Results in the case of some of the above salts have been also given or requoted by Timmermans (loc. cit). A comparison with our numbers is only possible in a few instances since we have not worked above 100°C., as pressure affects the initial solution temperature.

For potassium chloride one number only is comparable and this agrees with ours; in the case of potassium chloride the three values and potassium sulphate the one value which can be compared, show small differences. Our endeavour has been to arrive at strictly comparable numbers over a range of small salt concentration.

The importance of these figures lies, in the first place, in the value of E for the various salts and secondly in the characteristic curves for individual salts on plotting the change of E with increase in the concentration.

From the curves the following average values for E are obtained:—

	Mol. c. 0.03-0.1	Mol. c. 0:1-0.2
NH_4NO_3	46.5	40
KI	66	56
KNO_3	66	56.5
NH_4Br	68.5	59
NH_4Cl	75	66.5
KBr	87	75.5
KCl	93	83
NaCl	112.5	100
Na. H. Tartrate	145	128
K_2SO_4	256	—
Na_2SO_4	315 extrapolated	—

i. e. the same order is obtained for each concentration. The curves for potassium iodide and potassium nitrate, above very low concentration, are nearly identical.

The above results show that most of the effect must be due to ions and that the cations and anions may be arranged in order of their power of elevating the C. S. T.

Cations. Na > K > NH_4

Anions. SO_4 > H. Tartrate > Cl > Br > I = NO_3

This is the Hofmeister series with the exception that the iodide ion is equal to, instead of greater, than NO_3 ion. Thus such a phenomenon as the coagulation of neutral egg albumen is linked up with the mutual miscibility, in presence of electrolytes, of water-phenol mixtures and is also related to changes of surface tension.

Numerical values may be assigned to each ion and all the substances investigated will be found to be in agreement: an assumption is necessary however which the data are insufficient to justify; a criticism which applies in general to all such series.

(2) Substances which raise the Critical Solution Temperature Soluble in Phenol

Azobenzene

c	Mol. C	C. S. T.	e	E
.9747	.00536	67.6	1.6	299
1.885	.01035	69.0	3.0	290
3.748	.02059	72.0	6.0	290
9.262	.05089	80.6	14.6	287

Salol

c	Mol. C	C. S. T.	e	E
2.247	.01050	68.8	2.8	267
8.420	.03934	76.5	10.5	267
11.53	.05392	80.4	14.4	267

Naphthalene

c	Mol. C	C. S. T.	e	E
6.222	.04861	75.8	9.8	202
9.714	.0759	81.1	15.1	199
10.54	.0823	81.85	15.85	193
11.24	.0878	82.9	16.9	192
11.76	.0918	83.6	17.6	192
13.30	.1040	85.7	19.7	190

Camphor

c	Mol. C	C. S. T.	e	E
5.137	.0338	74.15	8.15	241
6.510	.0428	76.2	10.2	238
8.950	.0589	79.45	13.45	228
9.158	.0603	79.65	13.65	227
14.12	.0929	87.0	21.0	226

c	Mol. C.	C. S. T.	e	E
		Palmitic Acid		
1.731	.00676	67.8	1.8	266
6.039	.0236	72.3	6.3	267
8.923	.0349	75.2	9.2	264
16.41	.0641	82.0	16.0	250
		Stearic Acid*		
2.816	.00991	69.1	3.0	303
4.318	.0152	70.6	4.6	303
7.707	.0271	73.9	7.9	292
11.31	.0398	77.1	11.1	279

Among substances of this class azo-benzene and salol were tried since Boutaric and Nabot (loc. cit) make use of these compounds to show that the identical rise is obtained from equimolecular concentrations. An anomalous result in the case of naphthalene they explain by its solubility in water.

The figures given above, based on the maximum point of the binodal curve (not used by Boutaric and Nabot) show that equimolecular concentrations give different values for E.

The values are approximately constant for each individual substance. Timmermans has given values for azobenzene haphthalene and camphor.

(3) Substances Soluble both in Phenol and Water

c	mol. c.	C. S. T.	e	E
		Urea		
5.656	.0943	64.7	−1.3	−13.8
13.55	.2258	62.9	−3.1	−13.8
30.07	.5010	59.0	−7.0	−14.0
69.10	1.152	49.2	−16.8	−14.6
		$Hg(CN)_2$		
29.38	.1166	60.8	−5.2	−44.6
33.01	.1310	59.9	−6.1	−46.6
38.39	.1524	58.8	−7.2	−47.3
48.01	.1905	56.7	−9.3	−48.8
58.84	.2335	54.3	−11.7	−50.1
		Cane Sugar		
26.62	.0778	65.8	−.2°	−2.57
48.40	.1415	65.65	−.35°	−2.47
54.49	.1693	65.6	.4°	−2.51
		Phenyl-a-naphthyl-methyl-benzyl-arsonium iodide MW = 512		
1.267	.00247	64.0	−2°.0	−809
4.167	.00814	60.2	−5.8	−713
5.406	.0106	59.0	−7.0	−663
12.61	.0246	55.3	−10.7	−434

*Kahlbaum sample—not pure.

Cane sugar leads to a very small lowering of C. S. T. as it is soluble in both water and phenol. Bancroft (loc. cit.) had classed it with potassium nitrate i. e. insoluble in phenol. Phenyl naphthylmethylbenzylarsonium iodide is of interest as being of high molecular weight. It leads to anomalous values for E, decreasing with concentration; it extends the range of critical opalescence.

Viscosity

Comparative viscosity determinations were made (water at 17° being taken as unity) of (1) phenol-water mixture (as above) and also with the addition of each of the three classes of third component i. e. (2) sodium chloride, (3) naphthalene, (4) mercuric cyanide.

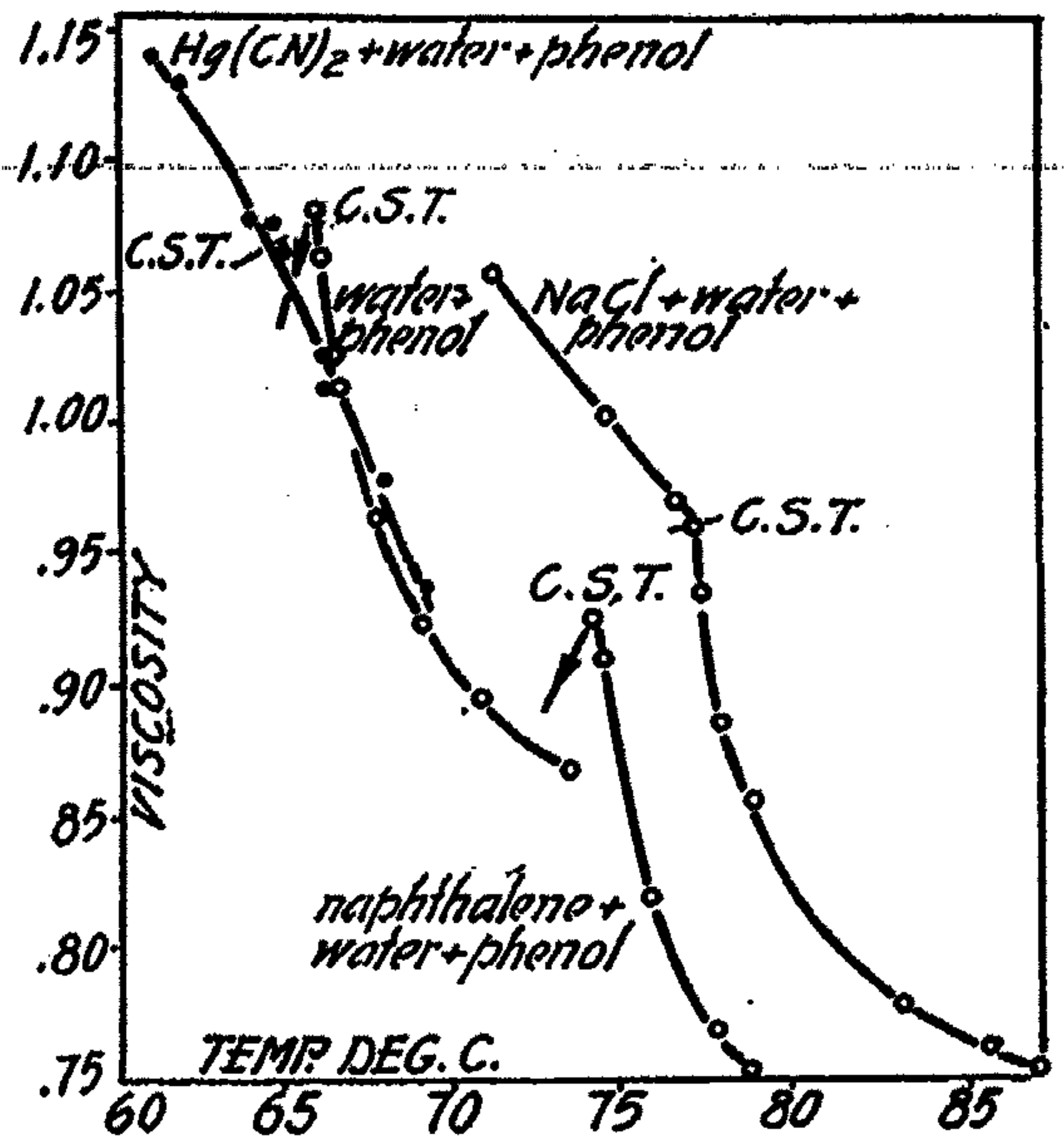

FIG. 1

(1) and (3) show inflection at the respective C. S. T.s i. e. 66°0 and 74°5 the viscosity of the heterogenous system just below the C. S. T. being less than the homogeneous phase just above the C. S. T.; (2) and (4) show points of inflection.

These results are shown graphically in Fig. 1.

Conductivity

Conductivity measurements were made with a dipping electrode in one or other of the layers or the homogeneous solution. In some cases the formation of an emulsion brought about discrepancies.

Fig. 2 shows variation of specific conductivity; the lower outer line the phenol phase with rising temperature the upper outer line the aqueous phase. The dotted lines extend this into the metastable region above the C. S. T. The straight middle line gives the values of K for the single phase by falling temperature (K being almost constant); the inner branches the respective conductivities of the two phases below the C. S. T.

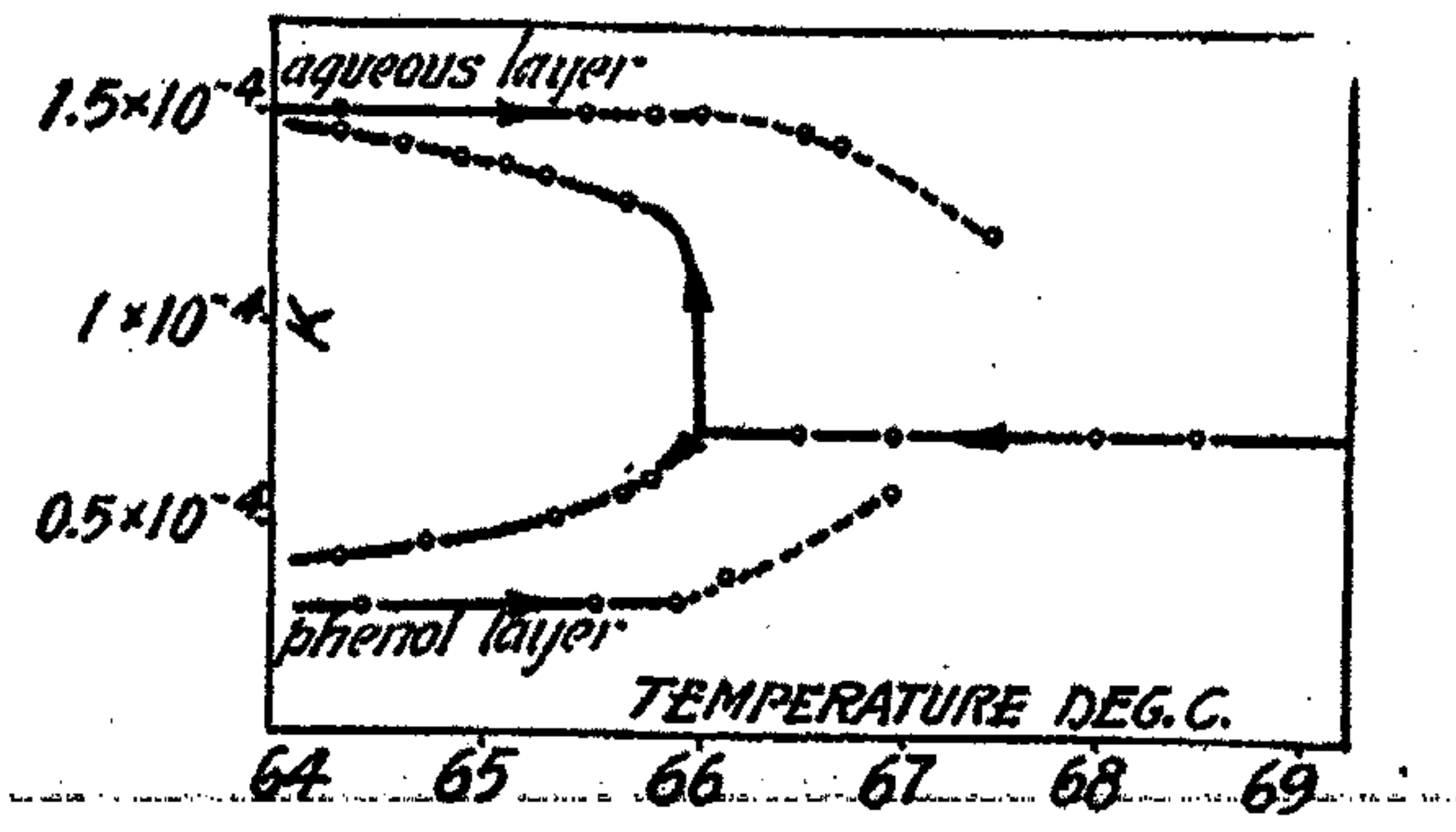

FIG. 2

It may be noted that the relative distances of the two outer lines from the middle line are in the same ratio in which phenol and water are mixed to give the maximum C. S. T. When a third substance is added, e. g. sodium chloride, this ratio is greatly changed.

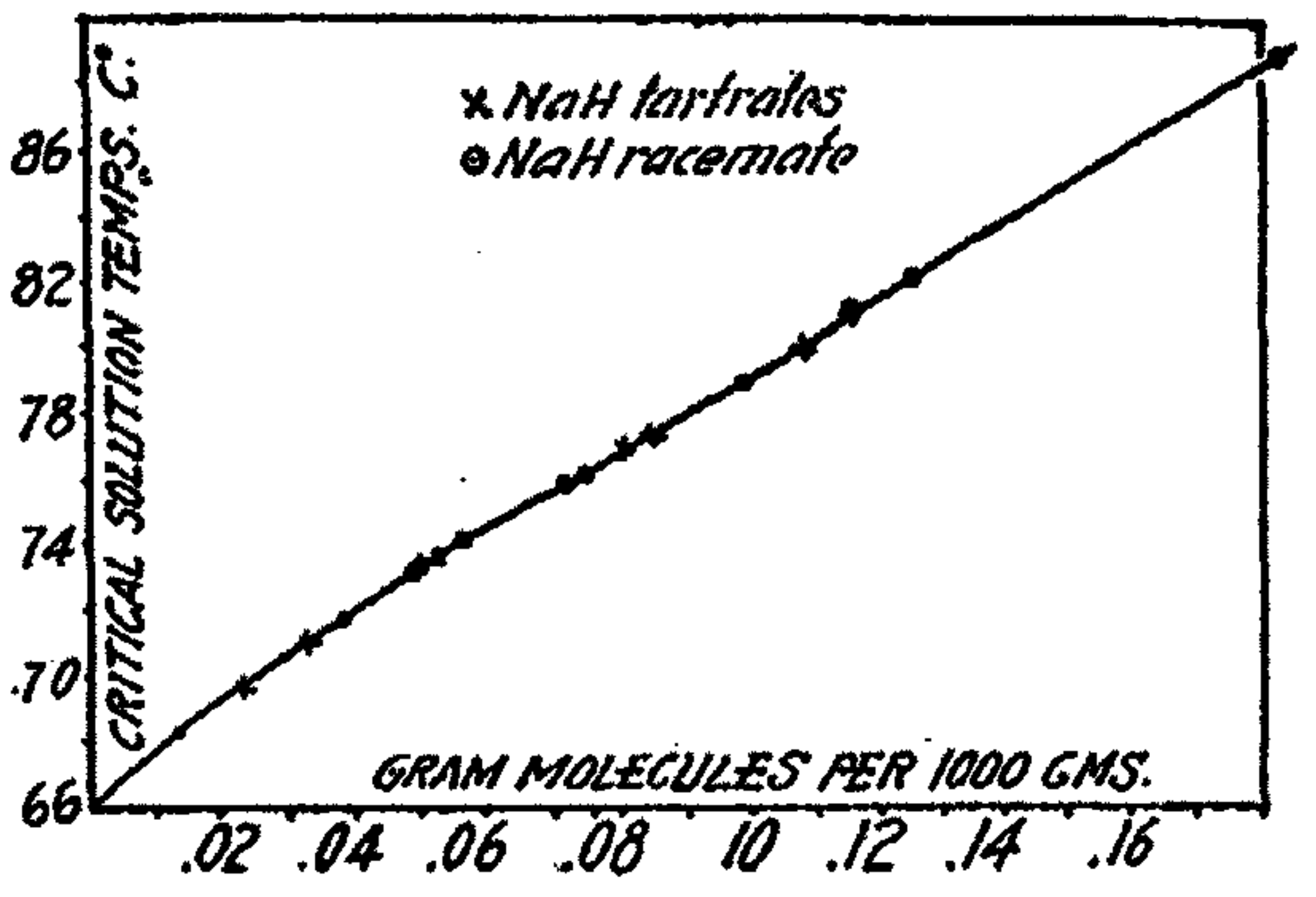

FIG. 3

Colloids

Dialysed colloidal gold, ferric hydroxide, and silver (by the Bredig method) were found to raise appreciably the C. S. T. The results are not included owing to difficulty in allowing for traces of electrolyte and changing stability.

Optical Isomerides

Fig. 3 gives the result for actual C. S. T. plotted against molecular concentration for sodium hydrogen racemate and d. sodium hydrogen tartrate. Both substances lie on the same curve.

Summary

The following are the main results:—

(1). In the region of critical opalescence phenol water solutions polarise light with a change in the angle at the C. S. T. The homogeneous solution above the C. S. T. is of the nature of an isocolloid.

(2). A series corresponding to the Hofmeister series is arrived at by examination of the effect on C. S. T. of substances soluble only in water.

(3). The change of C. S. T. by substances soluble in phenol only cannot be used for determination of molecular weight.

(4). An optically active substance and a racemate have the same effect on the C. S. T.

(5). Viscosity and conductivity changes in the region of the C. S. T. are shown by curves.

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A RELATIONSHIP BETWEEN ATOMIC NUMBERS AND THE PROPERTIES OF IONS IN THE CRYSTAL LATTICE[1]

BY ARTHUR F. SCOTT

The various relationships between the properties of ions and their atomic numbers have formed the subjects of a number of papers published during the last few years. The highly suggestive papers of Bragg[2], Davey[3], and Grimm[4] in particular have pointed out the relationship between the radii of ions and their atomic numbers, a relationship which the present communication purposes to establish in a somewhat more general, quantitative form. Of the factors that determine the distance between ions, the point centers in a lattice, the two primary ones appear to be the dimensions of the ions proper and their external electrostatic fields which control the equilibrium position assumed by ions in a crystal. Since both of these are characteristic properties of an ion, they must be intimately connected with the structure of the atom.

It is one of the canons of modern atomic theory that the internal structure of atoms up to the periphery is regulated exclusively by the positive nuclear charge, the atomic number. Positive ions, therefore, formed by the loss of peripheral electrons may be considered to have dimensions dependent on the atomic number. For the same reasons we may believe the residual, external field of an atom to be similarly related to the atomic number. But with an ion, the external action is also dependent on the number of electrons lost by the original, neutral atom; and, consequently, since periodicity is a function of the number of electrons in the outer shell, we would expect the external field to exhibit distinct periodic changes, and at the same time to undergo a regular variation with the atomic number. If our premise is correct, that the lattice distance of a crystal depends on the dimensions and external fields of the constituent ions, we may then, on the basis of the above reasoning, make the general statement that the controlling factors in determining the distance between a positive ion and a negative ion (anion or electron) are the atomic numbers of the two ions. A confirmatory illustration of this statement is found in the familiar fact that the atomic volumes of isotopes are identical.

Because of our fragmentary knowledge of the dimensions and external actions of ions, it would be difficult to establish what function the distance is of the atomic numbers. Nevertheless, an empirical rule which does express this relationship to an apparently quantitative degree is contained in the following general equation:

$$d_o = a \ln\left(Z_c - Z_a\right) + b. \qquad (1)$$

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[1] Contribution from Department of Chemistry of Reed College.

[2] Bragg: Phil. Mag., (6) **40**, 169 (1920).

[3] Davey: Phys. Rev., **23**, 318 (1924).

[4] Grimm: Z. physik. Chem., **98**, 353 (1921.)

where d_0 is the shortest distance between ions; $Z_c - Z_a$ represents the absolute value of the difference of the atomic numbers of the cation and anion; and *a* and *b* are constants. We thus have a linear relationship between the lattice distance and a function of the atomic numbers. However, in order to avoid any misunderstanding, it must be understood that there are sound theoretical grounds for believing that the above variation with the atomic numbers in any series will not always be regular but will show a marked discontinuity in the majority of cases. The reason for this discontinuity is to be found in Bohr's suggestion that in the elements following argon the electrons instead of always going into the outer shell commence to fill up the vacant places in the inner shell. Such a change in the sequence wherein the orbits are filled up must also be related to the magnitude of the atomic number. Nevertheless the elements that precede and follow argon differ so in performance, that it appears that the radii and external field of the ion cannot vary in the same manner in both cases:—even though they do vary regularly with the atomic number. Under these circumstances we would expect a discontinuity to appear in any group at the element with an ion structure similar to argon; and in the periods following argon we would also expect irregularities to appear corresponding to divergences from the normal rule on the part of the electrons. For the negative ions, such as the halogens, essentially the same principles would be true.

By far the most diverse group of crystalline substances to test Equation 1 with are the metallic elements. It is relatively simple to picture the lattice structure of one of the alkali metals if we consider it to be essentially similar to that of sodium chloride with the chlorine ion replaced by an electron. It is not so easy, however, to devise a satisfactory representation for more complicated cases, such as silicon, where we have four valence electrons to place. For want of a more definite hypothesis it will be necessary to make two assumptions in order that all the metals can be treated in the same manner. First, we will postulate that the negative charge of all the electrons is localized in one unit. For example, in the case of silicon with its four valence electrons, we will think not of four electrons but of one unit with four negative charges which we may term an electron-ion. Now it is patent that with this conception all the elements could be treated in the same manner as the alkali metals, were it not for the fact that the positive ions of the different elements have been shown to form various types of lattices. We shall therefore have to make a second assumption: We will imagine that an electron-ion is located between every pair of positive ions and that this electron-ion determines the distance between the positive ions (the equilibrium status) just as in the crystal of sodium chloride, the distance between the sodium ions has been shown to depend on the chlorine ion. One other aspect of the problem must be mentioned here. In some cases, as in the hexagonal lattice the distance between two positive ions is not the same for the different neighboring ions. There is, however, a minimum distance to which they can approach and it is this minimum distance which is implied in the second assumption above. Such a portrayal is not inconsistent with the general properties of

TABLE I

Nearest Approach of Ions in Metals

Element	Z	Z+e	ln (Z+e)	$2d_0$	Type of Lattice Known or assumed	Authority
Helium	2	2	0.693	4.13	Rock-salt	Calculated
Lithium	3	4	1.386	3.03	Body-centered cubic	Hull[1]
Beryllium	4	6	1.792	2.28	Hexagonal	McKeehan[2]
Carbon	6	10	2.303	1.50	Hexagonal	Debye[3]
Sodium	11	12	2.485	4.00	Body-centered cubic	Hull[1]
Magnesium	12	14	2.639	3.22	Hexagonal	Hull[1]
Aluminum	13	16	2.773	2.86	Face-centered cubic	Hull[1]
Silicon	14	18	2.890	2.35	Tetrahedral cubic	Debye[4] Hull[1]
Argon	18	18	2.890	5.26	Rock-salt	Calculated
Potassium	19	20	2.996	4.48	Body-centered cubic	McKeehan[2]
Calcium	20	22	3.091	3.93	Face-centered cubic	Hull[5]
Titanium	22	26	3.258	2.90	Hexagonal	Hull[6]
Vanadium	23	28	3.332	2.64	Body-centered cubic	Hull[7]
Manganese	25	32	3.466	2.53	Body-centered cubic	Calculated
Iron	26	34	3.526	2.48	Body-centered cubic	Hull[1]
Gallium	31	34	3.526	3.03	Face-centered cubic	Calculated
Germanium	32	36	3.584	2.43	Tetrahedral cubic	Kolkemeyer[8]
Krypton	36	36	3.584	5.60	Rock-salt	Calculated
Rubidium	37	38	3.638	4.93	Body-centered cubic	Calculated
Strontium	38	40	3.689	4.33	Face-centered cubic	Calculated
Zirconium	40	44	3.784	3.18	Hexagonal	Hull[6]
Molybdenum	42	48	3.871	2.72	Body-centered cubic	Hull[9]
Ruthenium	43	51	3.932	2.64	Hexagonal	Hull[9]
Silver	47	48	3.871	2.88	Face-centered cubic	Vegard[10]
Indium	49	52	3.951	3.24	Tetragonal face-centered	Hull[9]
Tin	50	54	3.989	2.80	Tetragonal cubic	Bijl[11]
Xenon	54	54	3.989	5.84	Rock-salt	Calculated
Cesium	55	56	4.025	5.34	Body-centered cubic	Calculated
Barium	56	58	4.060	4.52	Face-centered cubic	Calculated
Lanthanum	57	60	4.094	3.75	Face-centered cubic	Calculated
Cerium	58	61	4.111	3.64	Face-centered cubic	Hull[6]
Praseodymium	59	62	4.127	3.71	Face-centered cubic	Calculated
Neodymium	60	63	4.143	3.65	Face-centered cubic	Calculated
Samarium	62	65	4.174	3.56	Face-centered cubic	Calculated
Tantalum	73	78	4.357	2.83	Body-centered cubic	Hull[9]
Tungsten	74	80	4.382	2.73	Body-centered cubic	Debye[12], Hull[9]
Osmium	76	84	4.431	2.66	Hexagonal	Hull[6]
Gold	79	81	4.394	2.88	Face-centered cubic	Vegard[13]
Thallium	81	84	4.431	3.38	Face-centered cubic	Becker and Ebert[14]
Lead	82	86	4.454	3.48	Face-centered cubic	Vegard[13]
Thorium	90	94	4.543	3.54	Face-centered cubic	Bohlin[15] Hull[6]
Uranium	92	98	4.585	2.99	Body-centered cubic	Calculated.

[1] Hull: Phys. Rev., 10, 661 (1917). [2] McKeehan: Proc. Nat. Acad. Sci., 8, 270 (1922.)

[3] Debye: Physik. Z., 18, 291 (1917). [4] Debye: Physik. Z., 17, 277 (1916).

[5] Hull: Phys. Rev., 17, 12 (1921). [6] Hull: Phys. Rev., 18, 88 (1921).

[7] Hull: Jour. Franklin Inst., 193, 189 (1922).

[8] Kolkmeyer: Proc. Roy. Acad. Sci., Amsterdam, 21, 405 (1919).

[9] Hull: Phys. Rev., 17, 571 (1921).

[10] Vegard: Phil. Mag., (6) 31, 86 (1916).

[11] Bijl: Proc. Roy. Acad. Sci., Amsterdam, 21, 501 (1919).

[12] Debye: Physik. Z., 18, 483 (1917).

[13] Vegard: Phil. Mag., (6) 32, 65 (1916).

[14] Becker and Ebert: Z. Physik, 16, 165 (1923).

[15] Bohlin: Ann. Physik., 61, 421 (1920).

metals. For instance, if we conceive of all the electrons lumped together in electron-ions (which contain the maximum number of valence electrons) and if we think of the nearest approach of the positive ions as being determined by these electron-ions, then we can imagine electrons either in the form of these maximum units or singly, swarming throughout the lattice of positive ions without disarranging the structure permanently, the situation which obtains during the process of electrical conduction.

The above hypothesis has been developed to make the application of Equation 1 to the metals more understandable. Therefore, to evaluate the term $Z_c - Z_a$ which is equal to the difference in the atomic numbers or the positive charges of the ions concerned, it is necessary to ascribe a negative value to the Z of the electron-ion which will be equal to the number or valence electrons. In short, $Z = -e$ where e represents the number of valence electrons or the maximum valence of the element. Since e never exceeds the atomic number of an element, we can hereafter write Equation 1 in the form:

$$d_o = a \ln (Z+e) + b. \qquad (2)$$

From the foregoing deduction it will be seen that d_o is equal to one half of the distance which is commonly termed "the nearest approach" of ions. To avoid subsequent ambiguity this distinction will be maintained although the distances employed in the case of the metals will always be the "nearest approach" or $2\,d_o$.

Figure 1 depicts the results obtained when the distance between the ions, $2d_o$, is plotted against the natural logarithm of the term, $(Z+e)$. The source of the values for d_o is given in Table I which also contains the other essential data for the construction of Figure 1. It seemed desirable to supplement the meagre data from X-ray analysis and therefore a number of values for the d_o were computed in the usual manner from the atomic volumes of the elements. In all of these cases the value for the density employed in the calculations is taken from Landolt-Börnstein's Tabellen; and the type of lattice assumed is in each particular instance determined by the types of lattices known for the neighboring elements. The results of these two modes of determining lattice distances are usually in satisfactory agreement for metals and consequently they may be considered to be comparable. Only when an element has no definite crystal structure under normal conditions is any serious discrepancy likely to occur. Potassium is such a case, for McKeehan has found that this element has a crystal structure only at low temperatures, and he made a measurement of the lattice distance at about −150°C. With the atomic volume derived from this measurement it is possible to use the cubical coefficient of expansion of sodium as a rough approximation in order to get the value for d_o at a comparable temperature. This calculation has been carried out and since the values for three of the alkali metals are therefore necessarily obtained from calculations, those for lithium and sodium have also been calculated with the unusually precise density data so that this series can be on a more comparable basis. The solid inert elements were assumed to have a structure analogous to sodium chloride inasmuch as the salts formed by the ions of adjacent elements such as barium sulfide all exhibit the same tendency to form the simple cubic lattice. This assumption was made in spite of the preliminary notice published by Simon and von Simson[1] that solidified argon forms face-centered cubic crystals. The densities at absolute zero of the solid inert elements used in the calculations are those computed by Hertz[2] according to the method of Lorentz[3] which involves the density of the substance at its boiling point, melting point, and critical temperature.

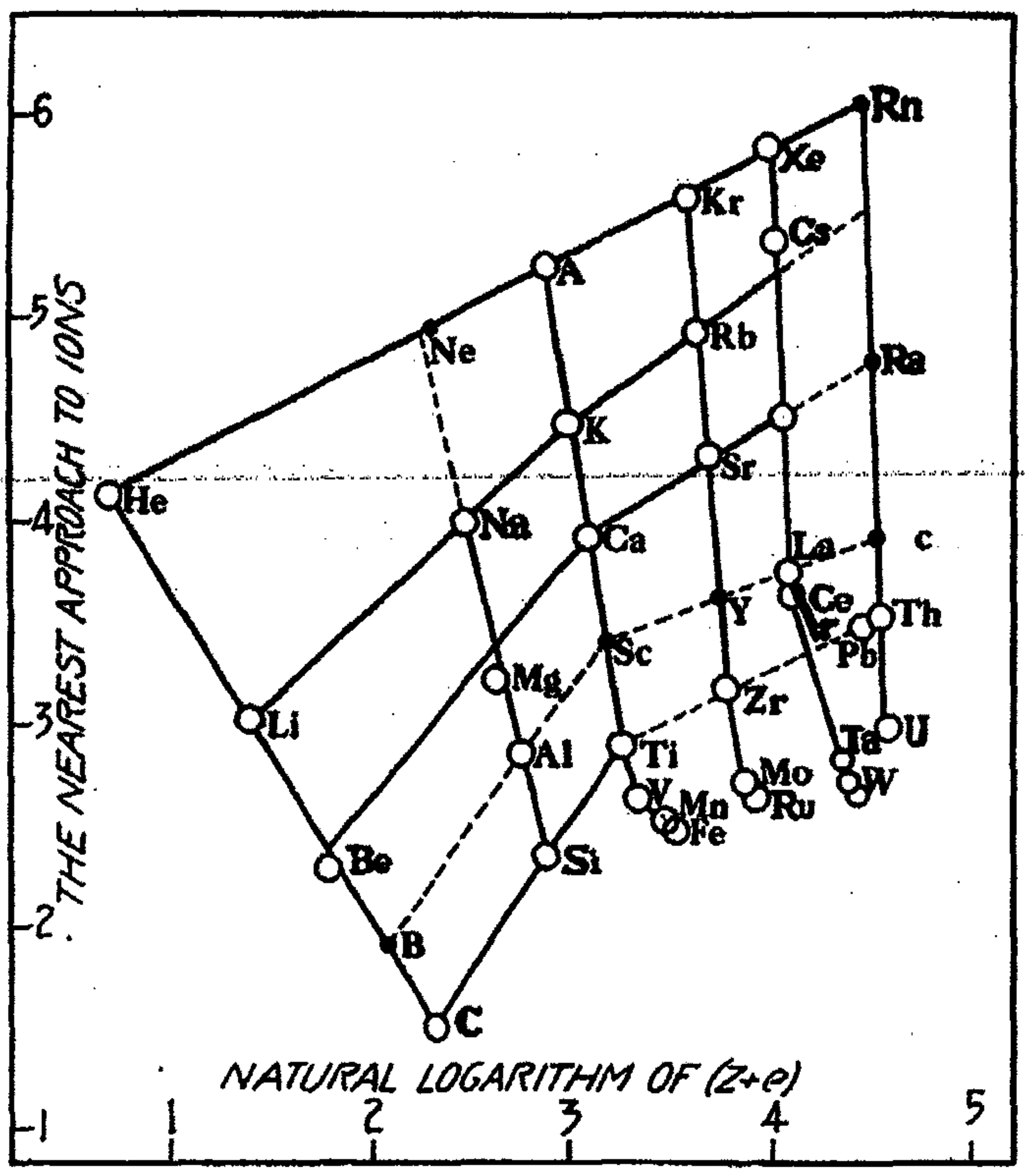

Fig. 1
The Periodic Variation of the Ion Radii of the Elements.

Figure 1 displays a new means of portraying the periodic variation of the radii of the ions. The horizontal lines are drawn through the points corresponding to the elements of each group; and the vertical lines place the elements of the different periods. The slight divergences exhibited by cesium, beryllium, and magnesium, must be attributed to the suspected inaccuracy of the data. The general characteristics of the two series of lines are quite apparent. Up to and including the fourth group we find all of the elements varying regularly with ln(Z+e) with the predicted discontinuity at the ion with the struc-

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[1] Simon and von Simson: Naturwissenschaften, **11**, 1015 (1923).

[2] Hertz: Z. anorg. Chem. **105**, 171 (1919).

[3] Lorentz: Z. anorg. Chem., **94**, 240 (1916).

ture of argon appearing at potassium, calcium, scandium, and zirconium, respectively. In the groups beyond the fourth the first two elements are wanting due to their non-metallic nature and the remaining elements exhibit a distinctly regular, although different variation. Concerning the vertical lines it is only necessary to note that the heavy black line marked *r* indicates the location of the points for praseodymium, neodymium, and samarium, which fall accurately and so closely together on a line that they cannot be shown. It is also because of this same mechanical difficulty that only the first element of each of the triads of the eighth group is shown.

By means of the data given in Table I a skeleton graph may be constructed on which the elements may be placed for which data are not available. The points for such elements are indicated in Figure 1 by black dots and are determined by plotting the correct values for the term, $\ln(Z+e)$, on the appropriate lines. Hence it is possible to compute the density or the atomic volumes of elements not hitherto known if we assume a type of lattice structure. Thus if we ascribe to radium a face-centered cubic lattice similar to the other alkaline earths, the density is found to be about 4.8 instead of the value, "nearly 6" recorded in the literature. Similarly the atomic volume of scandium is not known and according to Figure 1 it would be 16.7 when a face-centered cubic lattice is assumed. The value approximated by Sommerfeld[1] from Lothar Meyer's curve is 18.6.

No explanation can be offered at this time for the position of the inert gases on this chart. It can only be stated that the location of the points on the appropriate lines can scarcely be fortuitous; nor can the straight line drawn through the points corresponding to these elements be the result of chance. The divergence of the horizontal "group" lines from a straight line becomes less and less as the topmost line is approached, and this fact would indicate that the inert gases form the limit of this property.

Figure 1 does not contain points for any of the ions that do not have the electronic structures of inert gases because the introduction of additional lines would only obscure the striking symmetry exhibited by the figure. Moreover a separate graph is not given because of insufficient data and more especially because these ions do not display such obvious regularities. Nevertheless it is profitable to note a few of the more important characteristics of these ions. When the data for the elements of the first sub-group are plotted, it is possible to draw a straight line through the points of lithium, silver, and gold, the point for copper coming irregularly in the vicinity of those for vanadium and manganese. Likewise for the third sub-group it is interesting to observe that the points for aluminum, gallium, indium, and thallium all lie on a straight line. Finally, if the points for the elements of the fourth group are plotted, it is found that a line passes through the points for carbon, germanium, and tin, whereas lead falls on the line through the points for zirconium and thorium, as is shown in Figure 1. Owing to the lack of data and also owing to the fact that these elements which constitute the sub-

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[1] Sommerfeld: "Atom Structure and Spectral Lines." Footnote, page 105.

groups frequently exist in several different modifications, it is unwise to make any generalizations.

With this brief description of the relationship between the ionic radii and atomic numbers as a starting-point we will now consider those other properties of the elements which are commonly associated with the lattice distances; namely, the compressibility, and the melting point. Quite apart from theoretical grounds it is only necessary to recall the familiar Lothar Meyer curves for these properties in order to perceive their close connection with the radii of ions; and the marked parallel variation of all these properties with the atomic number is sufficient to suggest that, if the radii are related to the atomic numbers as has been shown, then all of these properties must likewise be ultimately dependent on the atomic number. We may assume that if the proper function could be ascertained, we could obtain a periodic representation for these physical properties similar to Figure 1. Unfortunately there are not sufficient data available to test this point although a preliminary examination with the data on hand shows that, by employing the cube root of these properties, representations analogous to Figure 1 would be obtained. At this time, however, only the data for the alkali metals will be considered because these data are probably the most trustworthy. In Figure 2 are shown the results obtained by plotting the values for 2 d_o, and the cube root of the compressibilities, and the reciprocal melting points of these elements against the term, ln(Z+e). The necessary data are given in Table II and are taken from Landolt-Börnstein's Tabellen.

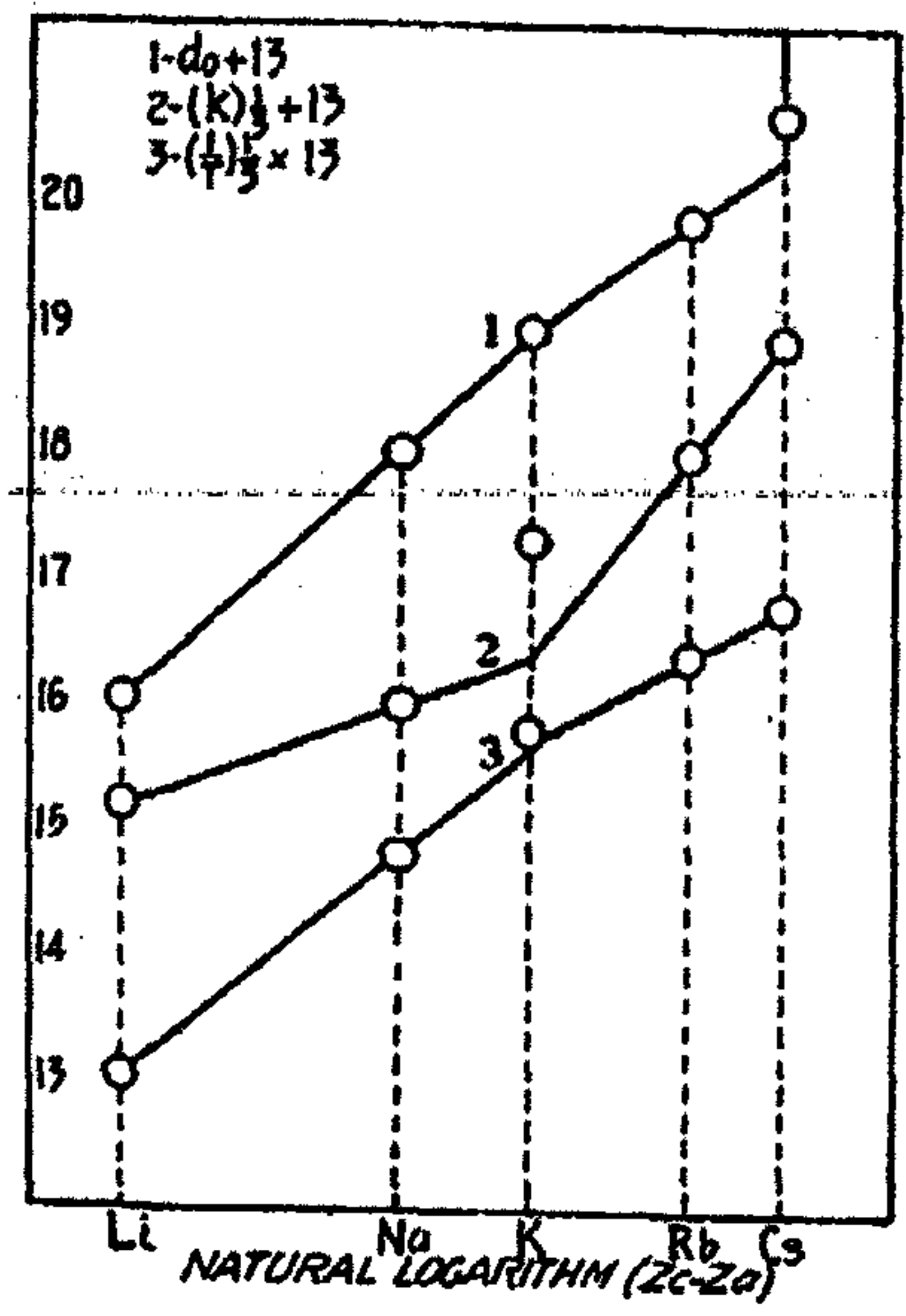

Fig. 2

The Variation of the Radii, the Compressibility and Reciprocal Melting Point of Alkali Metals.

Table II

The Radii, Compressibilities and Melting Points of the Alkali Metals

Element	ln (Z+e)	2d_o	Cube root of Compressibility in megabars ×10⁶	(Cube root of Reciprocal Melting point ×10
Lithium	1.386	3.03	2.08	13.0
Sodium	2.485	4.00	2.50	13.9
Potassium	2.996	4.48	3.16	14.4
Rubidium	3.638	4.93	3.50	14.7
Cesium	4.025	5.34	3.94	14.9

Apart from the discrepancy of the point for the radius of cesium which has already been mentioned, the point for potassium is irregular in both of the other cases. This is not at all disturbing if it is recalled that potassium has no crystalline structure at high temperatures, a fact which would necessarily cause it to behave abnormally. It is to be noted that with lines 2 and 3 the two branches intersect at the vertical line corresponding to the value of ln(Z+e) for potassium thus forming triple points which may be taken to represent the probable values for crystalline potassium in both cases. We have therefore these three properties of the alkali metals similarly related to the same function of the atomic numbers and this fact may be considered

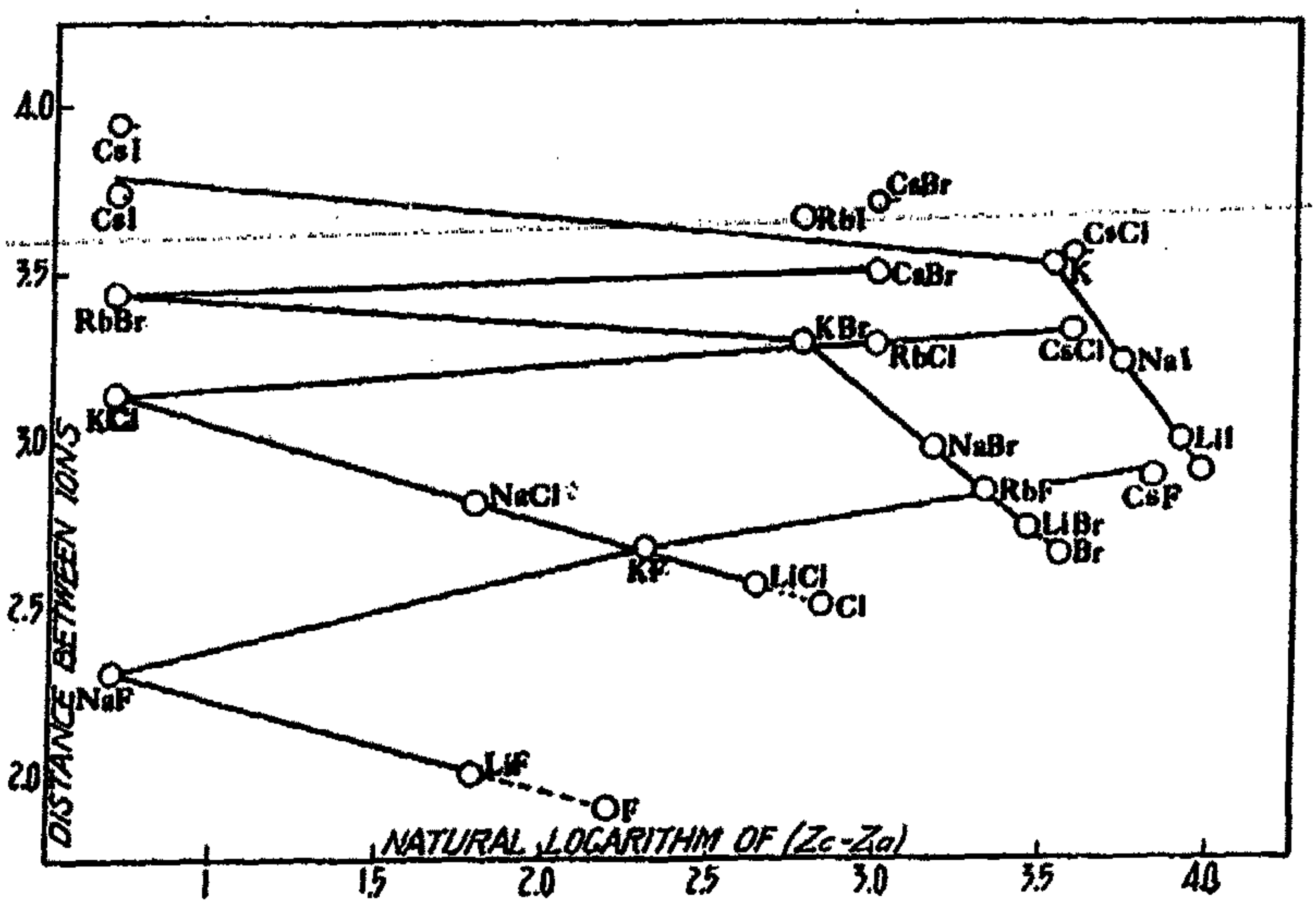

Fig. 3

The Variation of the Lattice Distances of a Series of Halide Salts of the Alkali Metals with with the Function ln (Z_c-Z_a).

convincing evidence of the validity of the extension of Equation 2 to apply to other properties than the radii.

Besides the metals there is the large class of polar compounds, the salts, which are characteristically crystalline. It can be seen at the outset that we have here far more complicated possibilities than exist with the metals, for the atomic number of the negative ion as well as that of the positive ion may vary over a wide range in any specific series of salts. However, to test the applicability of Equation 1 to such cases we will use the extraordinarily accurate data available for the alkali halides, and plot the distances between the ions against the natural logarithm of absolute value of $Z_c - Z_a$, as is shown in Fig. 3. The essential data are given in Table III.

TABLE III

The Lattice Distances of the Alkali Halides

	Fluoride			Chloride			Bromide			Iodide		
	ΔZ	$\ln \Delta Z$	d_o	ΔZ	$\ln \Delta Z$	d_o	ΔZ	$\ln \Delta Z$	d_o	ΔZ	$\ln \Delta Z$	d_o
Li	6	1.792	2.009	14	2.639	2.567	32	3.446	2.745	50	3.912	3.007
Na	2	0.693	2.311	6	1.792	2.816	24	3.178	2.982	42	3.738	3.233
K	10	2.303	2.680	2	0.693	3.140	16	2.773	3.294	34	3.527	3.527
Rb	28	3.332	2.85	20	2.996	3.291	2	0.693	3.441	16	2.773	3.668
α-Cs	46	3.829	2.88	36	3.584	3.32	20	2.996	3.51	2	0.693	3.74
β-Cs	46	3.829	2.88	36	3.584	3.567	20	2.996	3.719	2	0.693	3.952

With the exception of the fluorides the values for d_o are taken from a paper by Fajans and Grimm[1] and were in turn calculated by them from the very careful density measurements by Baxter and Wallace[2]. The values for the fluorides of lithium, sodium and potassium are from determinations by Spangenberg. No measurements of the densities of rubidium and cesium fluorides have been found in the literature; nevertheless, Fajans and Grimm have shown how their molecular volumes may be computed and the data given in the table are obtained in this way, using for the computations the new density determinations of the other fluorides by Spangenberg[3]. The cesium salts, excepting the fluoride which has the same structure as sodium chloride, have been shown to have a body-centered lattice structure. These salts are given in Table III as the β-salts and the values for d_o have been calculated by Grimm from the density measurements of Baxter and Wallace. However, it is not unlikely that these cesium salts, if not some of the other alkali halides, exist in more than one modification. If so, they would resemble the chemically related ammonium halides which the work of Bartlett and Langmuir[4] demonstrated could exist in two modifications; the stable compounds at the lower temperature have the same structure as cesium chloride, and above a definite transition point the structure changes to the rock-salt arrangement. These two types are termed the β and α salts respectively. Further evidence, also of a suggestive nature, is found in the recently published communication of Richards and Saerens[5] that the fused salts, rudibium bromide and iodide, and cesium iodide, undergo a permanent contraction amounting to somewhat less than one per cent. when they are allowed to stand for a relatively short period of time. This abnormal behavior is readily understandable if it is caused by the transition of the salt crystals from one form to another.

If these cesium salts can exist in two modifications, a condition which we will assume, it will be necessary to use the values of d_o for the α-salts because

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[1] Fajans and Grimm: Z. Physik., 2, 299 (1920).

[2] Baxter and Wallace: J. Am. Chem. Soc., 38, 259 (1916).

[3] Spangenberg: Z. Kryst., 57, 494 (1923).

[4] Bartlett and Langmuir: J. Am. Chem. Soc., 43, 2, 86 (1921).

[5] Richards and Saerens: J. Am. Chem. Soc., 46, 934 (1924).

the ions in salts of this type approach nearer than in the β salts. Although such salts are purely hypothetical, it is possible to compute values for d_o by utilizing the relationship of Fajans and Grimm[1]. This has been done, with the molecular volume of cesium fluoride, obtained as previously described, serving as the basis of the calculation and the results are given in Table III. In Figure 3 only these values for the hypothetical α-cesium salts are employed in the representation of Equation 1; the circles with the short side-tails indicate the β-salts and are inserted merely for reference.

A word needs to be said concerning the accuracy of these data. Of course, the calculated values are least certain; next to them in the order of uncertainty come the figures for the fluorides, the densities of which are difficult to determine. The accuracy of the other data would be indisputable were it not for the uncertainty introduced by the abnormal performance noted by Richards and Saerens in the case of salts of rubidium bromide and iodide, and cesium iodide. We therefore cannot have much confidence in the data for these salts.

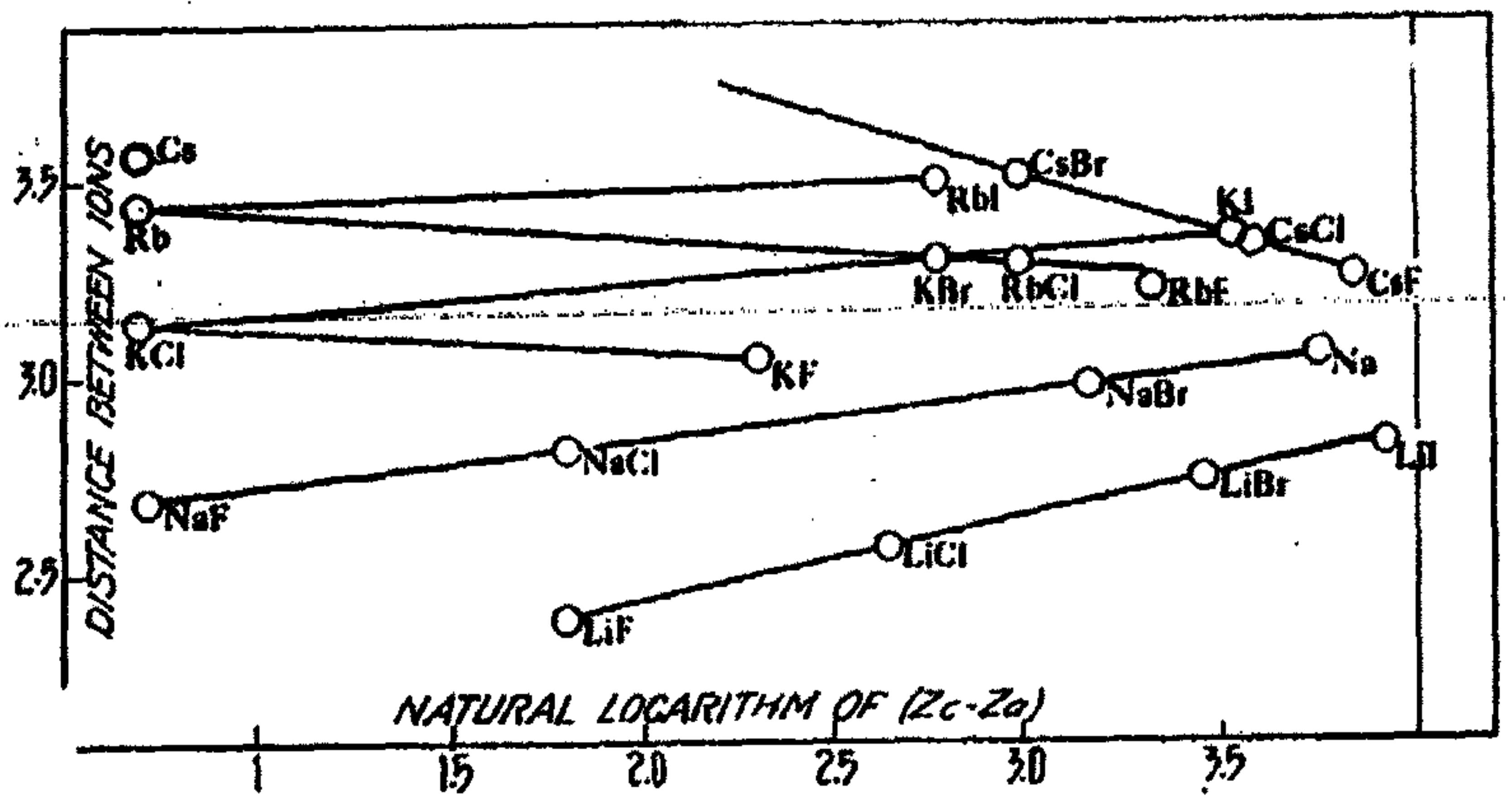

Fig. 4

The Variation of the Lattice Distances of a Series of Alkalihalidic Salts with the Function $\ln(Z_c\text{-}Z_a)$.

The characteristic features of the various lines in Figure 3 will become apparent through the consideration of two typical lines. We may take first the lines on which the points for the chlorides fall. The change and the reversal in the sign of the constant a at the point for potassium occurs similarly with all the other lines at the point where the difference $(Z_c - Z_a)$ changes sign; that is, wherever the atomic number of the invariant ion in a series is exceeded by the atomic number of the other ion. The other characteristic is the customary discontinuity in the lines at the potassium ion; in the case of the lines through the chlorides, this second characteristic is masked by the first.

Since the distances between ions show a regular variation with the atomic number of the varying cation, it is interesting to compute d_o by extrapolation

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[1] Fajans and Grimm: Z. Physik, 2, 299 (1920).

when the anion is in combination with a hypothetical cation of zero atomic number. Since d_o in all other cases represents the distance at which two ions are in equilibrium to each other, we must interpret it to represent in this special case the distance at which an anion is in equilibrium with a hypothetical cation of zero atomic number; or, it is equal to one half the distance between two similar anions in equilibrium in a crystal. The nearest approach to such a hypothetical situation is to be found with the almost identical analogs, the solid inert elements, where the only difference lies in the nuclear charge which is one unit greater for the inert element than for the corresponding anion. We have already computed (Table I) the distance between the atoms in the solid inert elements on the assumption that they form simple cubic crystals and it will now be interesting to compare these results with the values for 2 d_o obtained in the present case. The comparison is made below:

Chlorine	5.02	Bromine	5.32	Iodine	5.82
Argon	5.26	Krypton	5.60	Xenon	5.84

Further development of this interesting hypothesis will not be given at this time.

Up to this point we have not had occasion to consider any series of compounds in which the negative ion varied while the positive ion remained the same, a case that obtains with the halide salts of each of the alkali metals. An examination of Figure 3 shows the variation of d_o with the term, ln $(Z_o - Z_a)$ to be entirely different in such cases. However, it is found that by making the constant *b* depend on the anion of the salt it is possible to bring the points for all the salts of one element on the same line. In practice this is accomplished by assuming a line through the points for the chloride and bromide and by then determining the arbitrary correction for *b* necessary to bring the points for the fluoride and iodide on the line. These arbitrary corrections are the same in every case and are as follows:

Ion	Correction
Fluoride	−0.365
Chloride	.....
Bromide	.....
Iodide	+0.170

The results obtained when these corrections are applied are exhibited in Fig: 4. Here as in Fig. 3 the only marked defect in the figure occurs with cesium iodide.

In order to gain assurance that the relationships illustrated in Figures 3 and 4 are not illusory, the linear equations have been established by taking two points on each line as determining points; the values for d_o for the other points on the line have then been computed from the known value of ln $(Z_o - Z_a.)$ The data for the constants of these linear equations are given in Table IV.

TABLE IV

Values for the Constants of Equation 1

Equation No.	Determining Points	a	b
1	LiCl − NaCl	−0.2940	3.343
2	KCl − RbCl	+0.0626	3.097
3	LiBr − KBr	−0.8157	5.556
4	NaI − KI	−1.3981	8.458
5	LiCl − LiBr	+0.2152	1.999
6	NaCl − NaBr	+0.1198	2.581
7	KCl − KBr	+0.0740	3.089
8	RbCl − RbBr	−0.0651	3.486
9	CsCl − CsBr	−0.3197	4.466

In Table V we have tabulated the different values for d_o computed with the aid of these equations. No figures are included which were employed as a basis for determing the constants of the equations. Naturally the corrections for *b* for the fluoride and iodide salts are applied in the proper equations.

TABLE V

The Calculated Distances between Ions compared with Values from Other Sources

Salt	Equation Used	Distances between Ions (d_0)				
		Calc. Eq. 4	Densities Table III	Bragg's Empirical Law	X-ray Analysis	
					Davey	Wyckoff
LiF	5	2.020	2.019	2.17	2.007	2.07
LiI	5	3.011	3.007	2.90	3.537	3.03
	4	2.989	3.007	....	.....	....
NaF	6	2.299	2.322	2.44	2.310	2.31
NaBr	3	2.964	2.982	2.92	2.968	2.98
NaI	6	3.238	3.230	3.13	3.231	3.24
KCl	1	3.139	3.140	3.12	3.138	3.13
KI	7	3.520	3.527	3.47	3.525	3.55
RbF	8	2.90	2.85	2.92	.....	....
CsF	9	2.88	2.88	3.04	3.004	3.01
α-CsCl	2	3.231	3.32	3.32	.....	....

In selecting for the determinant points of the equations upon which the above calculations depend, the values for those salts that lie nearest together on a line, we have the least favorable condition, for an error in either one of the determining points is greatly magnified in the calculated results. Bearing this in mind, the concordance between the values calculated from the equations and those computed from the density measurements (which data should, of course, be the basis of comparison) is entirely satisfactory, and can be taken as evidence of the validity of the general equation. As a means of further reference, data for d_o from several other sources are also presented in

Table V. The data in the fourth column are computed on the assumption that Bragg's empirical law for the additivity of ionic radii is correct, and the values for the radii are taken from his compilation. The last two columns contain the data from measurements by X-ray analysis; the first series contains the values published by Davey[1] and the second, those by Wyckoff[2].

There is no reason to believe that the salts of the alkali halides are unique in respect to the relationship between the lattice distance and the atomic numbers of the ions. We would expect the same empirical rule to hold for all other classes of salts. Unfortunately, corresponding accurate data have not been determined for salts other than the alkali halides and therefore the point in question cannot be treated at the present time. Nevertheless it is possible to obtain data for the oxides, sulfides, selenides, and tellurides of the alkaline earths, and representations of these data, similar to Figures 3 and 4, exhibit without exception the identical characteristics which were noted with the alkali halides, when due allowance is made for the greater inaccuracy of the data. Similarly with the same qualification for the uncertainty of the data, the hydrides of the alkali metals behave in a normal fashion. Consequently we must conclude that Equation 1 is not singularly valid for the pure elements but that it is probably valid for the salts; its limitations cannot be ascertained at this time.

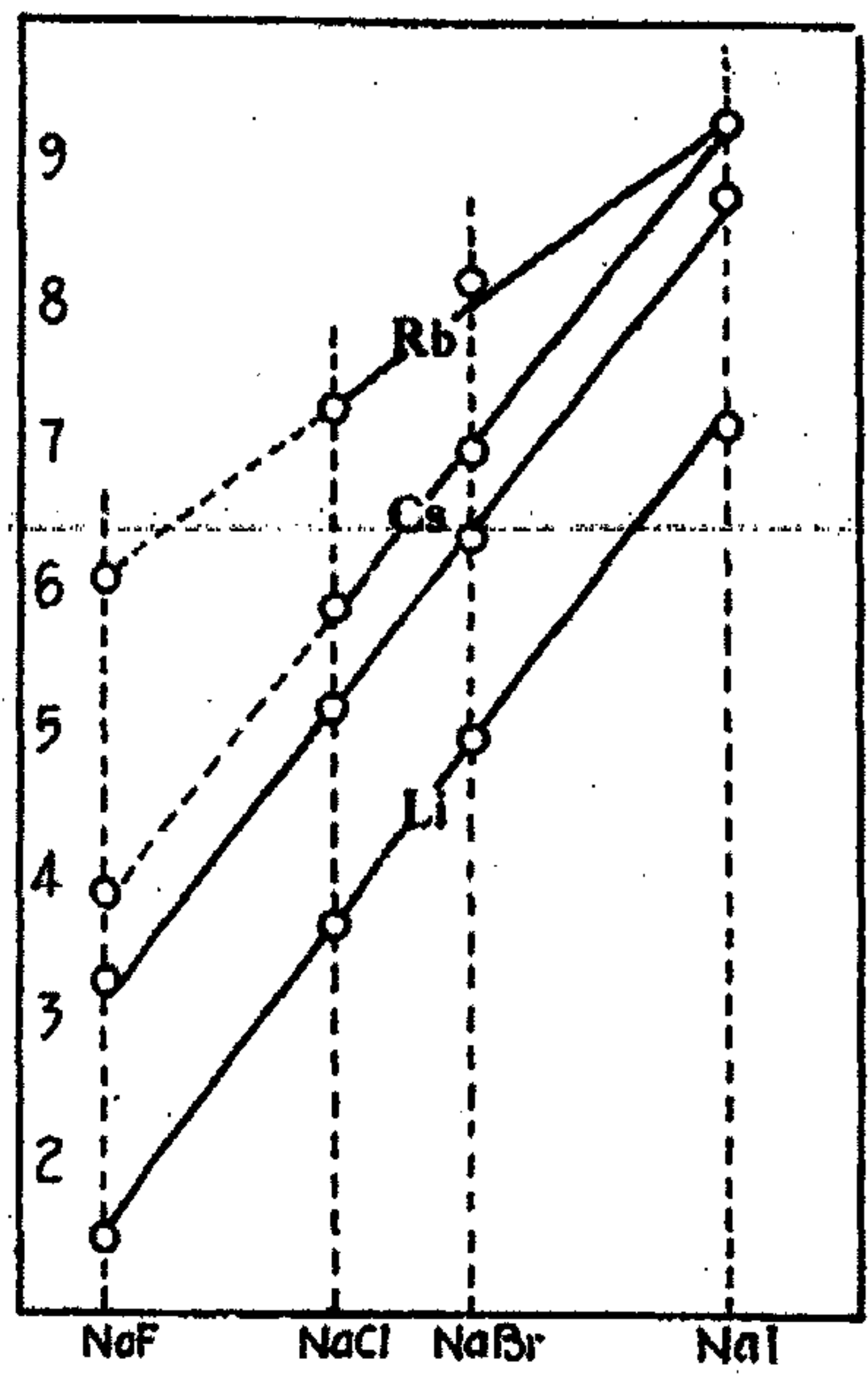

FIG. 5
Compressibilities of Alkali Halides Plotted Against Compressibilities of the Sodium Halides.

As an outgrowth of the study of the metals it was indicated how the various physical properties might be expressed by a relationship to the atomic numbers similar to the one found for the radii. This aspect of the problem was suggested by the parallelism of the Lothar Meyer curves for these different properties. The following discussion will be an attempt to demonstrate that a similar parallelism exists for many of the physical properties of the salts, a parallelism which, like the Lothar Meyer curves, must be fundamentally connected with the atomic number. Here, as previously, we will deal with the best known series of salts, the alkali halides.

A number of diverse properties of these salts may be expressed by the general equation:

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[1] Davey: Phys. Rev., 21, 143 (1923).

[2] Wyckoff: J. Franklin Inst., 195, 353 (1923).

$$P_{c_1x} = \alpha P_{c_2x} + \beta \qquad (3a)$$
$$P_{a_1y} = \alpha P_{a_2y} + \beta \qquad (3b)$$

where P represents any definite property, c_1 and c_2 represent definite cations in combination with any desired anion, x; and a_1 and a_2 represent definite anions in salts with a variable cation, *y*. In both equations α and β are constants. The validity of such equations was first pointed out by Fajans and Grimm[1] in the case of the molecular volumes of the alkali halides. Equations in which P was substituted by V, the molecular volume, were found to reproduce the data quantitatively. Another example which will serve also as an illustration of the nature of this relationship is the compressibility. Figure 5 depicts the compressibilities of the alkali halides plotted against those of the sodium halides.

TABLE VI

Compressibilities of the Alkali Halides in Megabars × 10^6

	Fluoride	Chloride	Bromide	Iodide
Lithium	1.53	3.7	5.0	7.2
Sodium	(2.6)	4.3	5.3	7.1
Potassium	3.31	5.2	6.4	8.8
Rubidium	(6.1)	7.3	8.2	9.3
Cesium	(3.9)	5.9	7.0	9.3

The accompanying data given in Table VI with the exception of the fluorides, are those recently published by Richards and Saerens.[2] The values for lithium and potassium fluoride are taken from determinations by Slater[3]. The figures for the other fluorides are merely approximations obtained by extrapolation and are enclosed in brackets. These data may be expressed by equations similar to (3a) and (3b) by substituting compressibility for P. The agreement in this case, as can be seen from Figure 1, is all that the accuracy of the experimental data warrants.

Besides the compressibility there are other properties of these salts which can be represented by Equation 3, and since this fact is not mentioned in the literature, they will be listed here: the contraction in formation from the elements; the contraction on solution; and the molecular refraction of solutions. In addition, Spangenberg has shown three other properties to follow the same rule, namely, the lattice constants of the crystals; the molecular refraction of the crystals; and finally the dispersion, the molecular refraction for different wave-lengths. In the case of this last property, it must be emphasized that only Equation 3a is valid and not 3b.

We have thus before us eight separate instances of properties all exhibiting the same regularity and, although this list is probably still incomplete, we have a basis for making a rather obvious general deduction. In no case can

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[1] Fajans and Grimm: Z. Physik., 2, 299 (1920).

[2] Richards and Saerens J. Am. Chem. Soc., 46, 934 (1924).

[3] Slater: Phys. Rev., 23, 488 (1924).

we speak of additive properties, of specific properties of ions. We always find that the property attributable to an individual ion is influenced by the ion with which it is in combination. It has been shown explicitly that the lattice distance of crystals can be expressed as a function of the atomic numbers, and, since the lattice constants are one of the eight cases mentioned above, it must be implied that the other properties can similarly be expressed by some function of the atomic numbers of the two ions of a salt.

Summary

The present paper must be considered a preliminary attempt to establish a quantitative relationship between the atomic numbers and the properties of ions. It is shown how the radii of ions in pure elements and the lattice distances of crystals may be expressed with certain qualifications by a linear equation involving the natural logarithm of the absolute difference of the atomic numbers of the ions in a crystal. Furthermore it is indicated how this same empirical relationship may be applied to other physical properties of the metals and salts.

The author wishes to take this occasion to express his indebtedness to his friend, Dr. Louis F. Fieser, for many valuable and helpful suggestions during the preparation of this paper.

THE PROTECTIVE ACTION OF SOAPS ON ZSIGMONDY'S GOLD SOLS

BY B. PAPACONSTANTINOU

Zsigmondy has shown that in aqueous solution a soap can act as a protective colloid towards a gold sol. The object of the present investigation was to extend these results, since a special interest attaches to the study of the protective action exerted by electrolytic colloids, and in the particular case of the soaps. The effects due to a number of substances of similar type can be compared.

The gold sols were usually prepared by the nucleus method of Zsigmondy, whilst the soaps were prepared from the carefully purified acids whose alcoholic solutions were neutralized by the requisite amounts of alcoholic sodium or potassium ethylate. The soaps then obtained were recrystallised from alcohol and carefully dried. In the present work the expression "gold number" has the meaning attached to it by Zsigmondy, *i. e.*, the number of milligrams of soap (or other protective colloid) just sufficient to protect 10 cc. of the red gold sol against colour change produced by the addition of 1 cc. of a 10 per cent NaCl solution under specified conditions. The greater the gold number, the less is the protective action due to the colloid. These numbers have been determined for a series of soaps at *different temperatures* and *concentrations*. Within the limits of the experimental error of the measurements and with the soap concentrations employed, the gold number of a given soap solution was not found to vary with time during the period required for a long series of measurements (see later).

Table I shows the influence of the concentration of a sodium oleate solution on the gold number towards three gold sols. In making these measurements 10 cc. of the gold sol were mixed with the requisite amount of soap solution and enough water added to make the volume up to 15 cc. After 3-4 minutes 1 cc. of the 10 per cent NaCl solution was added and the whole well mixed. The colour of the sol was observed after 15 minutes.

TABLE I

Sodium Oleate. Temp. 17°-18°

Concentration of soap solution in grams per 100 cc.	Gold Numbers Sol A	 Sol B	 Sol C
1.0	1.0	1.0	0.5
0.1	1.4	1.2	1.0
0.01	—	—	1.5

Sol C was a relatively coarse-grained sol prepared by the formaldehyde method without nucleus. Sols A and B have the same gold content and were prepared by the nucleus method, but Sol A contains smaller particles than Sol B. The results in this table show that increase in the concentration of the soap increases its protective action to a certain degree. To secure comparable results the soap solutions used in the following measurements possessed concentrations varying from 0.1 to 0.2 grm. of soap per 100 cc. of solution. The effect of the size of particle in the gold sol on the gold number for a definite soap solution is shown in Table II. In the sols D, E, F, A the size of particle increases regularly from D to A whilst all the sols have the same gold content. The graded sizes were prepared by varying the amount of nucleus solution added to the gold solutions before their reduction. Sol A was prepared by the formaldehyde method. The concentration of the sodium oleate was 0.1 grm per 100 cc.

TABLE II

Temp. 17°-18°C

Sol	D	E	F	A
Gold number for sodium oleate	0.4-0.5	0.7	1.1-1.2	1.0-1.4

Table II shows that the gold number increases with increasing size of particle of the gold sol. During periods of time up to at least 13 days, the soap solutions (preserved at room temperature, 17°-18°C) gave the same gold numbers towards a particular gold sol, as shown by Table III.

TABLE III

No. of Days	1	2	4	6	1.3
Gold number for sodium oleate	1.0	1.0	0.9-1.0	1-1.1	1.1
Gold number for sodium stearate	2.5	2.5	2.5	2.6	2.5

The concentration of the soap solutions were 0.1 grm. per 100 cc. of solution

Table IV shows the gold numbers towards a given gold sol for a number of different soaps at a series of temperatures.

TABLE IV

Soap	0	14°C	40°C	60°C	75°C	100°C
Sodium and potassium laurates (slightly acid solution)	—	12-14	—	10	—	—
Sodium myristate	—	10-12	—	7.5-8.5	—	1-0.9
Potassium myristate	—	12	—	8.5	—	1.2-0.9
Sodium palmitate	—	1.8-2	—	0.3	—	0.2
Potassium palmitate	—	2-2.2	—	0.3	—	0.3
Sodium stearate	—	3.0	—	0.6	0.5	0.4-0.3
Potassium stearate	—	3.8	0.4	0.3	—	0.2-0.1
Sodium oleate	1.25-1.3	1.0	0.5	—	0.3	0.2
Potassium oleate	1.4	1.2	—	—	1.0	0.9
Sodium linoleate	—	1.0	1.4	—	—	3.0
Potassium linoleate	—	0.82	—	—	0.9	1.8-1.6

Slightly alkaline solutions of the alkali salts of lauric acid do not show any marked protective action but a very slight one is observed in neutral or acid solution. It is of great importance to note in connection with these results that if a comparison is to be made between different soaps it is necessary to prepare them all in a neutral condition, the slightest excess of acid or alkali having a very great influence on the results.

The variation of the "gold numbers" with the concentration of the electrolyte has been determined for two soaps. As is to be expected, the number of milligrams of soap required to protect the sol increases with increase in the concentration of the electrolyte, the increase being at first rapid and then becoming slower. These results are shown in Table V. The numbers indicate the milligrams of the soap required for protection.

TABLE V

Temperature 17°-18°C

Total volume in all cases, 15 cc.

cc. of 10 per cent NaCl solution added to 10 cc. of gold sol	0.5	1.0	1.5	2.0	2.5	3.0	3.5
Potassium linoleate	0.35	0.8	1.8	2.7	3.9	5.4	7.5
Sodium oleate	1.0	1.2	1.3	1.5	—	Solution turbid	

General Discussion of Results

With the exception of the linoleates, all the soaps used exert a greater protective action at higher temperatures as is shown by the marked diminution in the gold number with rising temperature. McBain and his co-workers, from a study of the lowering in vapour-pressure and the electrical conductivity, have concluded that the ionic micelles of the soap decrease in size with rise in temperature. The increase in mobility (and possibly in number) of the ionic micelles with rise of temperature together with the increase in thermal agitation of the soap micelles and the gold particles may therefore be connected with the increase in protective action (viewed from a kinetic standpoint). The results in Table IV show that there is no very marked and general regularity between the protective actions of the sodium and potassium salts of the same acid. Potassium linoleate, however, seems to have a higher protective action than the corresponding sodium salt.

The gold numbers of the soaps show that on the whole they can be arranged as follows as regards their protective action at room temperature:—linoleate > oleate > palmitate > stearate > myristate > laurate. There is a variation, however, with temperature, and the nature of the alkali cation also exert an influence. It was found that the addition of alkali increases the gold number (and therefore lowers the protective action of the soaps.) This was found to be very marked in the case of the laurates, which in neutral or slightly acid solution show only a relatively small protective action.

If we adopt the theory of Spring, that the washing power of a soap is related to its power of forming "adsorptive compounds" with the dirt particles, it is probable that the relative washing powers of soaps will be connected with their relative protective actions toward a gold sol.

The thanks of the author are due to Professor F. G. Donnan for having suggested this work and for his kind interest and advice.

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THE PROTECTIVE ACTION OF SOAPS ON ARSENIOUS SULPHIDE SOLS

BY B. PAPACONSTANTINOU

In another paper[1] an account has been given of the protective action of a number of soaps on gold sols. It is desirable to ascertain how far the order of the protective action of the different soaps depends on the nature of the suspensoid. In the present paper the results are given for the protective action of some soaps on arsenious sulphide sols.

Zsigmondy has suggested the use of the gold number to characterise colloids of biological importance, like gelatine, peptones, etc. The sensitiveness of the coagulation of suspensoids to the protective action of traces of these colloids affords a promising method of detecting minute traces of these substances. It is also of interest in this connection to determine the protective action of such colloids on different suspensoids. The opinion has been expressed that the system suspensoid-protective colloid shows more the properties of the latter than those of the suspensoid. It will be seen from the sequel that the order of the protective action of the various soaps is not identical for the two sols, arsenious sulphide and gold. At the same time, certain regularities are noticeable. Thus, it is not possible to characterise one soap as having more or less protecting power than another, as the protective action depends on the nature of the suspensoid, and even for the same suspensoid the protective action depends on the temperature.

Experimental

The minimum amount of a soap necessary to prevent a perceptible change, in the arsenious sulphide sol by a N/6 solution of sodium chloride in 15 minutes, was taken as the measure of its protective action. 5 cc of arsenious sulphide sol were put in each of six dry test-tubes. The test-tubes were carefully cleansed with hot chromic acid and conductivity water. Measured volumes of a solution of the soap (containing 0.1 to 0.2 gr. of soap in 100 cc of water) regularly varying from one tube to another over a range of 0.5 cc to 3.0cc were added to these six test tubes. The volume of the mixture of sol and soap was then made up to 10 cc by the addition of the requisite amount of pure water. In each of another series of six test-tubes were put 5 cc of a N/3 solution of sodium chloride. The electrolyte was then added to the mixture of the sol and the protective colloid and the contents of the test-tubes thoroughly mixed by shaking.

The series of six tubes containing the same amount of suspensoid and electrolyte, but varying amounts of the protective colloid (in a given volume), were then compared after 15 minutes with a blank containing 5 cc of the sol

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[1] J. Phys. Chem. **29**, 319 (1925).

diluted to 15 cc with pure water. The minimum amount of soap which just sufficed to stop any perceptible change in the sol was determined in this manner. Each experiment was repeated three times and the results were concordant. Arsenious sulphide sols change in properties with time. This change is more rapid during the first few days after they have been prepared. When a certain amount of time has passed, the sol changes more slowly; sols which were about a month old were used. The comparison of the protective action of the different soaps was made on the same sol. Three different preparations of arsenious sulphide sol have been tried and the order of the protective action has been found to be the same. In the following table the minimum amounts in milligrams of the different soaps necessary for protection against perceptible change in 15 minutes are given.

At Room Temperature	
Sodium Linoleate	2.1
Potassium Linoleate	2.5 to 2.6 (3.2-3.4)
Sodium Oleate	2.2 to 2.3
Potassium Oleate	2.4 to 2.5 (2.8-3.0)
Sodium Myristate	2.0
Potassium Laurate	2.7 (4.2-4.4)
At 50°	
Na- and K-Laurates	2.5
Sodium Oleate	2.0
Potassium Oleate	2.1
Sodium Stearate	1.3 to 1.4
Potassium Stearate	1.6 to 1.7
Sodium Myristate	1.3 to 1.4
Potassium Myristate	1.8 to 1.9
Sodium Palmitate	1.4 to 1.5
Potassium Palmitate	1.6 to 1.7
Sodium Linoleate	4.8 to 5.0
Potassium Linoleate	4.2

(Note: In the brackets are given for comparison the results obtained with another arsenious sulphide sol).

Discussion of the Results

A comparison of the values given in the above tables with those observed with gold sols shows that the order of the protective action of the soaps is dependent on the nature of the suspensoid and on the temperature. The protective power of the other soaps, excepting laurates and linoleates, is nearly the same, although there is a slight but perceptible difference between them. The following similarities are, however, observed with both suspensoids:—

1) The effect of temperature is to increase the protective action.

2) Linoleates form an exception and with both sols show a decrease in protective action.

3) Laurates have a decidedly lower protective power, though the difference is more pronounced with gold sols than with arsenious sulphide sols.

Zsigmondy noticed that two colloids of the same family have roughly speaking gold numbers of the same order of magnitude. In the case of myristates, palmitates and stearates the difference in the protective action is light.

With arsenious sulphide sols the protective effect of the different soaps varies within narrower limits than is the case with gold sols. It is important in this connection to draw attention to the great protecting action of minute traces of alkali on arsenious sulphide sols.[1] Arsenious sulphide dissolves in alkali to form arsenites and thioarsenites. In the case of soaps, McBain and his co-workers have shown that the concentration of the free hydroxyl ions is very small and it may be assumed that this disturbing effect is not of any great importance. This assumption is justified by the fact that the sols do not show any perceptible clearing up on addition of the soap, an effect which can be easily perceived even when the amount of colloid dissolved is small. The protective effect of slight traces of alkali is, however, very great and the narrow limits of variation of the protecting power on arsenious sulphide suggest that the protecting action of the soap may be partly due to the small amount of alkali.

Such an effect would mask the actual difference in the protecting powers of the colloidal micelles of the different soaps.

The author's thanks are due to Professor F. G. Donnan for his kind advice and assistance.

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[1] Mukherjee and Sen: J. Chem. Soc. 115, 461 (1919).

ADSORPTION FROM SOLUTION BY SILICA IN VARYING DEGREES OF DISPERSIVITY

BY D. C. JONES

Silica adsorbs best from solution in solvents insoluble in water. The solvent from which the greatest adsorption occurs of any solute that has been investigated, is a high-boiling kerosene. In this respect it is markedly different from carbon which, as is well-known, adsorbs best from aqueous solution. Freundlich, generalising from the adsorption results, concluded that the greatest adsorption occurred in solvents of high surface-tension against air. It is clear that this should apply theoretically only if the interface at which adsorption occurs is a solvent-air interface. According to the thermodynamical theory positive adsorption should occur when the solute lowers the solid-solvent interfacial tension, and the greatest adsorption should tend to occur in solvents where this tension is greatest. If the adsorption interface is solvent-solid a lowering of the surface tension of the solvent against air would tend to increase the solvent-solid interfacial tension[1]: i. e. a solute that would be positively adsorbed at the liquid-air interface would be negatively adsorbed at the solid-liquid interface. From chemical considerations, and the values of the surface tensions of water and petroleum against air, it is to be expected that the interfacial tension between silica and water is much less than that between silica and petroleum.[2] The fact that silica adsorbs best from petroleum solutions seems then to be in qualitative agreement with the thermodynamical theory.

It is hoped to publish very shortly results that have been obtained on the adsorption from solution by silica gel. In this paper the adsorption of acetic acid from gasoline solution is investigated, using finely-ground quartz, precipitated silica, silica gel, and the gel material with varying degrees of water content, as adsorbents.

Figure 1 shows the various adsorption curves that have been obtained, plotted in the usual way. In Figure 2 the logarithms of the equilibrium concentrations and the adsorbed amount per gram of adsorbent are plotted against one another. It is clear that all the curves fit some equation of the Freundlich type very accurately except for one or two determinations at the highest equilibrium concentrations. Undoubtedly the solvent effect is becoming important here. In the case of the silica gel there is no evidence of any departure from the exponential relations up to the highest concentration used in these experiments. At higher concentrations, however, the solvent effect becomes very marked.

The values of the equation constants are put together in Table I. The product (a)(1/n) is also included. The significance of the constants is well-

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[1] See a discussion of an analogous case by Porter: Trans. Faraday Soc., 17, 394 (1921-22)

[2] See also J. J. Thomson: "Applications of Dynamics to Physics and Chemistry," 192.

known. "a" is the amount adsorbed per gram of adsorbent when the equilibrium concentration is unity. "1/n" is the slope of the logarithmic curve. It is clear also that $\frac{d(x/m)}{dc} = (a)(1/n)(c^{1/n-1})$ and therefore that (a)(1/n) is equal to the tangent to the adsorption curve when the equilibrium concentration is unity.

The value of "1/n" varies from 0.6 in the case of the finely-ground quartz to 0.18 in the case of the silica gel. At the same time, that the effective adsorption space has increased very largely, in the region of smaller equilibrium concentrations, is clear from the values of the constant "a" in Table I. At 1% equilibrium concentration the gel material adsorbs 16.8 grams of acetic acid per 100 grams of gel and the quartz 0.7 grams.

TABLE I

	a.	1/n.	(a)(1/n).
Silica gel containing 6.2% water and 3.5% water	0.168	0.18	0.031
Silica gel containing 1% water and the partly peptised gel.	0.1	0.36	0.036
Precipitated silica.	0.083	0.47	0.039
Ground quartz.	0.007	0.6	0.004

It is clear that if the adsorption were of the same type throughout, e. g. a plane solid surface effect either mono-molecular as postulated by Langmuir,[1] or a thick layer as suggested very frequently in the literature of adsorption,[2] the value of "1/n" would not change as the dispersivity of the adsorbent increased. In other words, if the adsorption effects were due in all cases to the specific surface only, the amount adsorbed, "x/m", if reckoned per sq. cm. would be constant in all cases, or if reckoned per gram of adsorbent would be proportional to the constant "a". The marked decrease in the value of "1/n" must be due to effects of increased surface contiguities. Thus if the ordinates for Curve 6, Figure 1, (ground quartz), be multiplied 11 times the 'similar' hypothetical Curve 7. is obtained. "1/n" would have the same value for this curve as for Curve 6., "a" would be increased 11 times. While the curve is almost coincident in the higher concentrations with that for silica gel, (Curve 1,) the much more effective adsorptive power of the gel in the lower concentrations is very evident. This means that the regions of stronger adsorptive forces have increased in a greater proportion as the dispersivity increased.

These results demonstrate quite clearly that the very marked adsorbing power of this type of porous adsorbent, in dilute solution, is due only partly

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[1] J. Am. Chem. Soc., 40, 1393 (1918).

[2] See papers recently by Polanyi: Ber., 16, 1012 (1914), etc.

to the increased specific surface. The main effect is dependent on the increased proximity of the solid surfaces, the radii of the capillaries so produced being less than the range of the attractive forces causing adsorption.

There would seem on current adsorption theories these possible explanations:—

If it were possible to extend the Zsigmondy liquefaction theory of adsorption from the vapour to adsorption from solution, then one would have the simple explanation that increase in dispersivity increases the proportion of the finer capillaries. On this view the adsorption of acetic acid from kerosene solution would be ascribed to the lowering of the solubility of the acetic acid in the kerosene due to the highly concave curvature presented by the acid in the fine capillaries.

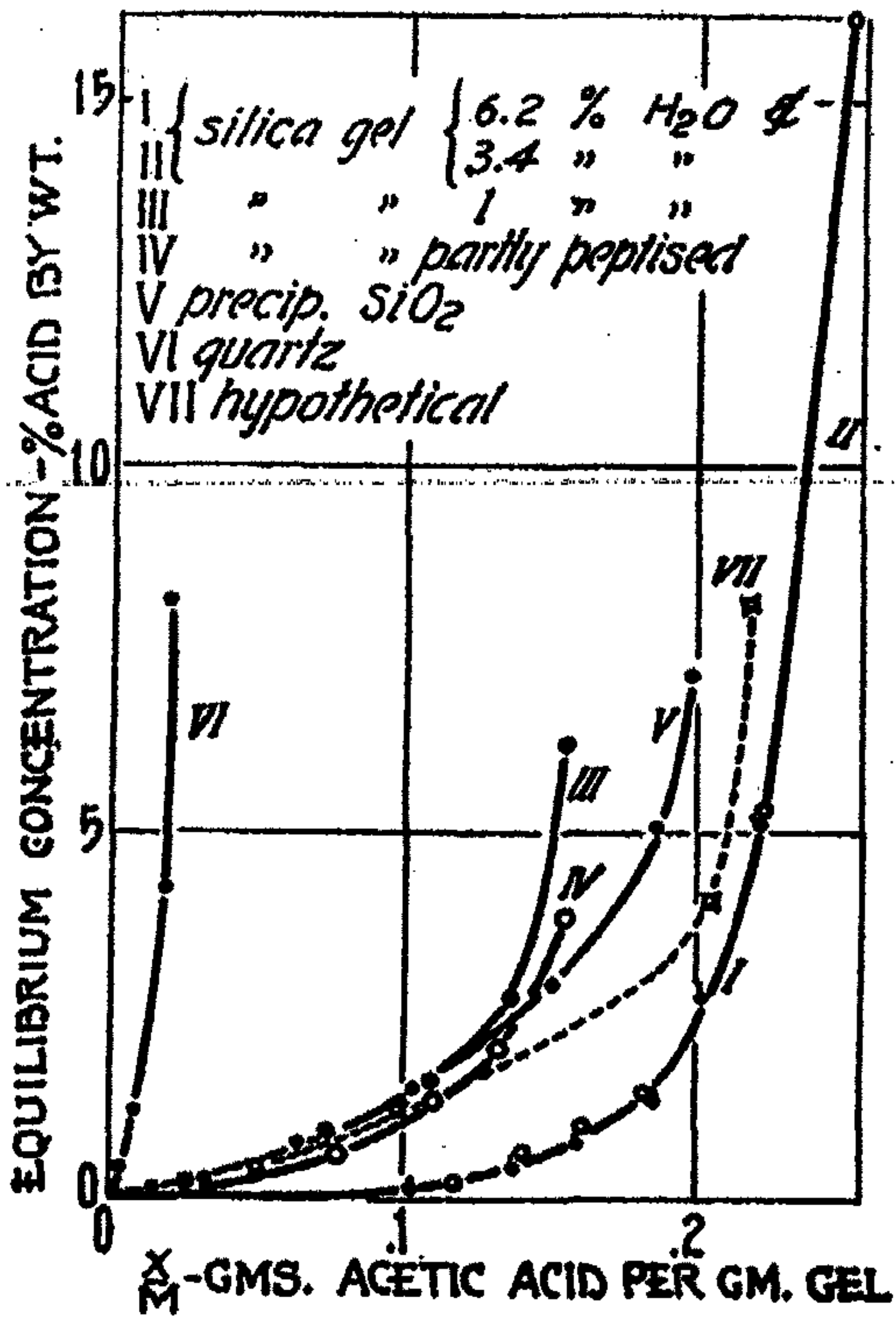

FIG. 1

Adsorption Curves with Silica in Varying Degrees of Dispersity as Adsorbents.

Langmuir has put forward the view that the adsorption layer is monomolecular when a plane surface is just saturated. However, as Langmuir himself points out, it would be impossible to apply his equations quantitatively to porous bodies because the varying proximity of the solid walls would cause the adsorbate molecules to be attracted by one or many solid surfaces, and no quantitative relations could be deduced in the absence of accurate knowledge as to the internal structure of the solid. The change in "1/n" would be ascribed on this view to a large increase in the proportion of the adsorbate that is attracted by two and more solid surfaces.

With regard to the theories of thicker adsorption layers, if the solid surfaces became closer to one another than twice the thickness of the adsorption layer, some of the less strongly held upper layers would be prevented by the proximity of the solid surfaces from being present. As dispersion proceeded there would be a greater proportion of the more strongly held layers.

There is evidence that porous adsorption consists of these definite types, liquefaction in capillary tubes, plane surface adsorption, and an adsorption in cavities gradually becoming more and more enclosed. In other words, one is dealing with the attractive forces of curved liquid surfaces, plane solid surfaces, and curved solid surfaces. The problem would seem to be further complicated by the uncertainty of the experimental evidence regarding the adsorption on a plane surface. In another paper some evidence will be given that would seem to show that the adsorbed layer on quartz is not greater than five molecules thick. It would greatly simplify the problem if this point could be settled.

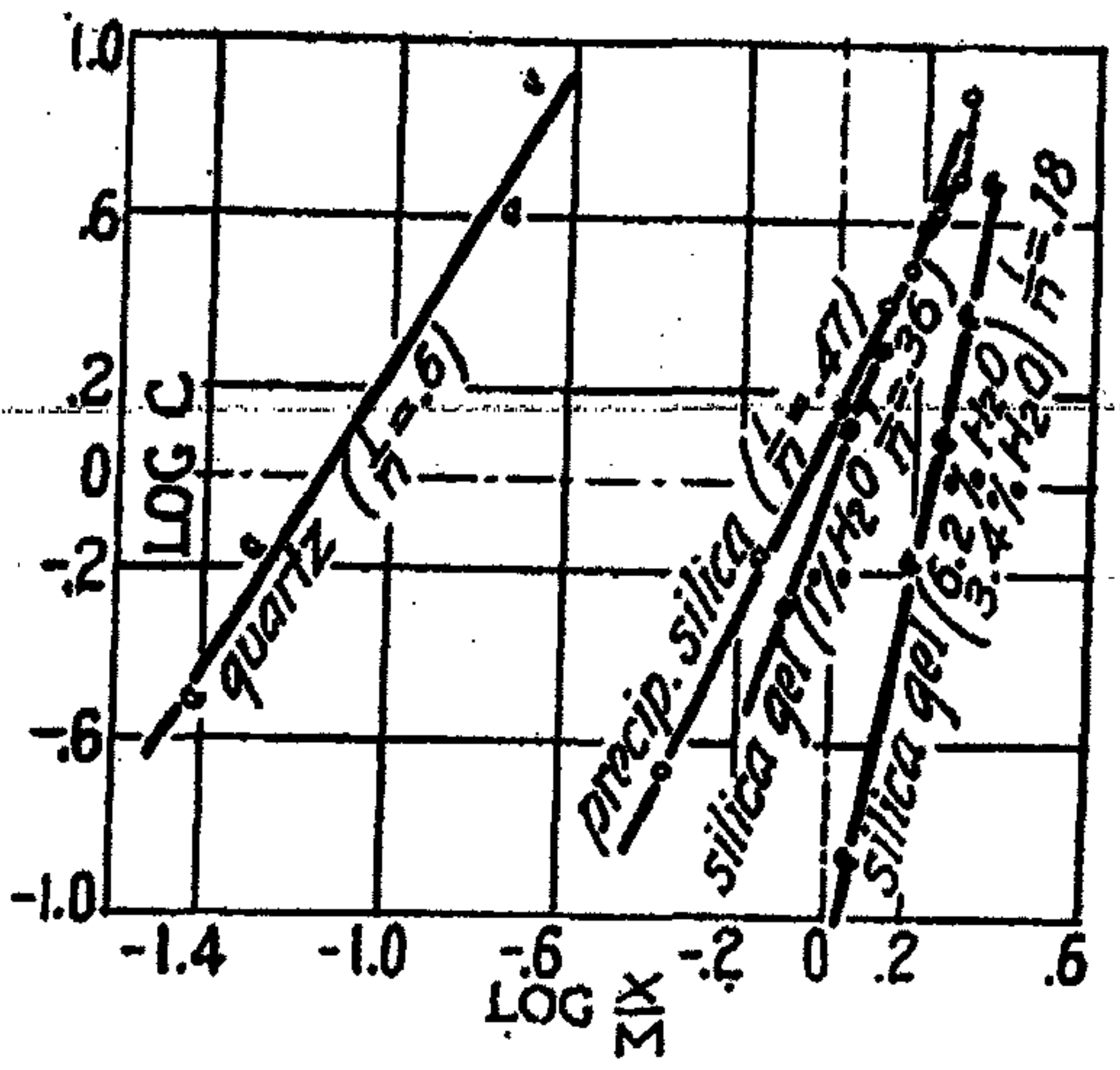

Fig. 2

Logarithmic Adsorption Curves

The Zsigmondean liquefaction theory is very attractive. Kelvin first suggested it and put forward a theoretical relation between the diminution of vapour pressure obtainable when a liquid surface was concave: e. g. if a liquid filled a capillary tube. Zsigmondy,[1] and later Anderson[2] suggested that it may be possible in this way to account for the adsorption of certain vapours by the gel of silicic acid. Anderson calculated the radius of the capillary tube that if filled with liquid capable of completely wetting the tube, would give such a reduction of vapor-pressure as would correspond to certain points on the adsorption curves of water, benzene, and ethyl alcohol. More recently

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[1] Z. anorg. Chem., 71, 356 (1911).

[2] Z. physik. Chem., 88, 191 (1914).

Patrick and McGavack[1] have attempted to extend the theory further to account for the adsorption by silica gel[2] of less condensible vapours like SO_2.

The equation giving the relation between the radius of the capillary tube and the reduction of the vapour-pressure, or rather p/P_0, is as follows:-

$$r = \frac{2\,T\,s_0}{s\,P_0 \log \frac{P_0}{p}}$$

where
r = radius of the capillary tube,
T = surface tension of liquid,
s_0 = vapour density at the plane surface,
s = liquid density,
P_0 = saturation vapour pressure,
p = pressure of vapour outside curved surface.

Anderson showed that with water, when the circular cross-section of the capillary was 5.5×10^{-7} cms., p/P_0 has a value 0.7. It can be readily calculated that when p/P_0 has the value 0.1 the diameter of the capillary for water must be 0.9×10^{-7} cms., or of the order of two to three molecular diameters. Similarly when p/P_0 is 0.2 the capillary diameter is of the order four to five molecules across. Of course it is doubtful how far the quantitative equation applies. Also it is undecided at present to what distance the attractive forces of the solid reach on a plane surface. It would seem quite out of the question to consider these effects occurring in capillaries whose diameters was less than four to five molecular diameters across. It would follow from this that a reduction of vapour-pressure to an extent that $p/P_0 = 0.2$ would be the greatest that could be accounted for on this theory. A little calculation shows that this applies approximately to all the vapours that have been used.

With the same gel material as used in these experiments, the adsorption curve for water has been determined. The curve has the normal adsorption form, (as opposed to the results Anderson obtained with his gel material). When the vapour-pressure has reached a value of 90% of its saturation value, 32% of water is adsorbed. When p/P_0 is 0.2 there is 19% of water adsorbed: i. e. one must consider that this 19% or approximately 66% of the adsorption cannot be ascribed to capillary condensation. The remaining 33% of the adsorption may be due to this cause or to a thickening of the adsorption layers in the sense of Polanyi.

A much clearer idea of the applicability of the Zsigmondean theory is obtained from a consideration of the isotherms for SO_2 on silica gel that have been investigated by Patrick and McGavack. The conditions at −54°C. with SO_2 are somewhat similar to those with water at, say, 27°C. The adsorption curve can be determined up to the saturation value, which is 88 mms. as compared with that for water of 26.7 mms, and if one goes into the calculation a certain portion of the adsorption curve from a value of p/P_0 of 1 to a value of 0.2 can be accounted for on this theory, if one is prepared to admit these effects continuing to about three to four molecules thick. On the 0°C. isotherm similarly a reduction of the vapour-pressure from 116.2 cms. to 23

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[1] J. Am. Chem. Soc., 42, 946 (1920).

[2] See Report of Discussion on "The Physics and Chemistry of Colloids," by the Faraday Soc., 1921, pp. 51, 55, and 57.

cms., which corresponds to a p/P_0 value of 0.2, would correspond to a capillary thickness of 13×10^{-8} cms. about three to four molecular diameters, and would account for the adsorption down to an x/m value of 120 ccs. about.[1] On the isotherm at 30°C. however, a value of p/P_0 of 0.2 would correspond to an equilibrium pressure of 90 cms., the diameter of the capillary necessary to produce this diminution of vapour-pressure being again 12×10^{-8} cms.: and therefore every point on the observed isotherm at 30° C. represents a reduction in vapour-pressure values smaller than could be accounted for by these very small capillaries. This applies much more strongly to the isotherms at the higher temperatures from 30° C. to 100° C.; e.g. the highest equilibrium pressure observed at 100°C. corresponds to a p/P_0 value of 0.03. Patrick and McGavack do not think it possible to extrapolate the quantitative equation to very fine capillaries and substitute an empirical equation to express their results with, however, a quasi-theoretical basis on these lines. It would seem better to limit the possibility of capillary condensation to a p/P_0 value of 0.2. This would mean in the case of the results that have hitherto been obtained with silica gel that in from 30 to 40% of the total adsorption space, the adsorption may either be capillary condensation or a thickening of the adsorption layer. In the case of the isotherms at the higher temperatures this portion of the adsorption space becomes partially, and finally completely, ineffective.

Acetic acid from dilute gasoline solution is adsorbed by silica gel to practically the same extent as that of water from almost saturated vapour. Curve 1. Figure 2. shows that at 5% equilibrium concentration there is 22% of acetic acid adsorbed; i. e. 0.22 grams of acid per gram of adsorbent. Undoubtedly here as in the case from the vapour the same portion of the gel structure will give adsorption either of the capillary type—a decrease of solubility instead of vapour-pressure at highly concave, liquid surfaces,—or of the Polanyi type. It would be very useful in this connection to know the partial vapour-pressures of acetic acid in various solvents. Unfortunately there are no data available.

It is rather interesting to calculate the total area that would be covered by an adsorbate one molecule thick. Taking water as an instance, one gram of the silica gel used in these experiments adsorbs, at 27°C., 0.3 grams of water when the vapour-pressure is 90% of saturation. Assuming a density for the adsorbed material of liquid water, Millikan's value for N of 6.06×10^{23} and Langmuir's value of 7.4×10^{-16} sq. cms. as the area covered by one molecule of water, it is readily calculated that 0.3 ccs. of water would cover 7.4×10^{6} sq. cms. one molecule deep. Patrick and Grimm,[2] from results on the heat of wetting have calculated a surface of 6.9×10^{6} sq. cms. per gram, and point out that the surface exhibited by one gram of SiO_2 particles of diameter $5\mu\mu$, taken from Zsigmondy's ultramicroscopic measurements, comes out to be 6×10^{6} sq. cms. If this calculated extent of surface is of the right order, it is clear that the adsorption of water from almost saturated vapour could be accounted for as forming on the average a layer one molecule thick.

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[1] See Patrick and McGavack: loc. cit. Fig. 2.

[2] J. Am. Chem. Soc., 43, 2144 (1921).

From the previous discussion it seems probable that some considerable portion, 30 to 40% of the adsorption, could be accounted for either by liquefaction in capillaries or by a thickening of the adsorbed layer. It follows therefore, that there must be also a considerable portion of the adsorbate held by two or more units of solid surface. This is completely supported by the low values of vapour-pressure associated with the more strongly held portions of adsorbate.

The effect of the water present in the gel on the adsorption has been very considerably studied, but no satisfactory conclusion, taking all the facts into consideration, seems to have been reached. This matter is discussed below in relation to the above suggestions regarding the character of the adsorption occurring in silica gel.

Effect of the Water present in the Gel on the Adsorption

The experimental results by all workers are in agreement on this question. Patrick and McGavack found that gel containing 8% of water had exactly the same adsorptive capacity as the same material heated to 300°C. for some hours and containing 4.86% water. In the experiments described in this paper, as Curves 1 and 2 show, (Figure 1.), the adsorption curves of acetic acid adsorbed from gasoline solution, are identical for gel containing 6.2% of water, (heated to 200°C.), and the same material heated for 18 hours at 375°C. and containing 34% of water. Curve 3, however, shows the very large decrease in the adsorption when a gel material is used containing only 1% of water, (heated to 680°C. for some hours). Patrick and McGavack found a marked decrease in the adsorption of SO_2 when the water content was reduced to 2.3%, and Patrick and Davidheiser,[1] in studying the adsorptive of NH_3 by a gel material containing only 0.33% of water record a very marked decrease in the adsorption.

The decrease in the adsorption on heating to high temperatures, is quite reasonably accounted for by a breakdown in gel structure,—a kind of crystallisation effect that only has an effect on the adsorption results when the gel is heated to about 400°C. At 700°C with the gel specimen used in these experiments, it is obvious to the eye that some change is occurring, a rounding of the edges of the gel pieces being seen. The water removed may be concerned either in some chemical way with the silica network, or be merely desorbed when the temperature rises and the internal structure breaks down.

The stationary values obtained while the water content changes from 3.5% to about 8% are very interesting. If the gel structure remained unaltered a removal of one adsorbent should tend to increase the capacity for another. Certainly if more water is present than 8% the adsorption diminishes and very probably for this reason. If the 8% or some of it were held in very fine capillaries in a Zsigmondean sense, or held in layers according to theories of Polanyi or Langmuir for adsorption on a plane surface, it seems very improbable that the removal of this water from the very strongly-adsorbent

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[1] J. Am. Chem. Soc., 44, 1 (1922).

portions of the gel would not increase the capacity of the gel for the other adsorbate. This 8 % of water is apparently occupying a portion of the adsoption space that is unattainable for most other adsorbents. It seems very probable that it is held in the very enclosed solid capillaries, other evidence for the existence of which has been brought forward. The size of the adsorbate molecule would be very important. It would be immaterial how much of this water remained in the gel, the adsorption would be unchanged until a high temperature begins the breakdown of the structure.

If a definite proportion of finest structure in the gel were eliminated, by peptisation or by structural breakdown on heating to a high temperature, it would be expected that the adsorption curve obtained with the resultant adsorbent would be related to the curve obtained with the original adsorbent in this simple way.

$$C + x/m = a\,c^{1/n}. \text{ (original adsorbent.)} \quad 1.$$

$$x/m = a\,c^{1/n}. \text{ (resultant adsorbent.)} \quad 2.$$

The curves would be parallel to one another throughout, but curve 2 would cut the x/m axis at the point x/m = the constant C. It is interesting to observe that in Davidheiser and Patrick's adsorption results on NH_3 at 0°C. with gel containing 4.93% of water and 0.33% of water, the curves are completely parallel down to the lowest equilibrium pressure used, (mm. approximately). At 30°C. with the same gel samples this does not hold quite so accurately. Comparing Curves 1 with 3 and 4 in this paper it is clear that they also are almost completely parallel down to the lowest equlibrium concentration examined. It would not be expected that at very low pressures or concentrations this would hold rigidly, because structural break-down would create of itself a small proportion of the finest structure. It would seem sensibly true that a certain portion only of the finest structure is affected, and that the portion associated with Zsigmondean or Polanyian adsorption seems quite unaffected. These considerations do not seem to fit in very well with the explanation that has been given for the large adsorption of NH_3 by silica gel.

It is suggested that the Zsigmondean adsorption theory should not be pushed beyond the limits of its legitimate application. It is possible to account for adsorption in a certain portion of the total adsorption space, not more than 30 to 40% certainly, of silica gel by this theory. However, it is not certain whether in the present state of our experimental knowledge of adsorption we can distinguish clearly between capillary condensation in this region and that of the occurrence of thicker adsorption layers. In the remainder of the adsorption space Zsigmondean adsorption is most improbable.

Experimental Results and Details

Materials used

The acetic acid and the gasoline were purified as described by the author,[1] the acetic acid having a melting point of 16.45° C, and the gasoline boiling between the limits 125°C–130°C.

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[1] J. Chem. Soc., **123**, 1379 (1921).

The quartz used was prepared by grinding silica glass in an agate mortar. It was sieved through a 350-inch mesh. Before being used it was boiled with nitric acid and afterwards washed with distilled water until free from acid. The final washings were done in a silica flash. It was then dried at 200°C in an air-oven.

The precipitated silica was prepared by adding hydrochloric acid solution to a solution of sodium silicate. It was washed with running water for many days. It was then treated with nitric acid washed until free from acid, and dried at 200°C in an air-oven.

The silica gel was prepared in the manner described by Patrick. After preparation the gel was filled with water by passing steam through, and then washed with distilled water. It was dried at 200°C in an air-oven. The water

Results.

Series 1.

Adsorbent—Silica gel containing 6.2% of water.

C_0	C	$\frac{C_0-C}{G}$	$\frac{X}{M}$
7.47	5.28	0.894	0.223
5.73	2.57	0.789	0.197
3.27	1.29	0.745	0.186
2.14	0.70	0.64	0.160
1.27	0.14	0.47	0.118

Series 2.

Adsorbent—Silica gel containing 3.4% of water.

C_0	C	$\frac{C_0-C}{G}$	$\frac{X}{M}$
7.47	5.05	0.88	0.22
3.61	1.41	0.74	0.19
2.37	0.98	0.64	0.16
1.31	0.27	0.55	0.14
19.20	16.10	0.997	0.25

Series 3.

Adsorbent—Silica gel containing 1% of water.

5.73	3.84	0.61	0.16
3.27	2.02	0.53	0.13
2.14	1.31	0.44	0.11
1.27	0.52	0.31	0.08

Series 4.

Adsorbent—Silica gel partially peptized.

7.47	6.23	0.61	0.15
3.61	2.68	0.55	0.14
2.37	1.51	0.44	0.11
1.31	0.93	0.29	0.07

Series 5.

Adsorbent—Precipitated silica.

8.31	6.84	0.79	0.20
6.20	5.01	0.76	0.19
4.21	2.88	0.61	0.15
2.12	1.52	0.43	0.11
1.07	0.68	0.27	0.07
0.48	0.22	0.17	0.04
0.15	0.04	0.11	0.03

Series 6.

Adsorbent—Ground quartz.

8.38	8.26	0.08	0.02
4.29	4.17	0.077	0.019
0.765	0.725	0.019	0.005
0.352	0.317	0.016	0.004

C_0 represents the initial concentration in grams per 100 c.cs. of solution.
C represents the equilibrium concentration expressed in the same units.
G represents the weight of adsorbent used in grams.
$\frac{X}{M}$ represents the weight of acid adsorbed per gram of adsorbent as calculated from the concentration changes.

content, as determined by blasting in a platinum crucible, was 6.2%. This material gave the adsorption results tabulated under Series 1, which are graphed in Curve 1, Fig. 1.

A portion of this gel was heated to 375°C in a stream of dry air for 18 hours. The water content was thus reduced to 3.4%. This material gave the results in Series 2, graphed in Curve 2. (Curves 1 and 2 are identical.)

A portion of the original gel was heated to 680°C in a stream of dry air for 18 hours. The water content was reduced to 1%, and the material gave the adsorption results in Series 3, graphed in Curve 3.

A portion of the original gel was refluxed in a glass tube with nitric acid and afterwards with water. Owing, undoubtedly, to adsorption of traces of alkali from the glass the gel was partially peptized, and on drying at 200°C in an air-oven it gave the adsorption results tabulated under Series 4, and graphed in Curve 4.

Method.

The adsorptions were carried out in an electrically-controlled air-thermostat at 27°C. The adsorbents were vigorously shaken, mechanically, with the solutions for several hours. The concentrations of the solutions were determined by the titration of pipetted portions with N/100 baryta in small stoppered flasks.

Summary

1. The adsorption curves of acetic acid in gasoline solution, with silica in various degrees of dispersivity as the adsorbent, have been determined.

2. The results are discussed in relation to current adsorption theories and their application to silica gel.

3. The effect of the water present in the gel on the adsorption is discussed.

Some preliminary experiments on these lines were carried out at Johns Hopkins University with Professor Patrick, to whom my best thanks are due for his constant help and encouragement.

I wish to acknowledge, also, the very helpful criticism given me by Professor Donnan and the "Colloquium" at University College.

During this research I was a National Research Fellow of the United States.

University College,
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THE ADSORPTION OF BUTANE BY SILICA GEL[1]

BY W. A. PATRICK AND J. S. LONG

The adsorption of butane by silica gel has been studied for several reasons. In the first place it was desired to test out, in the case of the adsorption of a widely different substance, capillary adsorption formulae which have been successfully applied to the adsorption of sulfur dioxide[2] and ammonia[3] by silica gel. The adsorption of both sulfur dioxide and ammonia was more or less affected by the solubility of the gas in the water present in the gel. Particularly was this so in the case of ammonia, which is soluble to the extent of 783 volumes in one volume of water under atmospheric pressure at 16°C. Therefore it was necessary to correct for the amount of ammonia dissolving in the gel water before the adsorption formula could be applied. It was further shown that the gel contained free mineral acid which was not removed by prolonged washing or by heating the gel for 3 hours at 300°C. This acid, of course, neutralized an equivalent amount of ammonia, thus making the apparent adsorption too high.

To eliminate the above effects, it was decided to study the adsorption of a gas or vapor which was only slightly soluble in water and which was not affected by acids or alkalies present. Butane was chosen for this purpose. It is soluble in water to the extent of 0.15 cc. in one cc. of water at 17°C under a pressure of 772 mm. Its boiling point, $-1.^{\circ}0$ C, moreover, was convenient in that it allowed adsorption measurements to be readily made in the neighborhood of its condensation point under one atmosphere pressure.

Apparatus, Materials and Procedure

The apparatus used and the method of carrying out the experiments has been previously described by Patrick and McGavack[4]. The volume of butane was measured to within 0.005 cc., and the pressure to within 0.03 mm. by means of a sensitive cathetometer. By adhering to the uniform procedure in preparing the gel sample for adsorption as described in the case of ammonia, results could be duplicated to exact checks in most cases. For the 0°, 30°, and 40° isotherms (see later), duplicate runs were made, and both series of points plotted together as one curve. In the case of ammonia, this uniform procedure was absolutely necessary to obtain checks, on account of the effect of the gel water in dissolving ammonia. For, the amount of water in the gel depends upon the temperature of activation, the degree of evacuation, and the length of time of activation. With butane, however, as will be seen, the water content of the gel had little effect upon the adsorp-

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

[2] Patrick and McGavack: J. Am. Chem. Soc., 42, 946 (1920).

[3] Patrick and Davidheiser: J. Am. Chem. Soc., 44, 1 (1922.

[4] Loc. cit.

tion: therefore it was not necessary, in the latter case, to obey the uniform procedure rigorously. The water content of the different gels used was determined for samples which were first subjected to exactly the same heating and evacuating treatment that was always used immediately before an adsorption run. These samples were transferred to platinum crucibles and ignited carefully to constant weight.

The butane used was prepared as follows. N-butyl alcohol from the Eastman Kodak Co. was distilled, and the fraction boiling between 115°–120°C taken. This fraction was introduced slowly below the surface of phosphoric acid held in a glass flask heated to 400°C. The phosphoric acid at the beginning was made to correspond closely to H_3PO_4. The dehydration of the alcohol proceeded smoothly and a steady flow of butylene was obtained.

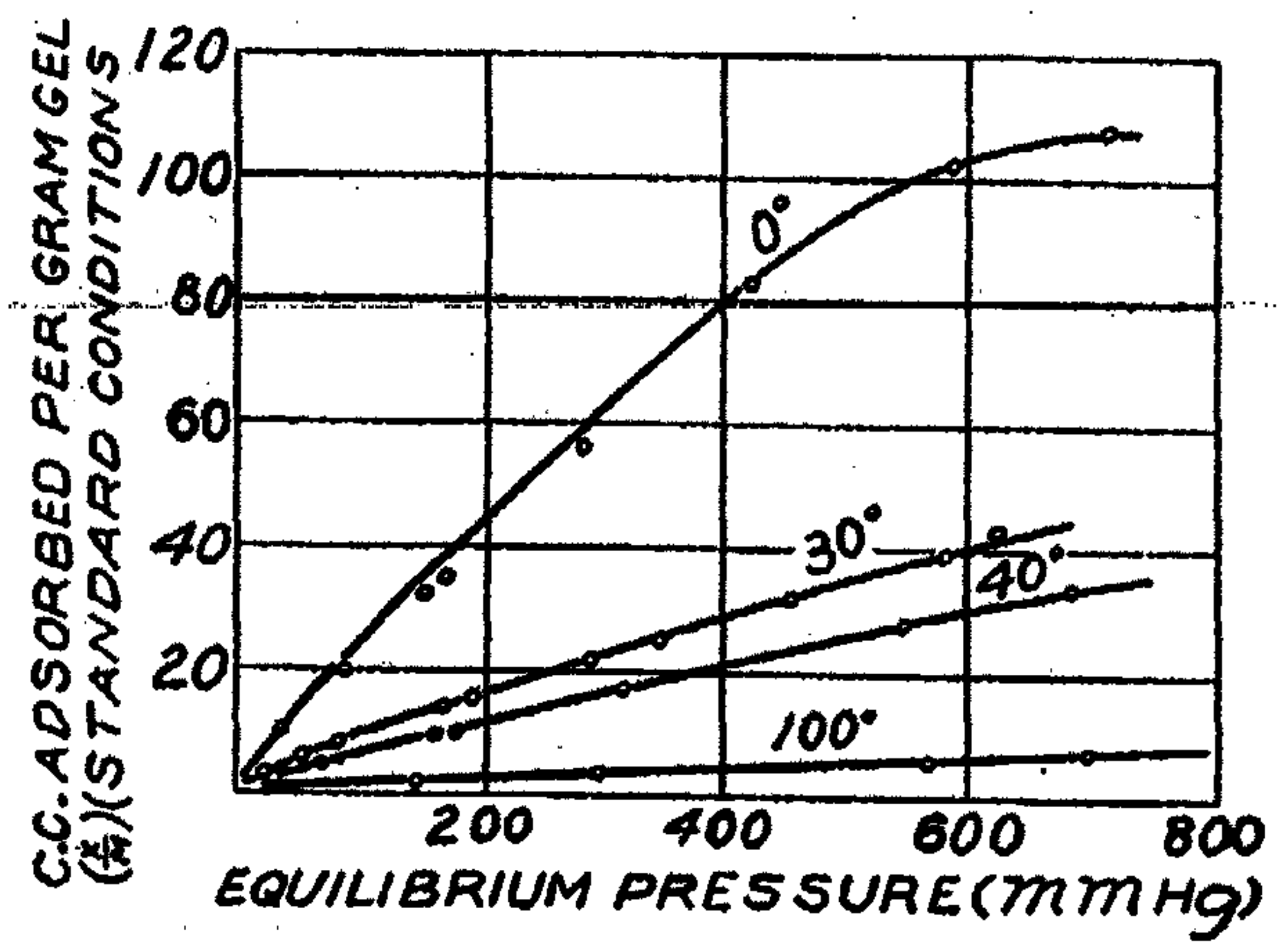

FIG. 1
Adsorption of Butane by Silica Gel.

The butylene was purified, dried, and mixed with an excess of hydrogen and converted to butane by calatylic hydrogenation. The catalyst used was finely divided nickel suspended in infusorial earth. This was made from nickel nitrate as described by Rather and Ried[1].

It was found that a temperature of 180°C, the hydrogenation was effected to the extent of about 70% when using a slight excess of hydrogen above that required by theory. The production, however, was slow when the mixed gases were held in a glass tube and heated by means of an electric furnace. Much more rapid production with the same percentage conversion was obtained by suspending a small quantity of the nickel catalyst in paraffin oil and bubbling the mixed gases through this while stirring at very high speeds (9000 to 11000 R.P.M.) by means of the high speed stirring apparatus described by Rather and Reid[2]. The mineral oil used was a commercial product, —liquid albolene (McKesson and Roberts Co.). This was found to be free

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[1] J. Am. Chem. Soc., 37, 2115 (1915).

[2] Loc. cit.

from sulfur, and although quite liquid at 180°C, the temperature used, did not distill in any appreciable amount from the reaction chamber. The catalyst remained effective after 72 hours continuous run. The butane thus produced was bubbled through three flasks,—the first containing fuming sulfuric acid to remove practically all of the butylene, the second containing strong sulfuric acid (96%) to remove SO_3, and the third containing sodium hydroxide. Finally the gas was absorbed in silica gel contained in absorption towers, and in this was separated from the excess of hydrogen.

To recover the butane, this gel was treated with a current of steam. The butane driven off was passed at the rate of 4 cc. per minute through a final purification train consisting of the same three solutions mentioned above, and finally through two long tubes containing phosphorus pentoxide. The gas thus purified was liquefied by means of a freezing mixture of ice and salt, and the liquid butane was then transferred to a steel cylinder fitted with a needle valve. The tank was filled to overflowing and the excess butane allowed to expand through the valve and escape, thus eliminating any possibility of having air admixed with the butane. After blowing off for a short time on two successive days, the cylinder was connected directly to the apparatus by means of glass tubing.

The silica gel used was prepared in the usual manner described by Patrick and McGavack[1], and purified by refluxing the dried material with aqua regia for eight hours. By heating for definite lengths of time, samples of gel containing various percentages of water (0.03% to 4.0%) were prepared. These samples were put into glass stoppered bottles, and the latter kept in a desiccator containing P_2O_5.

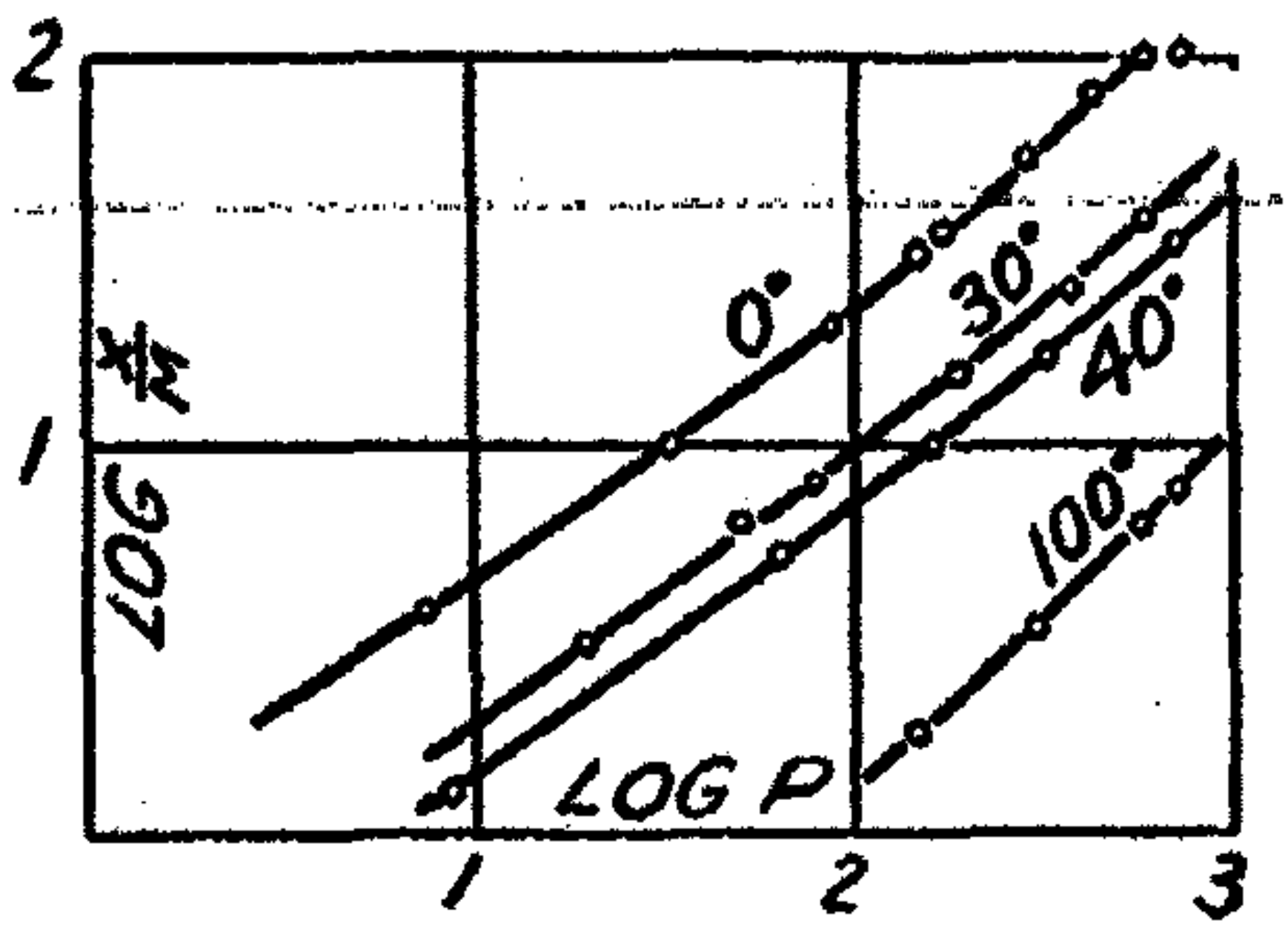

FIG. 2

Expression of Results

The results are tabulated in Table I, which deals with adsorption by the same gel sample at different temperatures, and in Table II, which gives data on adsorption by five gels of different water content. P is the equilibrium pressure in millimeters of mercury, and X/M the number of cc. of butane reduced to standard conditions adsorbed per gram of gel.

Discussion of Results

The results of the adsorption measurements may best be seen in Fig. 1, where the cubic centimeters of butane adsorbed (reduced to standard conditions) are plotted against the equilibrium pressure in millimeters of Hg. It is to be noted that the extent of the adsorption is much less than with sulfur dioxide although the boiling point of the latter gas is lower than that of butane.

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[1] Loc. cit.

When the log of the cc. of butane adsorbed per gm. of gel is plotted against the log of the equilibrium pressure (Fig. 2) fairly straight lines are obtained as demanded by the Freundlich equation $X/M = KP^{1/n}$. Nevertheless there is a distinct bending of the log curves towards the X/M axis. The direction of the curvature is quite opposite to the usual type of adsorption log curves.

In Fig. 3 are plotted the adsorption isotherms at 30°C. obtained with butane and silica gels of various moisture contents. On the same sheet (dotted line) the isotherm at 30°C. of butane obtained with a very dense gel is given. It is to be noticed that such a gel, although the water content is 3.38%, exhibits a greater activity than the regular material used in these experiments. At the higher equilibrium pressure, however, such a dense gel does not retain as much butane as the other gel, i.e. its capacity is less.

TABLE I

Run No. 6; Temp. 0°C.; Wt. gel 0.8884 g; H_2O—3.57%.

X/M	P
3.84	7.41
10.59	32.89
20.70	86.85
35.23	167.13

Run No. 10; Temp. 0°C.; Wt. gel 0.8877 g; H_2O—3.57%

X/M	P
32.70	151.76
56.09	281.58
83.54	421.40
103.35	584.94
106.60	710.49

Run No. 5; Temp. 30°C.; Wt. gel 1.1879 g; H_2O—3.57%

X/M	P
3.09	19.45
8.03	77.20
15.38	187.17
25.09	345.74
39.20	580.92

Run No. 8; Temp. 100°C.; Wt. gel 0.7975 g; H_2O—3.57%

X/M	P
1.87	145.39
3.44	294.66
6.16	566.89
7.45	696.46

Run No. 13; Temp. 30°C.; Wt. gel 0.9229 g; H_2O—3.57%

X/M	P
6.29	51.03
14.53	169.42
21.75	287.30
32.12	456.22
42.76	621.15

Run No. 1; Temp. 40°C.; Wt. gel 0.8040 g; H_2O—3.57%

X/M	P
10.19	157.53
17.16	314.61
28.07	548.33

Run No. 3; Temp. 40°C.; Wt. gel 0.9023 g; H_2O—3.57%

X/M	P
1.30	8.90
5.28	63.67
10.85	171.80
17.69	317.19
34.38	682.44

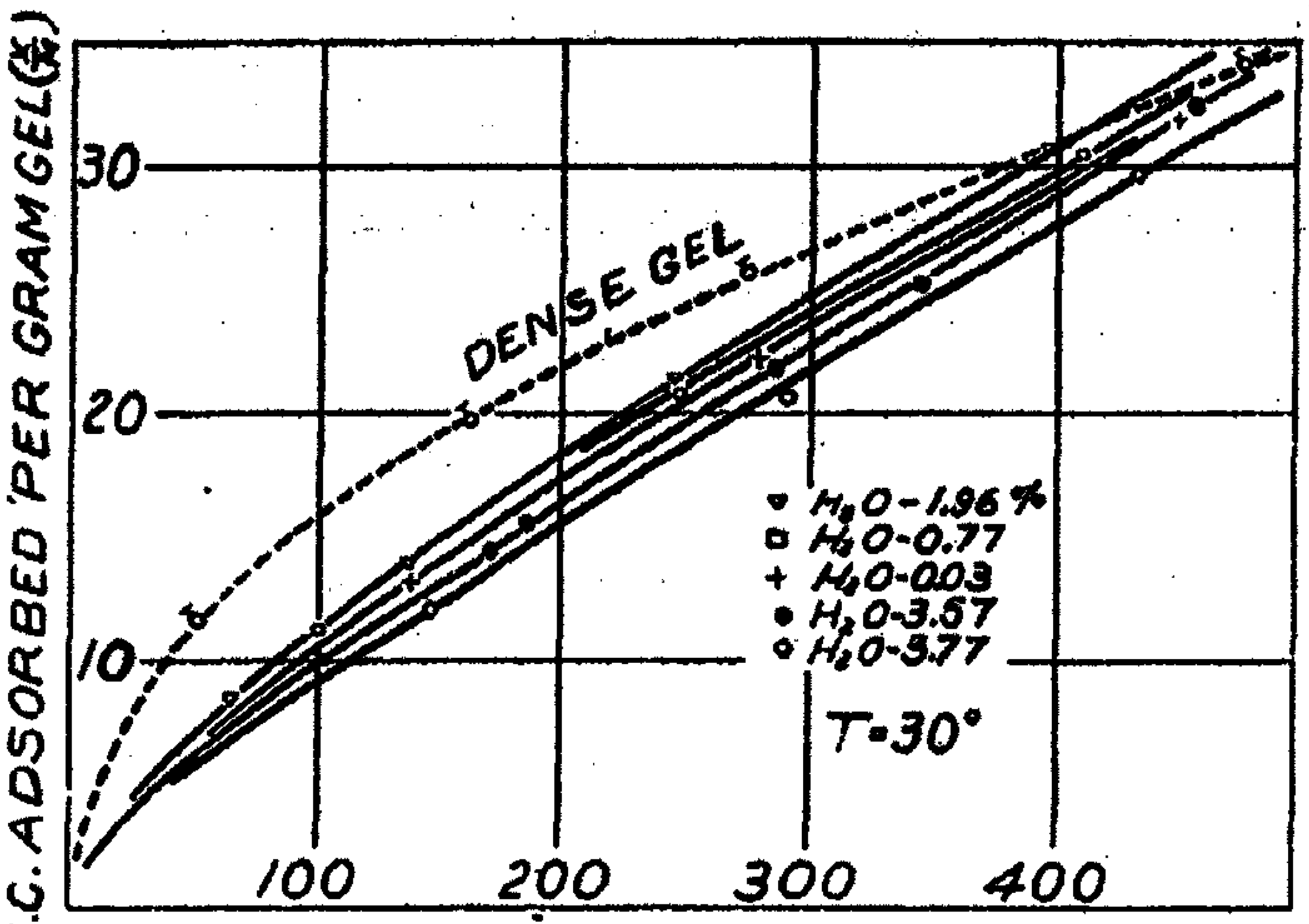

FIG. 3

Relation of Adsorption to Water Content of Gel.

TABLE II

30°C.

Run No. 16; Wt. gel 0.8766 g;
H_2O – 0.03%

X/M	P
7.17	58.20
13.22	138.28
22.32	283.32
32.01	453.63
43.16	649.60

Run No. 15; Wt. gel 1.0381 g;
H_2O – 0.77%

11.36	99.48
20.93	245.12
30.39	410.06
41.49	609.46

Run No. 11; Wt. gel 0.9811 g;
H_2O – 1.96%

3.41	16.02
8.52	66.11
13.96	137.68
21.23	245.72
30.69	395.34
45.05	634.68

Run No. 14; gel 1.1996 g;
H_2O – 3.38% (Dense gel)

X/M	P
10.60	51.13
19.85	162.85
25.78	272.97
34.01	478.40

Run No. 12; Wt. gel 0.9802 g;
H_2O – 3.77%

5.25	44.57
12.25	145.34
20.52	291.33
29.72	433.09
41.12	614.54

See also 30° run of Table I

It is brought out by a study of the five curves of the same gel but a different water content, that a gel containing 1.96% water possesses the maximum activity and capacity. Increasing the water content brings about both a decrease in the activity and capacity of the gel, while a decrease of water content to .77% apparently affects only the capacity of the gel. Anhydrous gel, however, shows a slight decrease in both properties. Whether or not this loss of adsorptive ability is due to a structural alteration caused by the higher temperature required in the dehydration is difficult to say. Leaving aside this latter point, it will be seen that the capillary theory affords a most simple and logical explanation of the above results.

According to the theory advanced in this laboratory to explain the adsorption of gases and vapors[1] the volume of liquid butane retained by silica gel should be the same as the volume of SO_2 or NH_3 retained as the same "corresponding pressure," or, the constants in the following equation should be equal for all three gases for the same sample of gel:

$$V = K \left(\frac{P\sigma}{P_0}\right)^{1/n}$$

In this empiric equation, V is the volume of liquid butane in cc. adsorbed per gram of gel (found by dividing the weight adsorbed by the density of liquid butane at the temperature), P is the equilibrium pressure, P_0 is the saturation pressure at the temperature, σ is the surface tension of the liquid butane and K and 1/n are constants dependent entirely upon the structure of the gel.

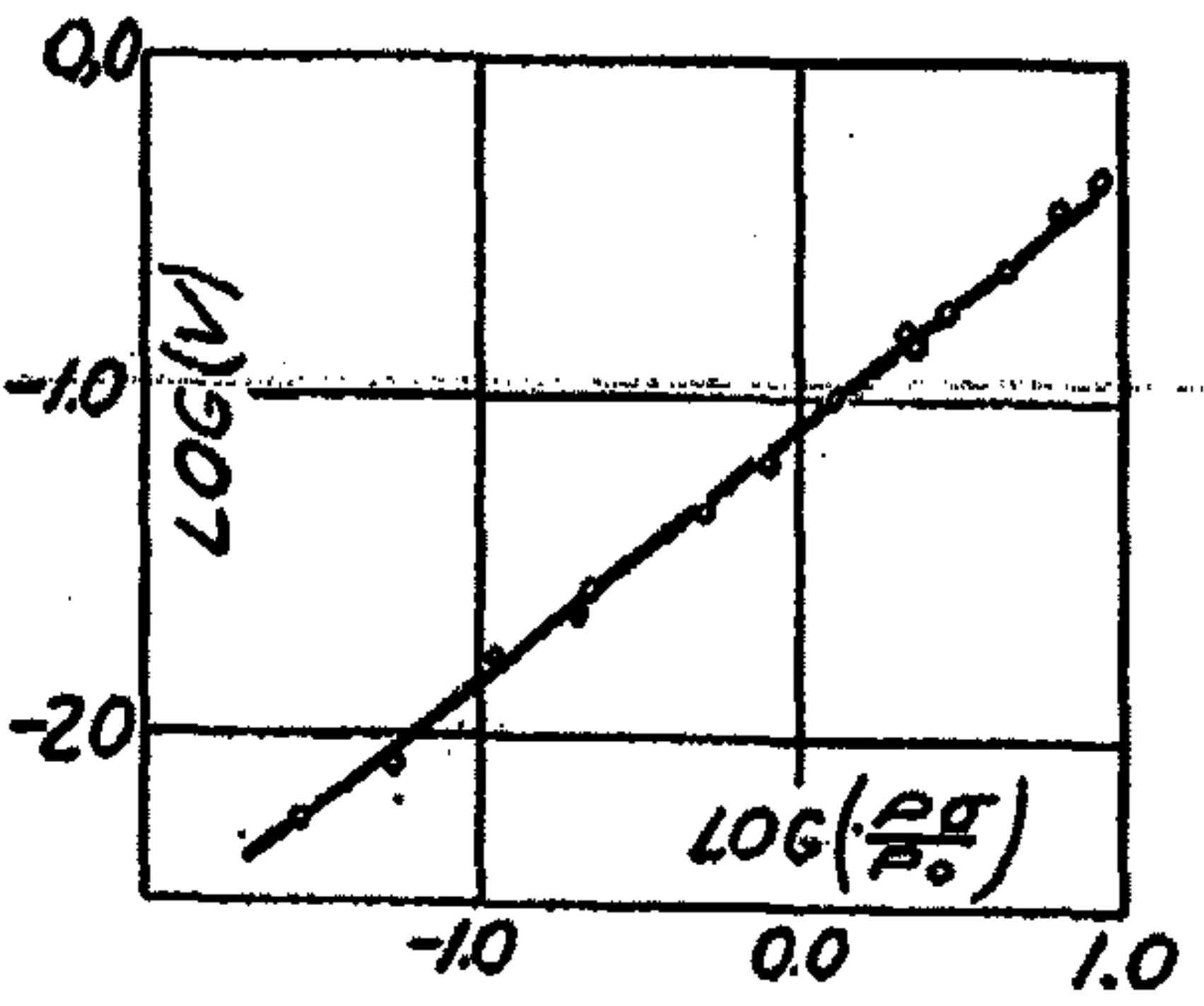

Fig. 4

Before comparisons are made it is necessary that the condensation pressures and densities of butane be evaluated. This was done as follows:

Values of the vapor pressure of butane at various temperatures were obtained from the measurements of Burrell and Robertson[2]. The logarithms of the pressures were then plotted against the reciprocal of the temperatures. From this curve were read off the vapor pressures (P_0) at 0°, 30°, 40° and 100°C. The surface tension was calculated from the Ramsay-Eötvös-Shields relation:

$$\sigma\left(\frac{M}{D}\right)^{\frac{2}{3}} = 2.12\ (Tc - T - 6)$$

at a temperature of 0° inasmuch as the density was known at this temperature. Values of the surface tension at the other temperatures were obtained by a straight line interpolation curve drawn between the temperatures 0°

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[1] Patrick and McGavack; Patrick and Davidheiser: loc. cit.

[2] J. Am. Chem. Soc., 37, 2188 (1915).

and $T_0 - 6$. The densities (D) at other temperatures could either be calculated by the Cailletet-Mathias relationship or by the above surface energy equation, using the calculated values of σ.

Table III gives the values, calculated as described above, to be substituted in the equation

$$V = K\left(\frac{P\sigma}{P^{\circ}}\right)^{1/n}$$

By plotting log V against $\log\left(\frac{P\sigma}{P_0}\right)$ a straight line is obtained (Fig. 4) which is the same for all temperatures. This is in entire accord with the results obtained in the case of the adsorption of SO_2 and NH_3. It therefore follows that the adsorption of butane by silica gel may be quantitatively accounted for on the basis of capillary condensation in the pores of the gel. Table IV gives a comparison of the values of K and 1/n found for three different substances.

TABLE III

Run No. 6; 0°C; $\sigma = 14.82$; $P_0 = 988.6$ mm.; D (liq) = 0.600

V	$\left(\frac{P\sigma}{P_0}\right)$
0.0166	0.1110
0.0457	0.4929
0.0894	1.3019
0.1523	2.5045

Run No. 10; as No. 6

V	$\left(\frac{P\sigma}{P_0}\right)$
0.1413	2.2748
0.2425	4.2207
0.3612	6.3162
0.4467	8.7674
0.4609	10.6496

Run No. 5; 30°C; $\sigma = 11.77$; $P = 2550.0$ mm.; D (liq) = 0.5980

V	$\left(\frac{P\sigma}{P_0}\right)$
0.0134	0.0897
0.0348	0.3562
0.0667	0.8639
0.1088	1.5948
0.1706	2.6812

Run No. 13; as No. 5

V	$\left(\frac{P\sigma}{P_0}\right)$
0.0273	0.2356
0.0630	0.7819
0.0943	1.3264
0.1393	2.1068
0.1854	2.8671

Run No. 1; 40° C; $\sigma = 10.75$; $P_0 = 3350.0$ mm.; D (liq) = 0.597

V	$\left(\frac{P\sigma}{P_0}\right)$
0.0443	0.5046
0.0746	1.0095
0.1219	1.7597

Run No. 3; as No. 1

V	$\left(\frac{P\sigma}{P_0}\right)$
0.0056	0.0286
0.0229	0.2049
0.0471	0.5512
0.0769	1.0179
0.1493	2.1897

Run No. 8; 100°C; $\sigma = 4.70$; $P = 12{,}500$ mm.; D (liq) = 0.590

V	$\left(\frac{P\sigma}{P_0}\right)$
0.0082	0.0546
0.0151	0.1107
0.0271	0.2131
0.0327	0.2619

TABLE IV

Gas	K	1/n	gel water content
SO_2	0.104	0.447	4.87%
NH_3	0.168	0.211	4.88%
	0.096	0.359	0.33%
Butane	0.075	0.759	3.57%

Summary

1. The adsorption of butane by silica gel of various water content has been accurately measured at 0°, 30°, 40°, and 100°C.

2. It is shown that a gel with about 2% water possesses the maximum activity and capacity.

3. A method of preparation of pure n-butane has been described in detail.

4. The capillary theory of adsorption has been applied to the above measurements and is found to be in complete accord with the experimental facts.

THE ELECTRODE, CONTACT, AND ELECTRO-KINETIC POTENTIALS OF GALVANIC CELLS

BY JAROSLAV HEYROVSKÝ

The application of thermodynamics to the various mechanisms through which the electrode potentials may be supposed to arise lead to different formulae. All such expressions are of course correct when they have been obtained from a strictly reversible cyclic process and, moreover, must give coinciding results, independently of the assumed mechanism.

Recently the author[1] deduced a formula by assuming ionisation by collision as the origin of the charge at an electrode; in that way the basigenic property of the metal could have been included[2]. A still simpler formula for the electrode potential can be deduced in the following way.

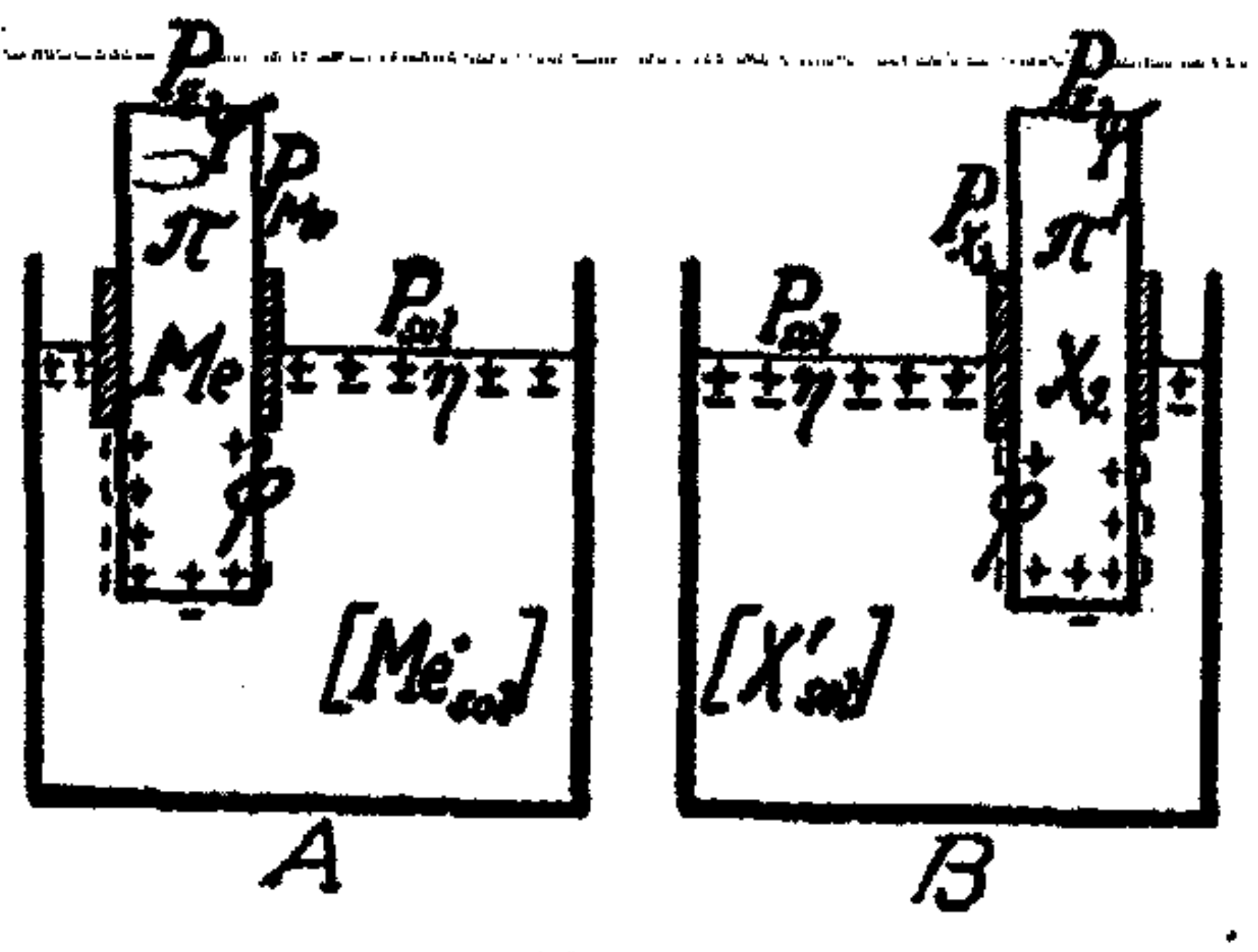

FIG. 1

The Electrode, Contact, and Electro-Kinetic Potentials

General Deduction of the Formula

Imagine a monovalent metal, Me, dipping into a solution of its ions (Fig. 1.A). Transfer one gram-atom of the metallic vapour from the metallic surface into an ionisation chamber, where the metallic atoms, the free metallic ions and electrons are all kept at a pressure p; the work we do in transferring is RT log p/P_{Me}, where P_{Me} denotes the metallic vapour tension.

Now ionise one gram-atom of the vapour into ions and electrons, effecting this by collision with electrons moving between the electrodes of the chamber with an energy I.e, where I denotes the "ionisation potential" of the metallic vapour under the physical conditions of the chamber and e the charge of an electron. In other words, the free energy of this process is for a gram-atom of the vapour $-$I.F or we have to do work $+$I.F (when F denotes one faraday) to ionise the gram-atom. Next condense the electrons from this chamber back into the metallic electrode, transferring them first to the pressure P_e, at which they exist in the vapour phase close to the metallic surface and passing them across the metallic surface. The two work terms are χ.RT log $P_e/p+\psi F$, the coefficient $\chi(=0.0417)$ has to be applied when treating the electrons as a gas[3] (ψ denotes the transition potential).

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[1] Proc. Roy. Soc., 102A, 628 (1923).

[2] This communication has been criticised by J. A. V. Butler, whose objections were shown to arise from an erroneous understanding of the transfer of metallic ions, where Mr. Butler confused concentration terms. (see *Chem. News* 128; 294; 129, 329, (1924).

[3] A. D. Fokker: Arch. néerl. (3) 4, 394 (1918); A. H. Lorentz: "Bericht Solvay 1911:" Abh. Bunsen Ges. No. 7 p. 32 (1914).

The gaseous metallic ions have to be brought from the ionisation chamber into the electrode solution with a vapour pressure P_{sol} and containing cations of the metal in a concentration $[Me^{\cdot}_{sol}]$. This transfer can proceed reversibly if the ions be brought from the pressure p, at which they existed in ionisation chamber to the very small pressure p', at which they are present unsolvated in the solution. This minute fraction of unsolvated bare ions must be in equilibrium with the solvated ions of the solution according to the action:

$Me^{\cdot}$ + n solvent molecules $\longrightarrow Me^{\cdot}_{sol}$, with an equilibrium constant

$$K_{sol} = \frac{[Me^{\cdot}_{sol}]}{p'.P_{sol}^{n}}$$

Thus to bring the ions from the chamber into the solution requires work RT log p'/p, or substituting from the equilibrium constant, it becomes

$$RT \log \frac{[Me^{\cdot}_{sol}]}{p} - RT \log K_{sol}.\ P_{sol}^{n}.$$

The latter term expresses the free energy change when the gaseous ions get solvated and can be denoted as the "free energy of solvation," $H_{Me^{\cdot}}.F$, of ions entering a solution of the vapour tension P_{sol}. If no such solvating action existed, $H_{Me^{\cdot}}$ would be zero.

When crossing the liquid-vapour interface, electric work might arise in overcoming a surface potential η, due to adsorption or to an orientation of solvent molecules.

Taking its sign as positive when the positive side of such a double-layer is closer to the surface, this work is $-\eta.F$.

To deposit the ions from the solution into the metal we have to bring them either directly from the unsolvated portion, or through this from the solvated one—across the interfacial double-layer potential, Φ, which exists at the electrode equilibrium between the metallic and the solution phase. If the positive side of this double layer lies in the metal the work is $+\Phi.F$.

Summing up all the work terms of this cycle, we have

$$0 = RT \log p/P_{Me} + I.F. + \chi.\ RT \log P_e/p + RT \log \frac{[Me^{\cdot}_{sol}]}{p} - RT \log K_{sol}.\ P_{sol}^{n} + \psi.F - \eta.\ F + \Phi.F \qquad (1)$$

The potentials $\psi - \eta + \Phi$ are very closely related to the electrode potential of the metal in solution; this becomes evident if we imagine the following transfers in a cell consisting of two metals, Me and Me′, both in solutions of their ions:

1. Transfer of one gram-ion of the metal Me into its surrounding solution $/-\Phi.F/$; the transport of one-half gram cation from this solution into the other, and one-half gram anion in the reverse direction $/(\eta-\eta').F/$ disregarding the diffusion potential between the two solutions; the deposition of one gram-ion of the second metal at the electrode Me′ $/\Phi'.F/$.

2. Transfer one F. of electrons from the first metal over the dry surface $/-\psi.F/$, condense it to the concentration of electrons existing above the second dry metallic surface $/\chi' RT \log . P'_e/P_e/$ and bring it into the second metal $/\psi'.F/$.

The result is that we have dissolved one gram-ion of the first metal and electrodeposited the equivalent of the second metal: thus the sum of the work terms in 1. and 2. must be equal to $/\pi'-\pi/F$, where π and π' denote the real electrode potentials of the electrodes Me and Me′, and $\pi'-\pi$ the E.M.F. of this galvanic cell.

We have thus:

$$\pi'-\pi=-\Phi+\eta-\psi-(-\Phi'+\eta'-\psi')+(\chi\cdot RT/F)\log P'_e/P_e$$

from which

$$\pi=\psi-\eta+\Phi+\chi.\frac{RT}{F}\log P_e+\text{a constant.}$$

Since we measure only differences of potentials, π will be characterised equally well without the constant, so that we can simplify equation (1) expressing:

$$\pi=-\frac{RT}{F}\log P_{Me}+I-H_{Me^{\cdot}}+\frac{RT}{F}\log[Me^{\cdot}_{sol}] \qquad (2)$$

Before verifying formula (1) by experimentally determinable constants, let us deduce similarly the potential of a metalloid electrode, (Fig. 1. B).

Evaporate from the metalloid electrode half a gram-molecule of the diatomic metalloid χ_2 bringing it first to atmospheric pressure, dissociate it into atoms χ and expand to a small pressure p_x, at which the metalloid atoms, their gaseous anions χ' and the free electrons coexist in an equilibrium box; bring out of the electrode one faraday of electrons under the small pressure P_e, at which they exist above the electrode and place them in the same equilibrium box expanding to p_e; let them unite to a gram-anion of χ', at the pressure $p_{x'}$ in the equilibrium box and remove this gram-anion from the box. Now allow the anions to be solvated to the vapour pressure of the solution and concentrate them from $p_{x'}$ to the concentration $[\chi'_{sol}]$ of the solvated anions in the solution. Finally dip them into the solution crossing the surface potential η and deposit them across the potential Φ at the electrode completing thus the cycle.

The sum of the free energy terms then is:

$0=1/2\ RT\log\ 1/P_{x_2}+D_{x_2}.F+RT\log P_x/1-\psi.F.+RT\log p_e/P_e-H_{x'}.F+RT\log(\chi^{+'}_{sol})/p_{x'}+\eta.\ F-\Phi.F.$ (D_{x_2} denotes the dissociation energy).

Here again, as in the previous case, we can substitute for

$$\eta-\Phi-\psi-\frac{RT}{F}\log P_e=\pi,$$

and for the logarithm of the constant of the equilibrium box, $-RT \log \frac{p_{x} \cdot p_{e}}{p_{x'}}$ the electron-affinity of the metalloid to the electron, $+E$.
We obtain:

$$\pi = \frac{RT}{F} \log \sqrt[2]{P_{x_2}} - D_{x_2} + E + H_{x'} - \frac{RT}{F} \log [X'_{sol}] \qquad (3)$$

It will be observed, that the influence of the pressure, solvation and concentration upon the sign of the potential is reversed to that which was deduced for metallic electrodes.

During these reversible processes, no attention was paid to the fact, that electrostatic attractions between the charged particles have to be overcome. However, these effects in the complete cycle almost cancel each other, so that their actual influence upon the potential must be small (hardly observable in concentration cells, if not compensated by the activity increase, which works in the opposite direction). The idea of introducing the photoelectric effect and ionization potentials into the theory of E. M. F. is due to I. Langmuir (Trans. Am. Electrochem. Soc. 29, 125 (1916)). In this work, however, the solution interfacial potential is disregarded. Fajans (l.c.) first used the thermodynamic cycle involving the "heat of hydration;" in this way he calculated the heat of hydration, from "absolute potentials" of potassium and hydrogen; this procedure was criticised by Haber (ibid. p. 750) owing to the disregard of the transition potentials from the metallic phase; however, as the difference of "absolute potentials" used by Fajans happens to coincide with the difference of the electrode potentials, his result has to be regarded as correct.

Calculation of the Electrode Potentials

If we could substitute in formulas (2) and (3) real values, we ought to obtain for different metals a series of potentials identical with the series of their "electrolytic potentials."

When looking for available data, we find it possible to calculate the electrode potentials of lithium, sodium, potassium, rubidium, caesium (thallium, silver) hydrogen, iodine, bromine and chlorine in aqueous solutions of their ions.

The following table gives the results as well as the values used in calculations:—

The Electrode M	Energy of hydration of chlorides H Cals, volts	$\frac{RT}{X_nF}\log P_{Me}$ volts	Energy of dissociation D volts	Ionization potential I volts	E. P. calculated	 observed
Li	187.000 =8.13	1.24 (1−0.17) = −1.03	— —	5.36	−1.74	−3.03
Na	180.000 =7.85	0.85 (1−0.29) = −0.60 0.62*	— —	5.11	−2.12	−2.75
K	159.000 =6.91	0.89 (1−0.29) = −0.63	— —	4.32	−1.96	−2.93
Rb	150.000 =6.52	0.80 (1−0.30) = −0.56	— —	4.15	−1.81	−2.93
Cs	151.000 =6.56	0.75 (1−0.30) = −0.52	— —	3.87	−2.17	—
(Tl	159.000 =6.91	1.71 (1−0.15) = −1.45	— —	7.30	+1.84)	−0.33
(Ag	=7.85	2.76 (1−0.14)	— —	7.41	+2.03)	+0.77
H_2	14.4 0.9 to 14.0 0.9	0	2.0 to 1.2	13.5	−0.6 +0.6	0
				Electron affinity E		
I_2	−20.000 = −0.87	−0.108	0.637	2.57	+0.96	+0.63
Br_2	− 9.000 = −0.39	−0.018	0.96	2.93	+1.56	+1.07
Cl_2	0	0	2.44	4.26	+1.82	+1.39

* The pressure of sodium is taken from Miller: J. Am. Chem. Soc. 45, 2323 (1923).

Notes to Table I

For the energy of hydration Fajans' values of the "heats of hydration" of chlorides were used (l.c.) which are the differences of heats of solution of the chlorides and their crystal-lattice energies.

The value for silver is not directly obtainable, and was taken as identical with that of sodium because of the similarity of their ionic dimensions, upon which hydration depends.[1]

The energy of hydration of hydrochloric acid was calculated from the energy necessary to ionise the gaseous molecule, I_{HCl}, taking into account, that the tension of a 2 *N* aqueous solution of hydrochloric acid[2] is 0.00117 mm Hg.

$$\text{Then } H_{HCl} = I_{HCl} + 2RT/F \log \frac{2 \times 2 \times 22}{0.00117/760} = I_{HCl} + 0.9 \text{ volts.}$$

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[1] Born: l. c., Herzfeld; Jahrb. Rad. 19, 310 (1923).

[2] Gahl: Z. physik. Chem. 33, 178 (1900).

The ionisation potential of hydrochloric acid was found by Foote and Mohler[1] to be 14.0 volts, by Knipping[2] 14.4v.

Fajans finds the heats of hydration of bromides and iodides to be by 9. Cal and 20.Cal resp. lower than for chlorides; therefore for Br_2 and I_2 the numbers have a minus sign.

The vapour pressure terms of metals are taken from Haber's communication[3] and are corrected to 300° abs. by using a Grüneisen's approximation, that

$$-RT \log P_{Me} = D_0 \ (1 - T/T_B),$$

where D_0 is the heat of sublimation at absolute zero, T_B the absolute boiling point; the vapour pressures of iodine and bromine are 0.2 and 190 mm. Hg resp. (at room temperature).

The energy of dissociation of hydrogen into atoms should be 2.0 volts, or 86,000 cal per gram. molecule are used; however, Horton and Davies[4] find this energy as 1.2 volt.

The energies of dissociation of halogens are those of Lewis and Randall[5], that of chlorine is taken as 2.44 volts (Knipping).

The ionization potentials of the alkali metals and of thallium are taken from Franck's report[6], the value of silver is that calculated by Haber. The electron affinities of the halogen atoms were derived by Knipping.

The numbers since calculated from the spectra, relate to total energies; however, at ordinary temperatures differences between the total and free energies in such processes vanish.

Although several data of the table are uncertain, e.g., the vapour pressures of metals, especially those of high melting points (Li, Ag, Tl), yet the calculated values show distinctly the same series of potentials as observed and in some cases the agreement is close showing a constant difference ca ½ volt. A principal uncertainty, however, lies in the use of "heats of solution" instead of free energies.

The Contact Potential

The metallic surface potential ψ is closely connected with the "contact potential," χ, which arises at the junction of two metals and becomes noticeable through the Peltier effect.

In such a join of two metals we can imagine the electrons being carried out of one of the metals (work $-\psi$), brought over to the second metal (work $\chi . \frac{RT}{F} \log P_e'/P_e$), put into its metallic phase $(+\psi')$ and finally sent through the contact potential ξ inside of the metals; the sum will then be zero.

$$-\psi + \chi . \frac{RT}{F} \log P_e'/P_e + \psi^1 + \xi$$

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[1] J. Am. Chem. Soc. 42, 1832 (1919)

[2] Z. Physik. 7, 328 (1921).

[3] Sitzungsber. Akad. Berlin, 51, 506 (1919).

[4] Phil. Mag. (6) 46, 895 (1923).

[5] J. Am. Chem. Soc. 36, 2259 (1914); 38, 2348 (1916).

[6] Physik. Z. 22, 388 (1921).

$$\text{Thus } \psi - \psi' = \chi.\frac{RT}{F}\log P_e'/P_e + \xi$$

The partial pressure of electrons, P_e, in the metallic vapour, P_{Me}, can be calculated from the constant $K = \frac{P_e^{0.04}.P_{Me^{\cdot}}}{P_{Me}}$ where $P_{Me^{\cdot}}$ denotes the partial pressure of metallic ions and the exponent 0.04 comes in as a necessary consequence of the corrected "electron-gas" treatment.

Remembering that $P_e = P_{Me^{\cdot}}$, we obtain $P_e = \sqrt[1.04]{K.P_{Me}}$

The free energy of the ionisation process, i.e., the affinity of the electron to the atom is experimentally determinable as the "ionisation potential" I; hence

$$-\frac{RT}{F}\log K = I.$$

$$\text{Then} \quad \psi - \psi' = \frac{0.04}{1.04}\left[\frac{RT}{F}\log P'_{Me}/P_{Me} - I' + I\right] + \xi.$$

Now the ionisation potentials of monovalent metals do not differ more than by about four volts and the logarithmic terms of metallic vapours by about one volt; the Peltier potentials amount only to millivolts.

Therefore the potential difference $\psi - \psi'$ cannot be greater than 0.2 volt, if the coefficient 0.04 can be relied upon. This shows that the electromotive forces due to the direct contact of metals and to the electron-transfer across the interface metal-vapour constitute only a small fraction of the total E.M.F. of galvanic cells, the largest part of their energy originating from the junction between the metallic conductor and the electrolyte, and being due to the solvation of metallic ions.

The Electro-Kinetic Potential

Consider now the interfacial potential Φ. From the carrying out of the cycle it is evident that not the absolute value of Φ, but $\Phi - \eta$ characterises the electrode potential (the small contact potential $\xi = \psi + \chi.\frac{RT}{F}\log P_e$ being disregarded); then we have $\pi = \Phi - \eta$.

If $\Phi = 0$, the interfacial tension between the metal and the solution must be maximal, however η is far from being zero under such conditions, equalling $-\pi$, which denotes the solution surface potential. This potential might arise from the normal surface orientation of the solvent "di-pole" molecules if "surface-active" substances are absent.

Suppose now we change the potential Φ by adding a "surface-active" substance, either containing ions, which are selectively adsorbed at the surface (like iodides or sulphides) or consisting of non-electrolytes (amyl alcohol, caffein) which change the surface tension of the solution, affecting its orientated molecular surface layer. The change of the interfacial tension of the metal (e.g. mercury) then shows, that Φ has changed by a certain amount, ζ, to Φ, but the electrode potential π of the metal remains unaffected, (Fig 2. A).

That such additions cannot change π becomes evident, if we remember that the new additional potential ζ, due to surface adsorption, (in other words Freundlich's "electro-kinetic" potential[1]) adds itself simultaneously also to the ordinary solvent surface potential η.

The $\pi = \Phi + \zeta - (\eta + \zeta)$ is unchanged; however the electrode potential π (denoted as "absolute zero") at which the new interfacial tension will be maximal (i.e. when $\Phi + \zeta = 0$) equals $-\eta - \zeta$ being now quite different from the "absolute zero potential" noticed when adsorption is absent.

Electro-capillary phenomena do not, therefore, inform us about π, but only about one of the constituents of the electrode potential, viz. Φ, which vanishes at the maximum of the interfacial tension; the so-called "absolute potentials" are not electrode potentials, since they include the "electro-kinetic" potential, which does not appear in the E.M.F., and cancels in the circuit as we enter (with a charged particle) and leave the solution (e.g. between the bottom mercury layer potentials in Fig. 2, A and B).

Two sufficiently quickly-running Helmholtz-Paschen mercury dropping electrodes (Fig. 2 D and D′) will therefore attain equal potentials only when in either solution adsorption is absent; if an adsorption potential arises in one of the solutions, then in transferring the electric charge through such a cell from one mercury reservoir (D) to the other (D′) we would have to cross from one electrode over its zero interfacial potential ($\Phi'' = 0$) into the first solution, then over the adsorption potential ζ, (which occurs only in one of the solutions) into the other and thence into the second mercury reservoir, through a zero-potential again.

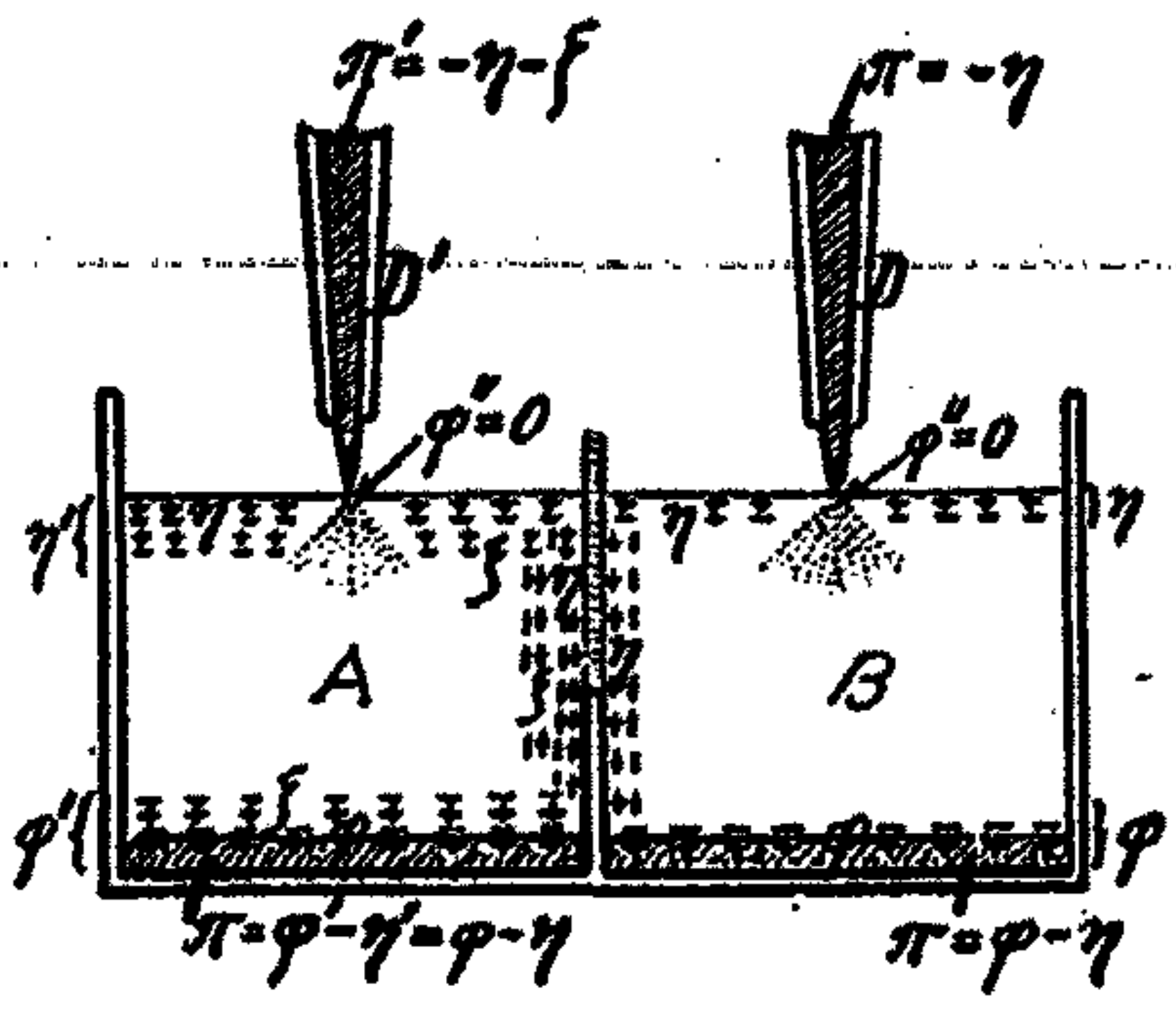

Fig. 2

The total potential encountered is ζ, although both mercury electrodes are kept uncharged by the vigorous dropping.

The Mechanism of the "Zero Dropping Electrode"

It remains now to explain how dropping mercury can acquire the potential of the maximal interfacial tension.

This electrode, consisting of a mercury jet splitting into numerous fine drops at the surface of the solution, represents a continually enormously increasing interface. The increase of mercury drops we can imagine to occur in quick installments, each consisting in adding to the electrode-surface new uncharged mercury surrounded by a new unorientated and absolutely mixed up water layer.

Consequently the electrode charge of the mercury will gradually disappear (just as according to the original Helmholtz's explanation) and the adsorp-

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[1] Freundlich "Kapillarchemie," 342 (1922.)

tion potential of the solution will be annihilated. In the limit, the electrode potential π, of the dropping electrode will be such, that its interfacial component Φ'' will totally vanish and consequently the value of π will be $-\eta$ in all surface inactive solutions, or $-\eta-\zeta$ in the case of surface-active adsorptions (see Fig. 2).

In these cases the dropping mercury has to be regarded as entirely uncharged, whereas stationary mercury when at the maximum of its interfacial tension in solutions (the same electrode potential π) is charged, having at the interface in reality two double-layer potentials (the ionic double layer and the surface potential), which cancel each other producing $\Phi = O$.

The author's warmest thanks are due to Professor F. G. Donnan for his encouragement and suggestive criticism.

Summary

1. From a reversible process consisting of energy terms concerning the ionization of the electrode vapour, the solvation of ions, concentration change and transfer of electric charges over the electrode-interphases a simple thermodynamic formula is deduced for the electrode potential of metals and metalloids.

2. This formula is verified from numerical data, all the terms being physically determinable.

3. The contact E.M.F. of metals is shown to constitute only a small fraction of the total E.M.F. of galvanic cells, the largest part of their energy being due to the ionisation and subsequent solvation of the electrode ions.

4. The rôle of the "electro-kinetic" potential is discussed and its relation to the so-called "absolute potentials" defined.

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THE DIELECTRIC CONSTANT OF LIQUID PHOSGENE

BY HERMAN SCHLUNDT AND ALBERT F. O. GERMANN

Beckmann and Junker[1], in a study of the ebullioscopy of phosgene solutions, have pointed out that phosgene probably belongs to the group of solvents which, like benzene, possess little or no ionizing power. This conclusion was based on the observation that phosgene conforms to the rule adhered to by the members of this group, that certain organic acids, such as acetic and benzoic, are associated to double molecules when dissolved in it, while their anhydrides are not. Germann recently found, on the other hand, that solutions of aluminum chloride in liquid phosgene conduct the electric current, the solvent being decomposed into carbon monoxide and chlorine in the process[2]. He has measured the conductivity of these solutions, and has found that the maximum conductivity is nearly one hundred thousand times the specific conductivity of the pure solvent, and hence it may be inferred that phosgene hardly belongs to the class of non-ionizing solvents, but rather to that of weakly ionizing solvents. In this connection a knowledge of the dielectric constant was of interest. But no measurements of this constant were available. Thwing's method[3] of calculating the dielectric constant did not furnish a solution of the problem, for depending on the interpretation made of its structure, Germann[4] has pointed out that liquid phosgene may have a dielectric constant in the neighborhood of 3.6 or in the neighborhood of 24.

Experimental

Approximately two hundred cubic centimeters of technical phosgene, as supplied by Edgewood Arsenal, were purified in an all-glass apparatus by a method similar to that described by Germann and Gagos[5], the only essential variation consisting in the use of a distilling tube in which effervescent evaporation instead of surface evaporation was employed for the fractionation of the sample. Fifty cubic centimeters of pure phosgene were thus obtained, whose vapor tension at zero remained constant at 557 mm. during distillation.

For the measurements of the dielectric constant, Drude's method[6] with the modifications made by Schmidt[7] was used. Four condenser bulbs, numbered 1, 2, 4 and 7, of which numbers 1 and 2 happened to have identical capacities, were filled with the purified phosgene. Two other bulbs were filled with impure phosgene, and the dielectric constant measured in order

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[1] Z. anorg. Chem. **55**, 371 (1907).

[2] Science, **61**, 70 (1925).

[3] Z. physik. Chem. **14**, 286 (1894).

[4] J. Phys. Chem. **28**, 879 (1924).

[5] J. Phys. Chem. **28**, 965 (1924).

[6] Z. physik. Chem. **23**, 267 (1897).

[7] Ann. Physik. (4), **9**, 919 (1902).

to determine the effect of the impurities usually present in technical phosgene as prepared by the Chemical Warfare Service. It was found that the dielectric constant of the pure and of the impure phosgene was very nearly the same.

For the calibration of the condenser bulbs, thiophene free benzene, and solutions of specially purified acetone in benzene were used, the dielectric constants of which are given by Drude[1] for use as standards. Five standards were prepared, three having values for the dielectric constant below that of phosgene, and two above. These values were plotted against the bridge readings for maximum resonance, and by interpolation of the bridge readings obtained with the four samples of pure phosgene, four values of the dielectric constant of liquid phosgene at 22° and 0° were obtained. Each bridge reading used in the curves is the average of ten concordant observations, five by each of two observers.

TABLE I

Bridge Readings

D. C. of cell liquid at 22°	Cell 1	Cell 2	Cell 4	Cell 7
6.82	46.58	46.77	39.50	30.86
5.04	49.60	49.29	43.32	35.97
3.53	51.65	51.65	47.48	41.12
2.94	52.87	52.93	49.28	43.86
2.25	54.30	54.36	51.50	47.05
$COCl_2$(22°)	50.25	50.35	45.25	38.35
$COCl_2$(0°)	49.72	49.62	44.05	37.37

Table I records the values used to deduce the dielectric constant of phosgene, and will be self-explanatory.

Table II contains the values for phosgene as read from the curves, dielectric constant values plotted against scale readings.

TABLE II

Dielectric Constant of Liquid Phosgene

Cell	22°	0°
1	4.368	4.704
2	4.352	4.832
4	4.320	4.760
7	4.312	4.600
Average	4.338	4.724

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[1] Loc. cit.

The four cells show remarkable agreement in the value given for phosgene at 22°, but the agreement is much less good at 0°, because the tubes had to be taken from the cooling bath and transferred to the apparatus, where temperature changes began to occur. The temperature coefficient calculated, −0.4% per degree at 22°, is sufficiently accurate, however, for most purposes.

Conclusion

The dielectric constant of liquid phosgene has been found at 22°C. to be 4.34 ±.02, and the temperature coefficient, −0.4% per degree.

Acknowledgment

Our thanks are due to members of the Chemical Warfare Service for supplying us with liquid phosgene for this investigation.

University of Missouri
and
Stanford University,
California.

NEW BOOKS

A Treatise on Physical Chemistry. *Edited by H. S. Taylor. 23×16 cm. pp. Vol. I, 652; Vol. II, 709. New York: D. Van Nostrand Company, 1924. Price: $12.00.* This is a co-operative work because in this way one can get a more authoritative presentation of the different fields and because it is possible to get the work done more rapidly by distributing it. The chapters in the first volume are: the atomic concept of matter, by H. S. Taylor; the energetics of chemical change, by H. S. Taylor; the gaseous state of aggregation, by Otto Maass; the solid state of aggregation, by Otto Maass; the liquid state of aggregation, by R. N. Pease; thermochemistry, by A. L. Marshall; the laws of dilute solutions, by J. C. W. Fraser; homogeneous equilibria, by Graham Edgar; heterogeneous equilibrium, by A. E. Hill; the measurement of electrical energy, by G. A. Hulett; conductance, ionization, and ionic equilibria, by J. R. Partington.

The chapters in the second volume are: the electrochemistry of solutions, by H. S. Harned; electrometric methods in analytical chemistry, by N. H. Furman; reaction velocity in homogeneous systems, by F. O. Rice; reaction velocity in heterogeneous systems, by H. S. Taylor, the quantum theory in physical chemistry, by Saul Dushman; the third law of thermodynamics, and the calculation of chemical constants, by W. H. Rodebush; photochemistry, by H. S. Taylor; infra-red radiation in chemical processes, by H. A. Taylor; colloidal chemistry, by W. A. Patrick; radiochemistry, by S. C. Lind.

Taylor considers, p. 54, that oxyhydrogen gas is reacting slowly all the time, and points out, p. 66, that if one million molecules of hydrogen are reacting with oxygen per second in a gas mixture, it will be sixty million years before there is a volume contraction of one cubic centimeter.

Taylor and a few—not all—of his fellow authors mis-spell Helmholtz's name consistently, p. 12. It is not clear from the text just what the first law of energetics really is, pp. 34, 36, or why it should not be called the first law of thermodynamics. If the calorie equals 4.182 joules, then the joule equals 0.2391 calories and not 0.2423, p. 36.

Maass rejects Lehmann's view that the substances forming "liquid crystals" melt first of all to form large aggregates, each of which is a crystal, the disappearance of turbidity being accounted for by the melting of these small crystals in turn at higher temperatures, p. 32. "This explanation is in opposition to the kinetic theory conception of a liquid. The liquid crystals would have to be enormous aggregates in order to give the optical phenomena observed. Yet, these liquid crystals have low viscosity (whereas liquids with large molecular weights have very large viscosities), and their variation of molecular surface energy with the temperature is in agreement with this low molecular weight. In fact, the variation of their physical properties, except for the rather sharp disappearance of turbidity, is continuous. In order to correlate his theory of liquid crystals with the properties of ordinary liquids, Lehmann was willing to abandon the whole kinetic theory of liquids. The real explanation of liquid crystals is given by the regional orientation of the molecules of the liquid taking place in a manner discussed above, an hypothesis which was put forward for the first time by E. Bose."

When a given film of palmitic acid, spread over a N/100 HCl solution, is kept under a constant force of 1.4 dynes and is heated, there is a sharp expansion between 28° and 35°, followed by a small steady expansion above 35°, p. 139. "The expansion coefficient above this temperature corresponds in magnitude to the thermal expansion coefficient of a gas. A change of state evidently occurred, analogous to the change of solid to gas."

When considering the latent heat of a liquid, Mills assumed that the force of attraction varies as the inverse square, p. 142. "In a recent paper, Edser has criticized these deductions on the ground that the variation of the constant with the temperature was neglected. He points out that the inverse square law obviously cannot hold and that the agreement obtained by Mills was due to the variation in molecular force of attraction with the temperature which just compensated for the error involved in using the inverse square law. . .Edser shows that the surface tension is equal to the intrinsic pressure multiplied by the diameter of the molecule and a known function of *n* where *n* is the power in the inverse distance law. By using the known values of the surface tension, the internal pressure given by the above equation, and an approximate value for the molecular diameter, sixty-five different substances gave the most probable value of *n* as being eight, so that the attraction apparently varies as the inverse eighth power."

Maass accepts the Ramsay and Shields formula as giving molecular weights of liquids, p. 127. He refers to the abnormal higher values of the constant obtained by Walden and others; but does not discuss them.

Pease says, p. 173, that "one reason for the partial failure of the law of Dulong and Petit lies in the arbitrary choice of room temperature as the temperature of comparison. Investigation of the change of the heat capacity with temperature has revealed that this law is subordinated to a more general one which states that atomic heat capacity at constant volume increases with the temperature to a maximum value which is in the neighborhood of six degrees per calorie for all substances. This constant maximum has already been reached at room temperature by those substances which obey the law of Dulong and Petit, and then heat capacities are nearly independent of the temperature at room temperature. The heat capacities of those other substances which deviate from the law are still increasing more or less rapidly with the temperature and presumably will reach a maximum at much higher temperatures. Thus, for example, the atomic heat capacity of diamond has risen to 5.45 calories per degree at 1169°K, from the value of 1.6 calories per degree at room temperature." A forward reference to p. 1167 would have helped the reader.

Pease wishes to substitute the words "mesomorphic state" for the term "liquid crystals," p. 175. "Mesomorphic substances are obviously not crystalline in the ordinary sense, nor are they under an externally applied stress. To account for their bi-refringence and therefore their anisotropic character, it seems necessary to assume that the molecules of such substances are not distributed at random as in an ordinary fluid but in some regular manner, however primitive the arrangement may be when compared to the arrangement of atoms in crystals. This assumption of molecular orientation is further borne out by the interesting forms which liquid crystals assume. Perhaps the most extraordinary of these are the so-called graded drops (*les gouttes à gradins*). When a small mass of ethyl para-azoxybenzoate, for example, is fused on a carefully cleaned glass plate or a freshly-cut cleavage surface of mica, it does not wet the surface but draws up into a drop whose upper edge is smooth and perfectly plane and whose edges are graded off into steps. The drop appears to be built up of a pile of planes which, when the drop is touched, glide over one another easily and recall the cleavage plane of crystals. It appears probable that these planes are of molecular dimensions in thickness (about 5$\mu\mu$). Their edges are made visible under the microscope by the fact that they are terminated by chains of very fine droplets which are bi-refringent," p. 176.

It is a pity to make the unqualified statement, p. 169, that "of two polymorphic modifications, that which is metastable in the melting point region has the lower melting point." This is not necessarily true in case there are two modifications in the melt.

Marshall has some very interesting pages on the heats of adsorption, pp. 220-223. Fraser defines a solution, p. 232, as a one-phase system consisting of two or more molecular species not transformable one into the other. This of course makes mixtures of gases gaseous solutions. The chief difficulty with the definition is in the application of it in these days of colloid chemistry. Unfortunately, Frazer does not give us any clue as to how we are to recognize a one-phase system. That can hardly be held up against him because nobody has a definite criterion as yet. On the other hand we may hold it up against Frazer that he cites Ostwald's whirligig proof without comment, p. 239, and that he implies, p. 275, that van't Hoff was hazy as to the volume term in the osmotic pressure formula. The Donnan equilibrium is treated at considerable length, pp. 283-290.

Edgar introduces us to the mass law, p. 292; but points out, p. 299, that "for many purposes it is convenient to consider the question of equilibrium in chemical reactions from the standpoint of the 'activities' of the reacting species." This is true enough; but the reviewer still feels that the activity is merely the figure which one has to substitute for the experimental one in order to make the equation come out right. There is a good table for the ammonia equilibrium, p. 334, and attention is drawn to the fact that the equilibrium constants for the ester formation are not the same for the liquid and the gaseous phases, p. 338. It might well have been added that one would get a third equilibrium constant in case two liquid layers were formed. The peculiarities of the distribution of silver perchlorate between water and benzene, water and toluene, and water and aniline are discussed, p. 358; but there is no explanation for the phenomena. When a small amount of silver perchlorate is added, the salt passes wholly into the water in the first two cases and wholly into the aniline in the third case. The word "isopleth", p. 400, for a line of equal concentrations, was new to the reviewer. Edgar does not believe in the constancy of the solubility product, p. 459.

Hulett has a short chapter, pp. 469-483, on the measurement of electrical energy. He, of course, favors making the volt and the ohm the primary units, and the ampere the derived unit. Some day this will be done; but electrical congresses meet seldom and act slowly.

Partington has a statement, p. 487, which is quite thrilling if true, that "some sulphides conduct metallically and others electrolytically, both solid and in the state of fusion." The reviewer fears, however, that Partington does not mean to say that some fused sulphides conduct metallically. It is interesting to read, p. 496, that "the influence of an added metal on the conductivity of a liquid metal is quite independent of the conductivity of the added metal. The determining factor seems to be tendency to compound formation. The alkali metals, having a strong tendency to combination, always lower the conductivity of a liquid metal to which they are added, whilst indifferent metals may either raise or lower it."

"Electrolysis of solutions of lithium carbide in molten lithium hydride leads to separation of carbon at the anode, whence it is concluded that the carbide is ionized. Nitrides of alkaline earth metals in the corresponding hydrides as fused solvents appear to be similarly ionized", p. 504.

Partington adopts the German spelling of cathode, p. 505, and not Faraday's. This error is now almost universal in England.

Harned follows Lewis very closely in his data on electromotive forces, making use of activity coefficients, p. 794, and considering the zinc electrode as positive, p. 798. Most of us used to do this; but it would have been better at least to have indicated that this had been given up officially in England and in Germany. Reference is made, p. 813, to the fact that an alternating current superimposed on a direct current lowers the overvoltage; but both overvoltage and passivity are considered as unsolved theoretical problems, p. 822.

"The preceding brief discussion of the phenomena of overvoltage and passivity has indicated that, up to the present time, explanations of the cause of these behaviors are divided principally into two distinct types. The first attributes the cause to the formation of chemical substances on the electrodes. In such cases as the anodic passivity of lead, this point of view seems to be unquestionably valid; but, in such cases as the anodic passivity of iron, the presence of an unstable compound cannot be regarded as established. The second theory takes these phenomena to be examples of irreversible processes, to depend on unstable physical states produced by electrolysis, and to be explained in terms of the velocities and catalytic acceleration or retardation of the electrolytic processes involved. Such a theory, although based on assumptions regarding the inner mechanism of the processes which must be regarded as highly conjectural, has been shown by Smits to be consistent with the laws of thermodynamics."

Rice does not approve of the Arrhenius method of accounting for the change of reaction velocity by postulating the existence of an active and an inactive form, p. 901. "Several objections to this hypothesis are immediately apparent; the assumption that the catalyst increases the rate of a reaction by shifting the equilibrium between the active and inactive molecules is contrary to one of the conceptions of catalytic activity, which is that a catalyst does not affect the equilibrium point of a reaction in dilute solution; further, the assumption that substances like cane sugar, ethyl acetate, etc., exist in two forms in solution is very artificial and is without experimental support; indeed, when considering multimolecular reactions we have nothing to guide us when selecting the reactant which is supposed to be present in two forms. For the reaction between cane sugar and water catalyzed by hydrogen ion, we might select any one of the three entities taking part in the reaction and by saying that it was present in two forms, active and inactive, we could deduce the Arrhenius empirical equation; there would perhaps be some justification for saying that the water exists in two forms, active and passive, for liquid water is ordinarily supposed to be a mixture of simple water molecules and various polymers; we might therefore postulate that the simple water molecules are present in very minute concentration and are the active molecules in the hydrolysis. This would account for the high temperature coefficients of hydrolytic reactions but it would also follow on the basis of this hypothesis that all hydrolytic reactions would have the same temperature coefficient; since this is not the case we cannot derive the empirical Arrhenius equation by postulating that the water is present in two forms. The remaining possibility that the hydrogen ion exists in two forms will be considered later.

"The Arrhenius hypothesis can hardly be regarded as anything more than an *ad hoc* explanation of the difficulty; from it we can conclude that each chemical reaction has a unique temperature coefficient depending on the heat of activation of the active molecules of the substrate but there does not seem to be any way of developing the hypothesis so that it can be tested."

Rice is assuming here that the active form is an ordinary chemical substance. Most of his objections vanish if we follow Baly's lead and consider the active form as due to the opening of the fields of force. The experiments of Van Name and Edgar on the rate of reaction of metals with iodine dissolved in potassium iodide, p. 945, are very conclusive as to the existence of a diffusion layer in this case. The work of Nacken on the rate of growth of crystal faces, p. 950, was new to the reviewer. Very interesting also is the discussion, p. 974, of the rate of sublimation of small spheres of iodine. The work of Knudson, Wood, and Langmuir on the velocity of condensation is given, p. 976, and Iredale's work on the adsorption of methyl acetate vapor on mercury, p. 1001.

Dushman says, p. 1005, that "our whole conception of atomic structure, of the mechanism of chemical and physical reaction of the significance of the laws of thermodynamics—all our previous ideas on these subjects have been completely revolutionized through the application of the quantum theory. Indeed, just as in the past we have had in the history of chemistry the period of the phlogiston theory, that of the dualistic hypothesis and so forth, so the historian of the future will undoubtedly be justified in designating the present as the period of the quantum theory."

Dushman closes the chapter, p. 1130, by saying: "Bohr's theory has been extended to the explanation of band spectra in terms of quantized molecular rotations. It may, in the near future, even be possible to treat chemical reactions as transitions between stationary states defined by certain quantum numbers and energy levels. The views initiated by Bohr have affected fundamentally all our previous ideas on atomic structure and radiation phenomena. But this is only a beginning and there is still with us the whole field of chemical phenomena in which there is plenty of scope for the extension of the same conceptions, and the results achieved in this manner will no doubt be just as wonderful and epoch-making as those already accomplished in the above-mentioned fields of investigation."

If the reviewer understands the situation rightly, the chemist has always played with quanta, though he did not call them that. The use of the equivalent weight and of the ion has meant a discontinuous absorption or emission of energy, though without the assumption of resonators, it is true. As for energy levels that has been a common-place to the chemist ever since it was shown that the electromotive force was a measure of the chemical affinity. It is true that the chemist did not express energy levels in terms of orbits; but that does not seem absolutely essential.

Rodebush has written an admirable chapter on the third law of thermodynamics. The reviewer was especially interested in the paragraphs on the heat capacities of supercooled liquids, p. 1142; in the heat capacity curves for metals, p. 1145; in the decomposition data for nitrates and carbonates, p. 1162; and in the relative heat capacities of graphite and diamond, p. 1166. On this last page Rodebush says that "the third law tells us that endothermic compounds are unstable at low temperatures; but the common belief that endothermic compounds are stable at high temperatures is scarcely more than a superstition. The important factor is ΔC_p formation and, even if it be positive, the compound will probably cease to be stable due to other reactions. In the sun, for instance, not only do molecules dissociate into atoms but atoms dissociate into electrons. Our generalizations in regard to specific heats assume that they approach the Dulong-Petit value as a limit at high temperatures; but this is only true for a short temperature interval. At still higher temperatures the amplitudes of vibration of the atoms become so great that the motion ceases to be simple harmonic, and dissociation analogous to evaporation takes place."

"When a metal is heated to a sufficiently high temperature, electrons are emitted in a manner that appears exactly analogous, from the standpoint of the kinetic theory, to the evaporation of molecules from the surface of a solid. There appears to be a definite heat of evaporation and a definite vapor pressure of electrons which increases with the temperature according to the well-known thermodynamic laws. Laue has shown that, under suitable conditions, the swarm of electrons emitted may be treated as a gas," p. 1192.

Taylor has written a good chapter on photochemistry; but the quantitative side overbalances the qualitative one too much for the reviewer's taste. Einstein's law of the photochemical equivalent is very important, p. 1210; but one should begin with depolarizers. The reviewer was interested in the statement, p. 1212, that short wave-length light produces both ionization and ozonization of oxygen, but that the two phenomena are independent. Weigert showed, p. 1232, "that phosgene, which is a colorless gas absorbing in the ultraviolet only, can be decomposed photochemically by visible light when chlorine is added to the phosgene. The chlorine absorbs the blue light and this energy is transferred by some mechanism to the phosgene, bringing about its decomposition. Weigert showed that this photo-sensitization is quite a general phenomenon in that the decomposition of ozone can be made sensitive in the visible region by addition of chlorine or bromine, the combination of hydrogen and oxygen and of sulphur dioxide and oxygen can be sensitized to visible light by chlorine."

Patrick defines solutions containing particles larger than single molecules or ions as colloidal solutions, p. 1277. He proposes to give a discussion of the theoretical aspects of colloidal chemistry. By a theoretical treatment he means the correlation of as many of the facts of descriptive colloidal chemistry as possible with a few fundamental assumptions, p. 1278, developing the theory of colloids around the postulates of molecular attraction and molecular kinetics, p. 1284. To what extent he succeeds in doing this will be left to the reader.

There is one place, however, where the reviewer wishes that a little more detail could have been given. Patrick accounts for the red color of certain gold sols by saying that there is a strong absorption band in the green, p. 1307. It would have been shorter and just as helpful to have said that they are red because they are red. What one wants to know is why finely divided particles of gold should absorb green strongly, when green is the color for which massive gold is most transparent.

Professor Taylor has done a good piece of work in getting this book written. It should be very helpful to students. The reviewer would not have objected to a somewhat less mathematical treatment; but he recognizes that he is a hopeless extremist on this point. This book is certainly exactly what many people want and that is, after all, what the editor was trying to furnish.

Wilder D. Bancroft

Photography as a Scientific Implement. *By Charles R. Gibson and others. 23×16 cm. pp. viii+549. New York: D. Van Nostrand Company, 1923. Price: $9.00.* The object of this book is to bring together in accessible form the methods of photographic technique developed by experts in astronomy, surveying, aeronautical observation, microscopy, metallurgy, engineering, physics, and other spheres of research. The chapters are: the history of photography, by C. R. Gibson; the elementary optics of photography, by S. E. Sheppard; photographic optics, by A. E. Conrady; the theory of photographic processes and methods, by S. E. Sheppard; astronomical photography by C. R. Davidson; application of photography in physics, by H. Moss; photography in the engineering and metallurgical industries, by J. H. G. Monypenny; photomicrography, by G. H. Rodman; photographic surveying, by H. S. L. Winterbottom; aeronautical photography, by F. C. V. Laws; colour photography, by W. L. F. Wastell; photography applied to printing, by W. B. Bishop; the technics of kinematography, by A. S. Newman; the camera as witness and detective, by W. M. Webb.

Surprise is expressed by Gibson, p. 19, that Wedgwood and Davy did not succeed in washing out the unchanged silver salt and thereby fixing the image. As a matter of fact they tried to, p. 14; but were not able to wash out all the silver nitrate in spite of its solubility. This was evidently due to the adsorption of silver nitrate by the material.

Under photographic optics, p. 52, it will be news to most people that "the natural sea horizon is not straight; it has the curvature of the earth, and from a high viewpoint this is extremely obvious even to the unaided eye."

On the next page, p. 53, we read that, "to secure the conventional and pleasing representation of buildings and tall natural objects, the sensitive plate must be in an accurately vertical position and not tilted. In portraits we assume that they represent the original as seen from a distance of ten feet or more; the unnatural appearance results when the lens is placed within a few feet or even less of the victim. The misleading effect of photographs of steamer-interiors is due to the use of wide-angle lenses; the pictures produced by painters and artists hardly ever embrace an angle of more than 30° or 40°, and accustom us to viewing pictures from a distance yielding a subtense not exceeding that angle. For that reason photographs covering a much larger angle never give a correct impression. As most people cannot see distinctly objects at a distance less than eight or ten inches from the eye, all pictures taken with a lens of a focal length below this minimum cannot be viewed from the proper distance, and therefore never look right until they are enlarged or magnified optically. That is the heavy penalty attached to snapshots taken by small cameras. It will thus be seen that the unsatisfactory types of photographs, whose perspective is usually condemned, are due to offences against well-established and thoroughly justifiable artistic conventions; the proper application of these conventions naturally is left to the user of photographic lenses. The designer can only render the perspective geometrically correct according to the criteria deduced above; when he designs a wide-angle lens, he knows perfectly well that the vast majority of the images (they can rarely be called pictures!) produced by them will be caricatures of the original subjects, but he has to meet a demand and does his best."

Sheppard's theory of ripening the emulsion, p. 131, is that "the chief function of ripening, which may also be effected with ammonia at low temperatures (ammonia being a solvent for silver halide), is probably to effect a combined process of partial recrystallization and incipient reduction of the silver halide to colloidal silver, in such a way as to secure a suitable dispersion of colloid silver in the silver halide grain."

"The use of films in the air, up to the present, has been limited. The main development of aerial photography having taken place under war conditions, the exigencies of the Service were necessarily the first consideration. The introduction of the F-type camera, as already stated, provided the initial attempt to use the film in the British Air Service, but was far from successful. Under the conditions ruling, the average risk of failure could not be taken. For a time, attempts to use film had to be curtailed, but in 1918 there was again a tendency to revert to it. The film was not used to any great extent either by the Allies or their adversaries, although both sides tried hard to produce an efficient film camera. Not merely are there mechanical difficulties when using film cameras, but it cannot be said that there exists an emulsion on film base equal to that on glass. Whilst it is admitted that in the air the film has many advantages, these are quite outweighed by the many difficulties in handling material of this nature in development. Given the necessary time for research, both with regard to the emulsion and the methods of mechanically developing and drying, the film will eventually take its place in aerial photography." p. 422.

"Light filters, when used in conjunction with panchromatic plates for aerial photography, are not primarily intended for colour correction purposes; that the colours are corrected by their use is purely incidental. With many of the uses to which filters are put in other classes of photography we are not concerned here. When taking photographs from the air, the special problem which presents itself is to find the best method of eliminating the effects of haze on the photographic plate, without at the same time unduly increasing the duration of the exposure. In taking photographs through this haze (or water vapour in suspension), on a panchromatic plate, without a filter, the results invariably lack clearness, contrast, and definition. The sole cause of this is the chemical action of the specially active ultra-violet, violet, and blue rays, which are scattered to a greater extent by the haze than rays which are chemically active.

"All plates are more sensitive to the rays in the blue end of the spectrum. Therefore the effect on the plate is that the more active rays from the haze make a greater impression on the plate than the less active, i. e., the green, yellow and red. It must also be remembered that the only image which the blue rays are conveying is a veil of fog. Obviously, then, a means must be provided to restrain the action of the more chemically active rays, and allow the remainder to pass unchecked, thereby adjusting, as may be necessary, the actinic power of all the colors throughout the spectrum in their action on the plate," p. 424. This is done by putting in a red filter or—speaking more accurately—a filter which cuts out a large portion of the blue.

The reviewer did not know that "a modified form of flash-powder is recommended by MM. Lumière and Seyewetz, perchlorate of potassium being substituted for the usual perchlorate. The light produced is richer in actinic rays and the mixture is safer in use," p. 448.

In the chapter on the technics of kinematography, p. 489, we read that "early cameras were quite simple compared with those now in general use. The modern camera will operate the film in the opposite direction by turning the handle backwards. This movement was at first only used for making trick pictures in which all motions appeared in their reverse order when thrown on the screen, but it is now an indispensable item, and is used in conjunction with the fade mechanism and for double exposures. Counters which indicate the number of feet of film which has been exposed were in most cameras, but the cameras today have quite elaborate indicators by which an individual picture in the series can be brought opposite the lens if desired, no matter how many times the film may have been run through the mechanism or 'reversed'. Double, triple, and sometimes quadruple exposures are made on the same film in the production of tricks, visions, and other effects. Another comparatively recent addition to the camera is the 'fade' mechanism. This, when set in action, causes one of the shutter discs to rotate slowly in relation to the other, so that the aperture in the shutter closes slowly till no light is admitted to the film. This has the effect of exposing each successive picture to a less extent till no light strikes the film. The effect known as a 'fade out' is thus produced. The opposite action—starting with the shutter closed—produces a 'fade in', and a combination of the two actions causes the appearance, now so much used, of one picture fading away and another taking its place, as in the well-known dissolving views."

"In the camera only one-half (generally somewhat less) of the movement of an object is recorded because the shutter obliterates the remainder of the movement. In the case of a small object moving across the picture at a high speed, no distinct rendering will be found on the developed negative. The distance moved during each exposure will be represented by a blur, the length of which will be equal to the amount of space passed through by the object in about 1/32 of a second. As the object moves while the shutter acts, the blur on the succeeding picture will be separated from the previous position by a blank space. When projected, a series of blurs, each separated by a space from the next one, will appear on the screen. A flying bird or a tennis ball is very inadequately reproduced. It might be supposed that so poor a record of the original could not give satisfaction, but as the eye views such a subject in nature it cannot distinguish details, nor can it hope to do so on the screen. As the eye follows the apparent movement of the object, the stronger part of the blurred images—the middle portions—impress themselves on the retina, and more or less remain and bridge over the spaces, and to an extent give the impression of continuity The longer the shutter remains open compared with its obliteration period, the longer in proportion will the blurs be and the shorter the spaces, and vice versa. It is doubtful whether any advantage would be gained by increasing the time of exposure to more than half. If the blurs could be made to join one another, owing to the persistence of vision, the appearance on the screen would be that of a blur more pronounced and longer in proportion.

"In the first days, movements of persons and things were rendered on the screen in a jerky manner. This was greatly due to a false idea—a desire on the part of the photographer to secure sharp pictures. In order to do this he reduced the opening of his shutter and recorded less than one-fourth of the total movement of the object. On projecting the picture, say of a moving ball so photographed, the appearance on the screen would not simulate the movement of one ball but present a string of balls, each one stationary, the first and last of the series faint, and the middle one well defined. The last of the series would disappear and others appear in front, each becoming stronger and fading in succession. With strong contrast perhaps six to eight images could be seen at a time. An image of a quick-moving limb appeared as if the owner was temporarily supplied with two or more, and the wheels of vehicles revolved in the wrong direction or not at all, as often as not.

"Animated pictures for a long time were much marred by flicker; the 16 per second flashes of light were painfully evident. Many devices were tried with the idea of curing the defect. It has been found that the eye cannot appreciate the intermittence of light and darkness, provided the changes take place at a greater rate than about 40 per second. By putting two extra blades on the projector shutter 48 obliterations take place in one second, and to the eye the light appears quite continuous. One thing, however, is of great importance—the obliterations must be of equal length, and quite equally spaced; if not, a certain amount of flicker will be evident. The three-bladed shutter cuts off just about one-half the light, each blade being about one-sixth of a circle; the change of picture takes place in a little over 1/100 of a second, while one of the blades is passing. The loss of light is certainly great, and has to be made up by increase of electric power," p. 500.

Wilder D. Bancroft

Vat Colours. *By Jocelyn F. Thorpe and C. K. Ingold. 22×14 cm; pp. xvi+491. London and New York: Longmans, Green and Co., 1923 Price: $5.50.* In the preface the author says: "Whatever the true nature of dyeing may be, whether, or no, it has a definite physical basis and involves some quantitative relationship between fibre and dye, it is certain that mere absorption, adsorption, or sorption of a dye base by the fibre, such as, for example, takes place when wool is coloured in a bath containing the hydrochloride of rosaniline, leads to an effect, which, from the point of view of fastness and stability, leaves much to be desired.

"In reality the fibre is, in such circumstances, stained by the dye, and like all stained material will readily part with its stain. In other words the dye is not fast and the fabric, therefore, unsuited to meet the conditions to which a dyed fabric usually has to be subjected.

"It has long been recognised that the only way in which fast colours can be imparted to fabrics is to cause the actual coloured compound to be formed within the fibre of the fabric, that is to say, by bringing about within the fibre the chemical reaction by which the dye is formed. There are, at the present time, many ways known by which this can be done. For example, a large number of azo-dyestuffs can be diazotised on the fibre, and the diazonium salts thus produced can be made to combine with other components thus leading to the production of new azo-dyes within the fibre. Many dyestuffs combine with metallic salts and can be stabilised on the fibre by after-treatment with these substances. Others form definite compounds with, for example, formaldehyde, and can be fixed on the fibre by the aid of this reagent. Again, the members of one of the most important and fastest series of colouring matters—the mordant colours—depend entirely for their value as colours on the property they possess of forming "lakes" with metallic hydroxides.

"Still, the art of dyeing, which is certainly one of the most ancient of the arts, did not await the advent of the chemist but arose by trial and error. The ancient enquirer would find to his hand many coloured substances and his desire would be to impart these colours to other material, and possibly to himself, at will. He would find that some served his purpose and that others did not. That some would impart colour, which, however faded rapidly or could be washed away, whilst others gave stable colours which survived all the weathering to which they were subjected. The colours he would find suitable were colours belonging to the vat series, and by using them he was discovering the process by which the fastest and most serviceable colours of the present day are imparted to the animal, vegetable, and artificial fibres. It is true that the ancient methods were hap-hazard and liable to give variable results; but the process by which, for example, the Hindu dyers used indigo was essentially the same as that by which the most modern colouring matter, say, duranthrene, is fixed on the fibre at the present day. For the vat dye is a substance insoluble in all the usual solvents, but is rendered soluble by reduction and, in this form, is caused to enter the fibre from the dye-bath. Reoxidation by the oxygen of the air is then alone necessary to reproduce the original colour within the fibre.

"In the modern vat, reduction is achieved by chemical means under well-defined and well-understood conditions, but the ancient dyers found their reducing medium to hand within, for example, their 'greening weed', and it was only necessary to steep their fabrics in the mixture and then to expose them to the air.

"Indigo, by far the most important and valuable colouring matter the world has known, was, up to the closing years of the last century, the sole representative of the vat series of colouring matters of commercial importance. The determinatiom of the constitution of this substance revealed the structure on which the property of vat dyeing was based, and the solution of the problem of its synthesis led, in the first instance, to the preparation of synthetic analogues of indigo having different shades of colour but similar properties. Later, the production of new types of compounds, notably from anthraquinone, placed the vat dyes in the fore-front of the synthetic colours and at the present day they are the fastest, most brilliant, and most valuable of all the colouring matters."

The subject is treated under four heads: indigoid vat dyes; anthraquinone; miscellaneous vat dyes; preparations. The volume is chiefly straight organic chemistry and therefore of importance to the physical chemist of today mainly as a reference book. The chapter on Tyrian purple is interesting, however; though one wishes that the author had hazarded some guess as to the effect of sunlight in developing the color. The chapter on natural indigo is good and the reviewer was interested to learn, in the chapter on synthetic indigo, that vanadium oxide is superseding mercuric sulphate in the oxidation of naphthalene.

"Until the beginning of the present century indigo remained the only known vat colour of any commercial value. The extreme fastness of indigo and of many of the colours produced by the vat process, towards light, and in the various vicissitudes which a dyed fabric may be called upon to undergo in daily use, naturally constituted a strong incentive towards research with a view to the production of other substances having similar properties. Researches with this object proceeded in three main directions. In the first place endeavours were made to prepare derivatives of indigo and in 1901 the first commercially valuable substance of this class, namely 5:7:5′:7′-tetrachloroindigo, was placed on the market by the Badische Anilin- and Soda-Fabrik. The second line of research had for its goal the production of analogues of indigo having a different carbon skeleton from indigo itself but a similar or at any rate a strictly analogous chromophoric residue. The first signal success in this field was the production of thioindigo by P. Friedländer in 1906. The third main objective was the preparation of vat dyes similar to indigo in the properties which render that substance of such great commercial value but possessing not only a different carbon skeleton but also an entirely different, chromophoric residue. The first two substances of this class to be prepared were indanthrene and flavanthrene, which were produced in 1901 by R. Bohn and placed on the market by the Badische Anilin- and Soda-Fabrik in the same year.

"All vat colours must contain a reducible carbonyl group, and the reducible carbonyl groups in indanthrene and flavanthrene are the carbonyl groups present in an anthraquinone nucleus. In fact, indanthrene and flavanthrene may be regarded as the parents (in the historical sense) of the class of vat colours derived from anthraquinone, a class the membership of which is now so large that it may be said to constitute the most important series of colours at present available. Almost every imaginable shade is represented.

"In fastness the anthraquinone vat colours are in no way inferior to the indigoid colours, in fact many of them are faster than indigo itself. Considered as organic substances they are amongst the most stable known, indanthrene for example surviving a temperature of 470° in the presence of air.

"There is one noteworthy difference between vat colours of the indigo class and those derived from anthraquinone; for whilst the vats formed by reducing indigo analogues are either colourless or only slightly coloured, the reduction products of the anthraquinone dyes are themselves strongly coloured substances substantive to cotton in alkaline solution," p. 173.

The reviewer was also interested in the paragraph on p. 281. "Since indanthrene A is the commercially valuable constituent of crude indanthrene, it was an important discovery that either the A- or the B-compound could be made the principal product of the alkali fusion of 2-aminoanthraquinone by suitably regulating the experimental conditions. If the fusion be conducted at 200°-250° without the addition of any other substance the product consists of indanthrene A to the extent of about two-thirds and indanthrene B to the extent of one-third. In the presence of oxidising agents, however, for example, if a stream of oxygen be passed through the melt during the fusion process, or if potassium nitrate be added, only traces of indanthrene B are produced and indanthrene A is almost the sole constituent of the precipitate obtained during the subsequent oxidation of the aqueous solution. On the other hand, if the fusion be carried out below 200°, and particularly if reducing agents are present then indanthrene B becomes the chief reaction product. This is the case, for example, when 2-aminoanthraquinone is heated at 150° with very concentrated alcoholic potassium hydroxide."

Wilder D. Bancroft

Spectroscopy. *By E. C. C. Baly. Vol. I, Third edition. 21×15 cm; pp. xi+298. London and New York: Longmans, Green and Co., 1924. Price: $5.00.* The second edition was reviewed twelve years ago (17, 88). In the preface of this edition the author says: "The science of spectroscopy during recent years has advanced to a remarkable extent. Since the last edition was printed, new fields of investigation have been opened and the limits of knowledge in the older fields have been pushed very far forward. It has not been possible to comprise within one volume any account, however, brief, of the whole, and it has therefore been decided to divide the book into two volumes. The present volume deals with the standard methods of work in the infra-red, visible, and ultra-violet regions of the spectrum and thus includes the first half of the original volume."

This is now the standard book on the subject and there are many things in it of special interest. "During recent years the technique of manufacture of optical surfaces, both plane and curved, has improved in a most remarkable way. This very striking advance is in the main due to Michelson and his work on interferometers, since this work may be said to rest on the fundamental basis of truly plane surfaces. The necessity for such surfaces, indeed, became the mother of invention so that it is now possible to obtain optical surfaces, both plane and curved, with an accuracy of figuring which would never have been obtained but for the pioneer work of Michelson. To a great extent this advance has been due to the English firm of Hilger and indeed Professor Michelson has stated that his measurements would have been impossible had it not been that this firm were able to produce interferometer plates of sufficient accuracy. This work has led to similar improvements in lenses and prism manufacture, and it is obvious that concurrently with such improvements an efficient system of testing the figuring of optical surfaces must be developed. Such a method has been worked out and is in use at the present time. It is not possible here to give a detailed description of the apparatus used, but the principle of the method consists in obtaining interference fringes with an interferometer of the Michelson type, one of the light beams passing through the surface under test. The interference bands give a contour map of the surface and from this map the nature of any imperfections can be recognized, that is to say, whether they are in the form of "hills" or "valleys". The treatment of the surface necessary for the removal of these can therefore be determined and a perfect surface obtained. The apparatus and method have been worked out by Twyman," p. 95.

"It must be remembered that all work of the highest accuracy demands the skill which can only be gained from understanding and experience. Understanding of the possible variations due to the many sources of error, and experience which alone can teach the best method of reducing all these to a minimum. At the outset many will find keen disappointment their portion, and indeed at times, as the late Lord Rayleigh said, one is tempted to doubt the constancy of Dame Nature herself. But there comes at length to all who possess true love for her a great uplifting sense of victory over the many pitfalls with which she bestrews the way of the unwary. To such is born a very perfect happiness, the birthright of the true scientist who, without thought of personal gain, follows new paths, and, seeking inspiration at the fountain's head, extends the confines of knowledge for the benefit of mankind," p. 149.

"The most recent results would seem to show that quite apart from its intrinsic interest investigation of the infra-red region holds out very great promise. At the present time the fascinating work based on the Bohr theory of the atom and the modern developments of X-ray spectroscopy have tended to focus the attention of scientific workers on to the most refrangible end of the spectrum, but I firmly believe that the time will soon come when the long-wave region will equal the short-wave region in interest. It has been shown that all substances possess powers of selectively absorbing infra-red rays to as far as $\lambda = 3000\mu$, and the integral relations between the many long-wave radiations selectively absorbed by a substance seem to prove that they are inherently characteristic of atoms and molecules. Up to the present no direct connection has been found between these very small frequencies and the very large frequencies dealt with in the Bohr theory. This connection will doubtless soon be discovered and I am brave enough to prophesy that the key to the problem of the absorption and radiation of energy by elementary atoms will be found in the infra-red. It is hoped that more workers will enter this field and take a hand in unravelling the mysteries that still lie hidden therein," p. 217.

"The application of the focal isolation method has enabled Rubens and von Baeyer to discover the existence of waves of exceedingly long wave-length in the emission spectrum of quartz mercury lamps. They investigated the radiation from a large number of sources, including sparks between various metal electrodes and the arc between carbon electrodes. It was at once found on trying with a quartz mercury lamp that there is present a very strong long-waved radiation, and it was soon discovered that this radiation must possess an essentially different composition from that of the Welsbach mantle, the mean wave-length of which is 108μ. For instance, a layer of quartz 14.6 mm. thick transmits 46.6 percent of the mercury lamp radiation and only 20 percent of the Welsbach mantle radiation. A number of experiments were carried out to test the transmitting power of various substances for these rays and for the rays from the Welsbach mantle. About seventeen different substances were experimented with, and in every single case the percentage transmission for the mercury lamp radiation was greater than for the Welsbach mantle radiation. Further, it was found that the percentage transmission was increased very materially if these radiations were previously passed through a 2 mm. layer of fused silica. It is evident, therefore, that the fused silica acts as a filter and cuts off some of the shorter wave-length radiation. Therefore, the percentage of transmission given by the same set of substances with the Welsbach radiation is very much smaller. Further experiments showed that the most effective ray filter is black cardboard, and the authors finally substituted for the silica a filter of black cardboard 0.38 mm. thick. In order to determine the average wave-length of these radiations attempts were made to measure them by the quartz interferometer, as already described. The interferometer curves obtained with the quartz mercury lamp without any filter showed a very irregular character. Nevertheless, it was evident that the main element of the radiation was about the same mean wave-length as that already dealt with from the Welsbach mantle. As soon as a 15 mm. layer of quartz was inserted a very considerable difference in the curve was noticed for the first minimum which previously was observed at a thickness of the air film of about 26μ now did not appear until the air layer was 42μ thick. If the thickness of the quartz filter was increased to 42 mm. the first minimum was not observed until the air layer of the interferometer was 68μ thick. At the same time the interferometer curve became more regular, and the faintly marked maximum began to make its appearance. With a filter of black cardboard 0.4 mm thick the periodic nature of the curve becomes more distinct. Here the minimum lies at a thickness of 78.4μ, and a strong maximum at 156.9μ, but even in this case an accurate determination is still very difficult. It is evident, as is previously deduced from experiments on transmission, that the radiation after filteration through black cardboard contains a greater amount of the long-wave radiation. It is still doubtful whether the long-wave radiation consists of rays of different wave-length such as would be expected if they arose from the luminiferous radiation of mercury vapour, or whether it is simply a continuous thermal radiation. It is, however, safe to deduce from the observations that a large portion of this radiation possesses a mean wave-length of 314μ, or very nearly one-third of a millimetre. It may be added that Rubens and von Baeyer satisfied themselves that the radiation in question has its origin in the mercury vapour itself and not in the hot quartz walls of the lamp," p. 236.

"The investigation of infra-red absorption spectra received a great stimulus in 1912 when Bjerrum enunciated his conception of molecular rotation. The fundamental basis of this theory is that in addition to the characteristic frequencies in the infra-red established by its chemical nature a molecule will also possess a frequency in the long-wave infra-red established by its rotation. Bjerrum stated that the result of this will be that the characteristic frequencies in the short-wave region will not evidence themselves as single absorption lines but as groups of three frequencies, $F + R$, F, $F - R$, where F is the frequency in the short-wave region and R is the rotational frequency. When as in actual practice a number of molecules are present there will be found at F an absorption band containing the frequencies $F + nR$, F, and $F - nR$, where $n = 1, 2, 3$, etc. Further, there will be found in the long-wave region a series of absorption lines with the frequencies nR. From investigations made by Miss von Bahr in Rubens's laboratory strong support was found for Bjerrum's theory and since then further important results have been obtained on the structure of absorption bands," p. 244.

Wilder D. Bancroft

The Constituents of Coal Tar. *By Percy Edwin Spielmann. 22×14 cm; pp. xii + 219 London and New York: Longmans, Green and Co., 1924. Price $4.25.* "The object of this book is to be useful to those chemists who are interested in the individual constituent substances that together form coal tar. This material is so often looked upon as being the source mainly of a series of fractions valuable in commerce, that little thought is given to the large number of chemical entities that are present with the exception of perhaps a dozen individuals."

The subject is taken up under the general headings: coal tar; hydrocarbons; oxygen compounds; sulphur compounds; nitrogen compounds. The main part of the book is, of course, straight information of a very valuable nature. There are a number of minor points, however, which are of general interest. "All the benzene derivatives tested proved to be more toxic to insects, molecule for molecule, than carbon disulphide", p. 9. "*Bacterium aliphaticum* and *B. aliphaticum liquefaciens*, both present in the earth, destroy the straight-chain hydrocarbons and leave the napthenes and aromatic hydrocarbons unattacked.... Others will destroy aromatic hydrocarbons preferably and even hydroxyl compounds," pp. 10, 29.

"The independent polymerisation of acetylene to form benzene is a change of fundamental theoretical importance. In practice, the conversion does not proceed far; but if activated wood charcoal is present, a whole series of products, from benzene to anthracene, result," p. 16. "In all the work that has been done, in no case does naphthalene appear in a primary reaction. At a low temperature, the main products are paraffins, naphthenes, and olefines, the higher pure aromatic and hydrogenated hydrocarbons and phenols; and only above 750° does naphthalene begin to appear. It cannot be formed by hydrogenation of naphthenes and of hydrogenated aromatic hydrocarbons, so that it may result from the decomposition of substituted naphthalene, though this is not likely. In fact, the mode of its production is not clear, unless it be supposed that the initial distillation of coal gives small 'bricks', such as acetylene, from which this substance can be built up," p 19.

"That 'free carbon' is not carbon is commonly known; but there are very few facts published about it. It is the material left insoluble after pitch has been treated with hot benzene, though a better preparation is obtained by solution first in carbon bisulphide and finally in benzene.... When coumarone resin is destructively distilled and the pitch is extracted with solvents, the composition of the residue is probably closely similar to that of the free carbon of ordinary pitch," p. 107.

The reviewer is sceptical as to the existence of a phenol-water compound, $C_6H_5OH.55H_2O$, p. 117. "The formation of red colour in phenol is due principally to the presence of quinone and catechol produced as impurities by oxidation, the colour itself being most probably due to phenoquinone, $C_6H_4O_2(C_6H_5OH)_2$. Contributory evidence of this is found in the fact that an oxidizing substance has actually been detected in measurements of electromotive force of red phenol in alcoholic solution," p. 119.

The effect of carbon disulphide on the soil is remarkable. "After a temporary reduction of micro-organisms, there is an enormous increase, as well as an increase of soluble compounds of nitrogen and sulphur. In its employment against undesired plant and soil life care must be taken lest the nitrifying bacteria of the soil be also killed. In sufficient quantity carbon disulphide will kill *Azotobacter*; but not all nitrifying bacteria are equally easily destroyed. Whilst its action varies towards different soils and crops, there is an undoubted improvement in sulphur crops, for instance, mustard," p. 147.

"It is remarkable, though the significance is not immediately apparent, that the majority of the nitrogen compounds in coal tar are nitrogen ring compounds and not substitution products of the aromatic series. This is contrary to what has been described among the oxygen compounds, where the phenols form an important proportion. They have not been fully worked out; there are still certain higher boiling alkyl derivatives that await identification," p. 156.

"Most remarkable is the fact that many substances, more particularly nitrogen compounds, dissolve to a much greater degree in a pyridine-water mixture than in either liquid separately, and a few, some sugars, for instance, in a smaller proportion. The matter is complicated by there existing at least three solvents—pyridine, pyridine-water as a pyridonium compound, and water; together with the capacity of pyridine to form additive compounds," p. 181. "Quinoline is an unusually good solvent for a large number of substances, behaving like pyridine in a complex manner, as the result of formation of additive compounds. In some cases a substance may be more soluble in an equimolecular mixture of quinoline and water than in each liquid separately," p. 188. *Wilder D. Bancroft*

Physical Chemistry for Students of Medicine. *By Alexander Findlay. 22×15 cm; pp. ix+227. New York and London: Longmans, Green and Co., 1924. Price: $2.60.* "The great advances which have been made in recent years through the application of the methods and teachings of physical chemistry to the study of physiology, bacteriology, and other branches of biological science underlying medical practice, have made it imperative for the student of medicine to acquire some knowledge of that branch of chemistry. In the present volume, those parts of physical chemistry which have found important applications in the medical sciences are discussed in an elementary manner, but also in sufficient detail to enable the student to read with profit larger and more specialized works. The treatment of the subject is based on the course of medical physical chemistry pursued by medical students in the Univeristy of Aberdeen, and regard is had throughout to the physiological and medical bearings on the subject.

The chapters are entitled: the gas laws; the aqueous milieu of the life processes; diffusion and osmotic pressure; osmotic pressure in the living organism; the behaviour of electrolytes in solution; the law of mass action and chemical equilibrium; law of mass action applied to solutions of electrolytes; hydrion; velocity of reaction and catalysis—enzyme action; the colloidal state; adsorption; the permeability of the cell membrane.

Any book by Findlay is sure to be good and this one is no exception to the rule. The last three chapters are entirely colloid chemistry. In the chapters on the colloidal state the subheads are: crystalloids and colloids; suspensoids and emulsoids; heterogeneity of colloid sols; the ultra-microscope; ultra-filtration; Brownian movement; osmotic pressure of colloid electrolytes and membrane equilibria; production of colloidal sols; electrical properties of colloids; mutual precipitation of colloids; precipitation of suspensoids by electrolytes; emulsoids; precipitation of emulsoids by electrolytes; protective action of emulsoids; formation of gels; imbibition. *Wilder D. Bancroft*

AN UPPER LIMIT FOR THE THICKNESS OF THE ADSORPTION LAYER ON SILICA

BY D. C. JONES

A large amount of interest has been shown recently in the thickness of the adsorption layers on solid surfaces. In this paper some discussion is given of experimental results on this question, and a preliminary attempt is made to measure the thickness of the adsorption layer on silica in contact with a solution.

The experimental results themselves are very conflicting. The methods that have been adopted in the case of a vapour have been to measure either the changes of pressure produced by adsorption on a known surface, or to actually weigh the adsorbed material. The adsorbent is usually in the form of a powder, and the increases in weight obtained by this latter method are often quite large, (0.001–0.01 grams per gram of adsorbent). Ihmori[1] used a microbalance to weigh the very small adsorptions he obtained on plane crystal surfaces, (area approx: 12 sq. cms.), and plane metal surfaces of similar small extent. Langmuir[2] measured the adsorption of a large number of gases on mica, glass, and platinum surfaces at very low pressures and temperatures, using a McLeod gauge to estimate the pressure changes obtained. The actual adsorptions he obtained are all very small, the highest value representing a layer of the order of 0.01 molecules thick. Extrapolating to the saturation value by means of his equation the thickness of the adsorption layer is of the order 0.1 to 0.5 molecules thick.

These results do not agree well with many former experimental results, and recently Evans and George,[3] have measured the adsorption on a large glass surface (glass wool) of CO_2, with the explicit intention of testing Langmuir's theory. The experiment was done at one pressure only, 121.6 m.ms., at 0°C., but the result gave them a 5 molecule thick layer. Langmuir does not give any values for the adsorption of CO_2 on glass and so a direct comparison is impossible, but he has given the adsorption curve of CO_2 on plane mica surfaces at 155°K. In the adsorption results of all other gases on glass and mica at liquid air temperatures, glass always adsorbs considerably less than mica. The highest equilibrium pressure of CO_2 on mica that Langmuir observes is 0.04 m.ms., but although the absolute value of the pressure used is much smaller than in Evans and George's experiment the temperature of adsorption is at the same time very low, and it can be calculated easily that p/P_0 where p is the equilibrium pressure and P_0 is the saturation pressure at that temperature, is equal to 1/200 in the case of Evans and George, and 1/450 in Lang-

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[1] Wied. Ann., 31, 1006 (1887).

[2] J. Am. Chem. Soc., 40, 1393 (1918).

[3] Proc. Roy. Soc., 103 A, 190 (1923).

muir's case. The CO_2 adsorption observed by Langmuir at this value of p/P_0 corresponds to a layer less than 0.01 molecules thick as compared with the 5 molecule thick layer found by the other workers. Former adsorption has shown that with p/P_0 constant, at lower temperatures the adsorption is either constant, as in the experiments of Trouton[1] and Orme Masson[2] on swelling adsorbents, or in the case of non-elastic porous adsorbents like charcoal or silica increases.[3] There appears then to be very large differences in these two sets of experimental results. It may be thought that the porous spaces present when glass wool was used would cause a liquefaction of the type that is suggested by Zsigmondy.[4] But an examination of the quantitative equation, a slightly approximated form of which is used by Anderson,[5] shows that the diameter of the capillary would have to be of the order of less than molecular size to account for adsorption at this value of p/P_0, i.e. 1/200. The contiguity of the solid surfaces would on the other hand reduce the total available surface.

It is very important to know to what treatment the glass-wool used by Evans and George was subjected before the adsorption, apart from heating it in the adsorption chamber to 300°C. in a vacuum. Ihmori's results, (loc. cit.), show very large adsorption variations on rock crystal and glass surfaces, according to the preliminary surface treatment. The adsorption on rock crystal surfaces decreased a hundred times when the surface was washed with water. Merely brushing or polishing the surfaces had very considerable effect. Langmuir has already drawn attention to Ihmori's result on the adsorption of water-vapour by platinum surfaces. When the platinum surface was cleaned thoroughly by heating to red-heat the adsorption was too small to be measured. It is, perhaps, a little questionable whether glass surfaces and gases of the nature of CO_2 and NH_3 should be used for this kind of investigation.

A large number of other investigations in the literature deal with the adsorption of water-vapour on glass and quartz and some metal surfaces. The results have always given an adsorption thickness of the order of 10^{-6} to 10^{-7} cms., corresponding to layers thirty to a hundred molecules thick. Langmuir has suggested two reasons, 1. that there may be an actual condensation in the capillary spaces present in the powders used, or in the thin crumpled solid surfaces used, especially if the equilibrium, gaseous pressures are near to saturation, or, as in many of these cases, actually saturation pressures are used, 2, that in the case of some materials it was possible for the gas to penetrate the surface for some distance at any rate, and thus the effective surface would be increased, or a kind of solid solution occur.

The conditions under which capillary adsorption may occur is very important. The investigation of adsorption on plane surfaces is experimentally

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[1] Proc. Roy. Soc., 77 A, 292 (1906).

[2] Proc. Roy. Soc., 78 A, 412 (1907).

[3] Vide, for instance, Patrick and McGavack: loc. cit.

[4] Z. anorg. Chem. 71, 356 (1911).

[5] Z. physik. Chem. 88, 191 (1914).

very difficult. However, an increase of specific surface to any considerable extent means the creation of capillary spaces. In the case of porous adsorbents it has been considered by Zsigmondy that the main portion of the adsorption may be of this nature. This theory has had a quantitative application by Anderson,[1] and Patrick and Mc. Gavack,[2] and will be discussed elsewhere. It appears, however, that the attraction exerted by curved surfaces of this nature can account for considerable reductions of the vapour-pressure, e. g., for water-vapour Anderson shows that when the diameter of a capillary tube of circular cross-section is 5.5×10^{-7} cms., p/P_0 has the value 0.7, or, with a capillary tube of this kind, approximately twenty molecules thick, there is a reduction of vapour-pressure to 7/10ths of its saturation value. However it can be calculated readily that when p/P_0 has the value 0.1, the diameter of the capillary must be 0.9×10^{-8} cms., or of the order 2 to 3 molecules across. Without going into the matter fully here it is very clear that assuming the correctness of the quantitative relation, capillary condensation cannot affect results such as those of Evans and George where p/P_0 has a value of 1/200. Experiments with saturated vapour using adsorbents having capillaries of whatever kind would give very high results for this reason, especially if the temperature control was not exact. Also the numerous results that have been obtained using approximately 90% of the saturation pressure of the vapour, and fine powders as absorbents will clearly be in some error owing to this cause, but only with extremely finely grained powders would this result in any appreciable error in the amount adsorbed. For values of $p/P_0/$ below 0.1 it is clear that no adsorption of this type could occur, however finely divided the adsorbent, and this is probably a low value. Clearly then it is not difficult to avoid capillary condensation and still have large specific surfaces of solid adsorbent. But of, course, by using low values of p/P_0 the maximum thickness of the adsorption layer would not be measured perhaps. This can only be done on a plane surface.

In the experiments of Parks,[3] glass wool and precipitated silica are exposed to a saturated atmosphere of water-vapour. It is very obvious that it would be quite possible for very large capillary liquefaction to have occurred. Martini[4] under the same experimental conditions, found an increase of weight of 80% with precipitated silica,—an obvious instance of actual condensation. Moreover in these experiments the temperature control was not exact. Therefore it seems without doubt that Parks' value of 13.3×10^{-6} cm. as the film thickness must be considerably too high. It is extremely probable also that precipitated silica has a considerable internal surface.

In the experiments of Katz[5] the adsorption of water-vapour on very finely-ground quartz was determined. One m. gram of powder contained 140×10^6 particles. From Katz' calculation that one gram of powder had

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[1] Z. physik. Chem. 88, 191 (1914).
[2] J. Am. Chem. Soc. 42, 946 (1920).
[3] Phil. Mag. (6) 5, 517 (1903).
[4] Phil. Mag. (5) 47, 329 (1889).
[5] Proc. Amsterdam Akad. 15, 445 (1912.)

3260 sq. cms. of surface, the adsorbed layer was reckoned to be 22 molecules thick at 2% of saturation and 32 molecules thick at 92% of saturation. There seems, however, to be an error in the calculation. From the given data one gram exhibits 18,000 sq. cms. of surface approximately. This reduces the thickness of the adsorbed layer to 4 molecules when the water-vapour pressure is 2% of saturation, and to 6 molecules when the vapour-pressure is 92% of saturation. There are two further points to which attention may be drawn. Katz first completely wetted his adsorbent and then left it to come to equilibrium with the sulphuric acid-water mixture that gave him the vapour-pressure he wanted. In the absence of any evacuation of the system this is known to be a very slow process. Also the surface area as calculated from the number of particles per gram, assuming the particles of the same average size, would give a lower result than the true one. These results would not seem to support a very thick adsorption layer on quartz.

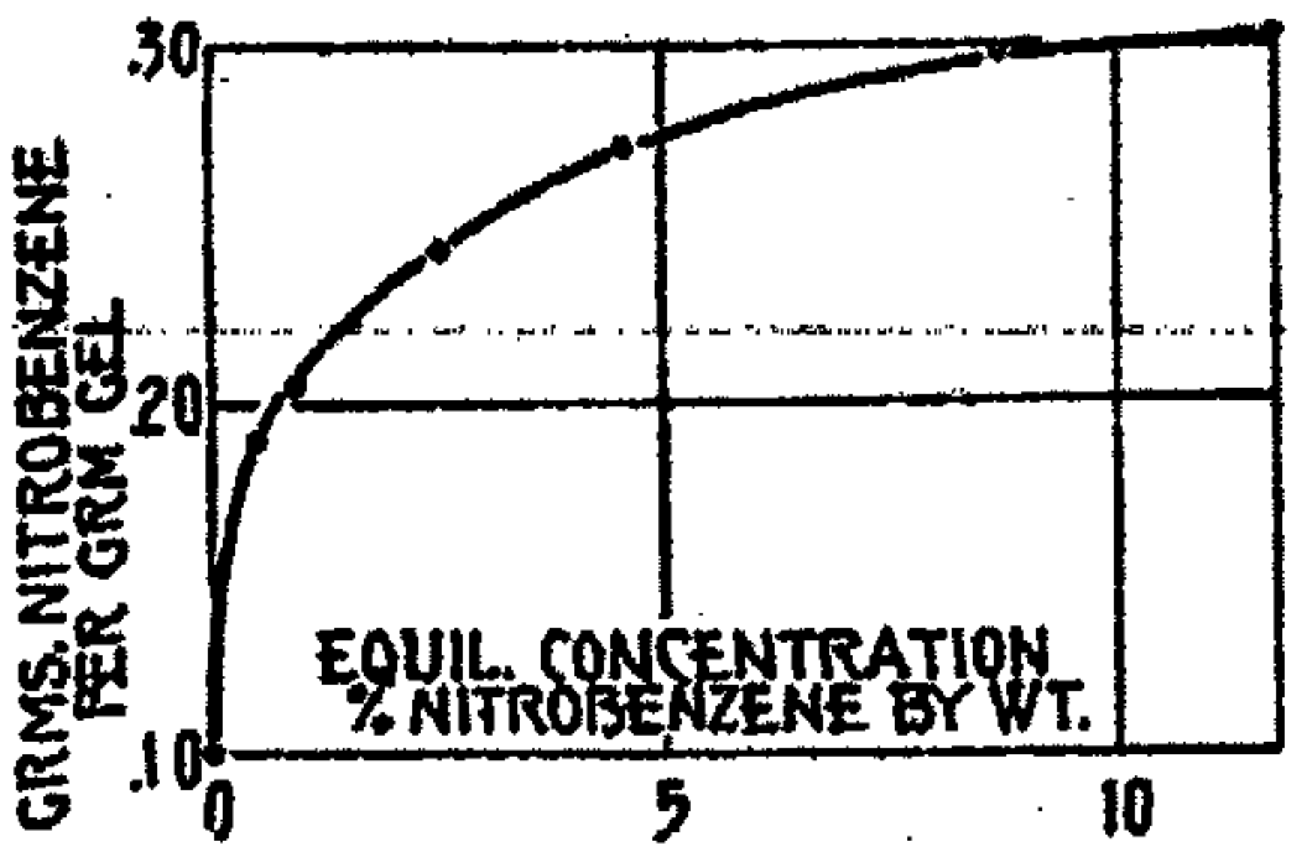

Fig. 1

Adsorption Curve of Nitrobenzene from Kerosene Solution by Silica Gel

No experimental data seem to be recorded on the thickness of the adsorption layer on a solid in contact with a solution with the exception of a preliminary paper by Bancelin,[1] who examined the adsorption from aqueous solution of certain unnamed dyestuffs by glass threads, using a colorimeter as a means of estimation of the concentration changes. His values in certain solutions were of the order 1 to 4 $\mu\mu$.

In view of the work that has been done on the adsorption from organic solvents by the gel of silicic acid, the measurement of the adsorption occurring on an almost plane surface of silica seemed to be of interest. The very sensitive Hilger interferometer was used as a means of detecting any changes of concentration that may occur.

In these experiments nitrobenzene and acetic acid in kerosene were found to be adsorbed very strongly from dilute solution by the gel. The former system, nitrobenzene in kerosene solution, was chosen for this test because of the greater sensitiveness of the interferometer to concentration changes, due to the larger difference in refractive index between the solute and the solvent, and also the danger of chemical interaction between acetic acid and the glass of the adsorption vessel and the interferometer cell would be avoided.

The adsorption curve of nitrobenzene in kerosene with silica gel as the adsorbent is shown in Fig. 1. When the equilibrium concentration of the solution is 3.5% of nitrobenzene, the adsorbed amount is 0.27 grams of nitrobenzene per gram of the gel. The total adsorption space per gram of gel is equal to 0.33 c.cs.; i. e. at this low equilibrium concentration 88% of the total adsorption space is occupied by nitrobenzene. It is extremely probable that the greater portion of the remaining space is ineffective for adsorption

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[1] Compt. rend. 158, 791 (1914).

at this low concentration and is filled with a solution of the equilibrium concentration, or slightly differing therefrom.

In all these direct determinations of the thickness of the adsorption layer from the vapour, the assumption is made that the adsorbed material has a density corresponding to that in the liquid state throughout the whole of the adsorption space. In adsorption from solution the corresponding assumption is that pure solute only is adsorbed. The thicknesses as actually measured by concentration changes give results that are too low. Thus from the vapour phase the more condensible gases give high values for the adsorption layer thicknesses, and it would be expected that in adsorption from solution the solubility of the solute in the solvent will be correspondingly important.

From the adsorption results of nitrobenzene in kerosene solution by silica gel, the solvent adsorption in this system is very small indeed, and this system would seem very favourable for demonstrating, by concentration changes, the maximum thickness of an adsorption layer from solution on quartz.

The negative results obtained in these experiments show definitely that the adsorption layer is not greater than 5 molecules thick. This is the limit of sensitiveness of the interferometer under present conditions. It is hoped by the introduction of thinner movable plates to increase the sensitiveness of the instrument.

The experimental details are as follows:—

Within the concentration range of 3% to 4% of nitrobenzene in kerosene, one division on the interferometer drum corresponds to 0.00429% of nitrobenzene in kerosene:, (the movable plates had a diameter of 4 m. m.s, and the cell thickness was 4 m.ms.). For this degree of accuracy sufficient time must be given for temperature to be established, and the slit must be carefully adjusted to give the clearest image of the bands. The optical path from the collimator to the movable plates was enclosed in a wooden box which during the course of the experiment could be maintained at constant temperature. Certain suggested alterations in the cell were carried out very successfully by Messrs. Hilger. The comparison beam was made to pass through the glass at the bottom of the cell instead of over the top, and a cell-cap was constructed ground to fit the top of the cell without at any point touching the inside edges. This last precaution avoids creeping of the liquid. These structural changes were very effective in preventing concentration changes due to volatilisation during the time allowed for temperature equilibrium to be established. Even with systems like methyl alcohol in kerosene no concentration changes could be detected by the interferometer after several hours. Also much less liquid was necessary in making a test with the new arrangements. The sides of the interferometer cell are adhesed, no cement of any kind being used in the cell construction.

Materials

The silica was ordinary silica glass ground in an agate mortar and carefully sieved. The particles used for the experiments were of a size between 100 and 120 mesh. This silica was then boiled up with strong nitric acid for several hours, and then with boiling water until no acidity could be detected. The last washings were done in a silica flask. The material was then dried in a steam-oven, and after being heated for one hour to red-heat in a platinum crucible was transferred at once to a desiccator over P_2O_5.

The nitrobenzene and kerosene were materials that had been purified as described.[1] Both these liquids were then shaken for long periods with silica gel in order to remove impurities removable by a silica surface. An interferometric test showed no change in the reading before and after treatment of the nitrobenzene, but the kerosene showed marked variations at first. After several treatments it finally gave no change in readings on being treated with silica purified as above and of 120 to 150 mesh, in quantities comparable with those used in an actual adsorption experiment.

Method of Experimentation

The interferometer was standardised with a series of solutions of known concentration made up by weight. The solutions were made up and kept in double ground-glass stoppered bottles of 12 c. cs. capacity. The change in interferometric reading per 0.1% concentration change, in the range 3 to 4% nitrobenzene concentration, having been determined, 7 c. cs., approximately, of a solution in this concentration range was made up, and its interferometric reading taken on two separate samples. In one experiment 3.376 grams. of a 3.45% solution remained after two samples had given 10.36 as the interferometric reading. To this solution 4.65 grams of ground silica were added. This was done in the desiccator, it being of the utmost importance to avoid a preliminary adsorption of moisture from the atmosphere. There was just sufficient free liquid available, capable of removal by a pipette, for making the test. The contents were shaken vigorously for half an hour and at intervals for two hours. The interferometric reading was now repeated. In three experiments of this kind no change in the interferometric reading could be detected.

A calculation of the thickness of the adsorption layer, capable of being detected by the interferometer is as follows: The interferometer will detect a change of concentration of 0.00429 grams of nitrobenzene in 100 grams of solution. 3.376 grams of solution were used and 4.65 grams of silica.
Therefore the weight of nitrobenzene removed by the silica and detectable by the instrument per gram of silica is equal to:

$$\frac{0.00429 \times 3.376}{100 \times 4.65} \text{ grams.}$$

Assuming the particles are cubes the surface presented per gram is equal to 132 sq. cms.

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[1] J. Chem. Soc. 123, 1379, 1389 (1923).

Therefore the number of molecules of nitrobenzene per sq. cm. of surface assuming Millikan's value for N, and 123 as the molecular weight of nitrobenzene, that is capable of detection by the instrument is equal to:

$$\frac{\text{Weight per sq. cm.} \times 6.06 \times 10^{23}}{123}$$

or 1.163×10^{15}.

From the density of the liquid, and assuming the molecules cubical, the area of liquid surface per molecule comes out to be approximately 30×10^{-16} sq. cm. Therefore the number occupying 1 sq. cm. of liquid surface is equal to 0.33×10^{15}: i. e. the interferometer could detect a layer three or four molecules thick. Since there was no change in the reading before and after adsorption it can be concluded that the layer is less than this thickness.

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INDUCED REACTIONS AND DIABETES FROM THE VIEWPOINT OF INDUCED OXIDATION

BY N. N. MITTRA AND N. R. DHAR

In previous papers[1] the phenomena of induced oxidation and their importance in biological phenomenon have been studied.

It is well known that oxalic acid cannot reduce a solution of mercuric chloride even in boiling solutions in the dark; we have shown that if a few drops of potassium permanganate are added to the mixture, the permanganate acts on oxalic acid and at the same time mercurous chloride begins to separate out. In other words, the chemical change between oxalic acid and permanganate induces the reaction between oxalic acid and mercuric chloride. We have investigated several cases of this type of reactions.

Moreover, we have induced the oxidation of substances like sugar, starch, alcohol, etc., by air or oxygen at the ordinary temperature by mixing the above substances with sodium sulphite, ferrous hydroxide, cerous hydroxide and other reducing agents. Hence the slow oxidation of these reducing agents sets up the oxidation of sugar, starch, alcohol, etc. We have tried to establish that induced oxidations are of very general occurrence.

In this paper we have investigated some more induced oxidations and their induction factors and we shall see whether any relation like Schönbein's law of autoxidation[2] is discernable in these reactions. Moreover, we shall prove that not only induced oxidations are very common, but that induced decompositions, induced precipitations, etc., also occur frequently. In this paper we have also advanced a suggestion about the etiology and treatment of diabetes based on our experience in these oxidation reactions. According to the customary nomenclature the faster reaction is called the primary reaction and that which appears to be forced along or induced by contact with the primary change is called the secondary reaction. The substance which takes part in both the reactions is called the actor, the substance which takes part in the primary reaction is called the inductor and the substance which takes part in the secondary reaction is called the acceptor.

Experiments

A. In each of the following reactions, the mixtures were made up to 70 cc with distilled water and boiled for thirty minutes, acidified with 4 N acetic acid (in cases of oxidation with sodium sulphite and sodium phosphite).

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[1] Dhar: J. Chem. Soc. 111, 694 (1917); Proc. Acad. Sci. Amsterdam, 29, 1023 (1921). Z. anorg. Chem. 128, 207 (1923); J. Phys. Chem. 28, 943 (1924); Mittra and Dhar: Trans; Faraday. Soc. 17, 676 (1922); Z. anorg. Chem. 122, 146 (1922).

[2] Pogg. Ann. 100, 1 (1857).

The precipitate obtained on boiling was then filtered and washed, digested with caustic soda, and filtered again. The filtrate was then neutralized with nitric acid, made up to 200 cc and titrated with $\frac{N}{40}$ $AgNO_3$.

1. $HgCl_2+Na_2SO_3 \longrightarrow HgCl_2+Na_3AsO_3$

Primary reaction Secondary reaction.

	N/5 $HgCl_2$	N/1 Na_2SO_3	Na_3AsO_3 sol. 1cc::28.5cc N/10 I_2	Acetic acid 4 N.	Total ppt. of Hg_2Cl_2 in gram.	Ppt. of Hg_2Cl_2 due to primary reaction + acid (blank experiment) in gram	Ppt. of Hg_2Cl_2 due to the secondary reaction by difference. in gram
a	50cc	1cc	5cc	2cc	0.3659	0.0944	0.2715
	50cc	2cc	5cc	2cc	.4013	.1770	.2236
	50cc	3cc	5cc	2cc	.4308	.2302	.2006
	50cc	4cc	5cc	2cc	.4603	.2832	.1771
	50cc	5cc	5cc	2cc	.4839	.3362	.1477
b	50cc	1cc	10cc	4cc	.6670	.1242	.5428
	50cc	2cc	10cc	4cc	.7435	.2419	.5016
	50cc	3cc	10cc	4cc	.7670	.2893	.4777
	50cc	4cc	10cc	4cc	.7789	.3186	.4603
	50cc	5cc	10cc	4cc	.8081	.3659	.4422

2. $HgCl_2+HCOOH \longrightarrow HgCl_2+Na_3AsO_3$

N/5 $HgCl_2$	10% Formic acid.	Na_3AsO_3 sol. 1cc::28.5cc. N/10 I_2	Distilled water.	Total Ppt. of Hg_2Cl_2	Ppt. of Hg_2Cl_2 due to primary reaction.	Ppt. of Hg_2Cl_2 due to secondary reaction by diff.
50cc	2cc	5cc	13cc	.9618	.3305	.6313
50cc	3cc	5cc	12cc	.9736	.3422	.6314
50cc	5cc	5cc	10cc	.9943	.4277	.5666
50cc	6cc	5cc	9cc	1.0200	.4957	.5243
50cc	10cc	5cc	5cc	1.0009	.5606	.4403
50cc	5cc	10cc	5cc	1.2030	.4189	.7841

3. $HgCl_2$+Sodium phosphite ⟶ $HgCl_2$+Sodium arsenite

N/5 $HgCl_2$	N/1 Sod. phosphite	4N. Acetic Acid	Sol. Arsenite soln. 1cc = 28.5cc. N/10 I_2	Distilled water	Total Ppt. of Hg_2Cl_2	Ppt. of Hg_2Cl_2 due to primary reaction +acetic acid.	Ppt. of Hg_2Cl_2 due to secondary reaction — by diff.
50cc	1cc	2cc	5cc	12cc	.5668	.3127	.3541
50cc	2cc	2cc	---	11cc	.6673	.4423	.2250

B. In each of the following cases the volume was made up to 100 cc with distilled water and the solution was either exposed to air for 24 hours, or boiled and then exposed to air; and then titrated with 0.4 N$KMnO_4$.

Na_2SO_3+air ⟶ $NaNO_2$+air.

1.	N/10 Na_2SO_3	N/10 $NaNO_2$	Distilled water.	Boiled for	Exposed to air for	Titration reading with 0.4N. $KMnO_4$		Amount of oxidation in terms of 0.4N $KMnO_4$
Exposure								
In beaker	50cc	5cc	45cc	1 hr.	24 hrs.	0.5cc		
	50cc		50cc	1 hr.	24 hrs.	4.0cc	6.8cc	6.3cc
		5cc	95cc	1 hr.	24 hrs.	2.8cc		
2.	50cc	5cc	45cc		24 hrs.	3.6cc		
Exposure	50cc		50cc		24 hrs.	2.0cc	4.8cc	1.2cc
In dish		5cc	95cc		24 hrs.	2.8cc		
3.	75cc	2cc	23cc		24 hrs.	1.1cc		
	75cc		25cc		24 hrs.	0.3cc	1.4cc	0.3cc
		2cc	98cc		24 hrs.	1.1cc		

C. In each of the following cases vol = 100 cc, made up with distilled water, and the exposure to air = 24 hours. After exposure each solution was treated with excess of acetic acid and calcium chloride, the precipitate obtained was filtered and washed. The residue of calcium oxalate was dissolved in dilutulphuric acid, and filtered. The filtrate was then titrated with 0.4N $KMnO_4$.

Na_2SO_3+air ⟶ $K_2C_2O_4$+air.

1. N/1. Na_2SO_3	N/1. $K_2C_2O_4$	Distilled water	Titration reading with 0.4N. $KMnO_4$		Oxidation in terms of 0.4N. $KMnO_4$.	
			(a)	(b)	(a)	(b)
75cc	2cc	23cc	4.8cc	5.0cc	0.6cc	0.5cc
75cc		25cc	0	0		
	2cc	98cc	5.4cc	5.5cc		

2. In the following experiments oxygen gas was passed through hot solutions before exposing them for 24 hours to air and titration with 0.4N $KMnO_4$.

N/1 Na_2SO_3	N/1 $K_2C_2O_4$	Distilled water	Titration reading with 0.4N. $KMnO_4$.	Oxidation in terms of 0.4N. $KMnO_4$.
30cc	0.1cc	69.9cc	0.0	
30cc		70.0cc	0.0	0.3cc
	0.1cc	99.9cc	0.3cc	
50cc	0.1cc	49.9cc	0.0	
50cc		50.0cc	0.0	0.3cc
	0.1cc	99.9cc	0.3cc	

D. Experiments given below exhibit the remarkable phenomenon of retardation of the oxidation of sodium sulphite in presence of either potassium oxalate or sodium arsenite.

N/1 Na_2SO_3.	N/1 $K_2C_2O_4$	Distilled water	Boiled for	Exposed to air for	Titration with 1/4N. $KMnO_4$.	Amount of retardation in terms of ¼N $KMnO_4$
30cc	5cc			24 hrs.	41.9cc	22.5cc
30cc		5cc		24 hrs.	0.0	
	5cc	30cc		24 hrs.	19.4cc	
30cc	5cc		20 min.		41.8cc	0.9cc
30cc		5cc	20 min.		21.6cc	
	5cc	30cc	20 min.		19.3cc	

N/1 Na_2SO_3	N/1. Na_3AsO_3	Distilled water	Boiled for	Exposed to air for	Titration reading with N/10 I_2	Retardation in terms of N/10 I_2
30cc	5cc	65cc	45 min.		119.2cc	48.4cc
30cc		70cc	45 min.		26.0cc	
	5cc	95cc	45 min.		44.8cc	
30cc	5cc	65cc		24 hrs.	113.6cc	68.1cc
30cc		70cc		24 hrs.	0.5cc	
	5cc	95cc		24 hrs.	45.0cc	
65cc	5cc			24 hrs.	203.0cc	153.1cc
65cc		5cc		24 hrs.	4.9cc	
	5cc	65cc		24 hrs.	45.0cc	

E. In each of the following mixtures, the volume was made up to 100 cc with distilled water, solutions exposed to air for 24 hours and then titrated with $KMnO_4$.

Sodium sulphite+air ⟶ Ferrous ammonium sulphate+air

30 cc Fe $(NH_4)_2$ $(SO_4)_2$=22.08cc N/8 $KMnO_4$

N/1 Na_2SO_3	N/10 $Fe(NH_4)_2(SO_4)_4$	Titration reading with $KMnO_4$	Oxidation in terms of $KMnO_4$
5cc	30cc	19.84cc N/8 $KMnO_4$	2.24cc N/8 $KMnO_4$
10cc	30cc	20.16cc ”	1.92cc ”
15cc	30cc	20.16cc ”	1.92cc ”
	30cc	22.08cc ”	
15cc		0.0 ”	
20cc	10cc	25.4 cc N/40 $KMnO_4$	12.6cc N/40 $KMnO_4$
20cc		0.1cc ”	
	10cc	37.9cc ”	

F. In the following the vol. in each case=50cc and the solutions exposed to air for 24 hours and then filtered. Cobaltic hydroxide washed and dissolved in strong HCl. Potassium iodide was then added and the liberated iodine corresponding to the cobaltous changed into cobaltic state titrated with N/10 $Na_2S_2O_3$.

Sodium sulphite+air ⟶ Cobaltous hydroxide+air

N/1.Na_2SO_3	$Co(NO_3)_2$	NaOH	Water	Exposed to air for	Titration reading with N/10$Na_2S_2O_3$
30cc	2cc	10cc	8cc	24 hrs.	2.2cc
30cc		10cc	10cc	"	nil
	2	10cc	38	"	1.4cc

G. Each of the following mixtures was made up to 100cc solutions either boiled or exposed to air for 24 hours at the room temperature and then titrated with N/8.$KMnO_4$.

Strength of sulphurous acid used—20cc = 19.5cc N/8 $KMnO_4$

Strength of ferrous ammon. sulph.—30cc = 22.08 do.

Sulphurous acid+air ⟶ Ferrous ammonium sulphate+air.

H_2SO_3	N/10 Fe Ammon sulph.	Water	Boiled for	Exposed to air	N/8 $KMnO_4$ titration reading	Oxidation in terms of N/8$KMnO_4$
20cc		80cc	40 min.		0.2cc	0.5cc
	10cc	90cc	40 min.		7.5cc	
20cc	10cc	70cc	40 min.		7.2cc	
20cc		80cc		24 hrs.	0.0	1.8cc
	10cc	90cc		24 hrs.	7.5cc	
20cc	10cc	70cc		24 hrs.	5.7cc	

H. Volume in each case = 50cc. Solutions exposed to air and then titrated with N/10 I_2.

Sulphurous acid+air ⟶ Stannous chloride+air.

Strength of sulphurous acid – 5cc = 5.1ccN/10 I_2

H_2SO_3	$SnCl_2$	Water	Exposure to air for	Titration reading with N/10 I_2	Oxidation in terms of N/10 I_2
10cc		40cc	3 hrs.	0.1cc	4.9cc
	2cc	48cc	3 hrs.	12.2cc	
10cc	2cc	38cc	3 hrs.	7.4cc	
30cc		20cc	24 hrs.	0.0	15.5cc
	5cc	45cc	24 hrs.	18.0cc	
30cc	5cc	15cc	24 hrs.	2.5cc	

I. In each of the following vol = 100cc Solutions exposed to air for 48 hours, acidified with dilute sulphuric acid and titrated with N/10 $KMnO_4$

Strength of H_2SO_3 − 90cc = 9.5cc N/10 $KMnO_4$

Strength of $FeSO_4$ − 5cc = 9.4cc do. do.

$H_2SO_3 + \text{air} \longrightarrow FeSO_4 + \text{air}$

H_2SO_3	$FeSO_4$	Water	Exposure to air for	Titration reading with N/10 $KMnO_4$	Oxidation in terms of N/10 $KMnO_4$
90cc		10cc	48 hrs.	0.0	
	5cc	95cc	48 hrs.	9.4cc	
90cc	2cc	8cc	48 hrs.	2.2cc	1.6cc
90cc	5cc	5cc	48 hrs.	6.2cc	3.2cc
90cc	10cc		48 hrs.	14.2cc	4.6cc

N. B. In E, F, G, H, I the secondary reactions actually take place but slowly; they are however accelerated in presence of primary reactions.

J. In the following experiments, nickelous hydroxide was suspended in 15cc N/1 sodium sulphite soln. and then oxygen gas was passed for 5 min. through the two bottles one containing the mixture of sodium sulphite and nickel hydroxide and the other only the sulphite. The contents of the bottles were then filtered and washed separately. The filtrates acidified with H_2SO_4 and titrated with N/10 $KMnO_4$.

N/1 Na_2SO_3	$Ni(OH)_2$	Oxygen gas passed	Titration reading with N/10 $KMnO_4$ of the filtrate
15cc	A little of the hydroxide	5 min	0.1cc
15cc	freshly prepared.	5 min.	3.1cc

In this case, the oxidation of the sulphite is accelerated in presence of nickelous hydroxide, which in its turn is oxidised to nickelic hydroxide.

K. $Na_2SO_3 + \text{oxygen gas} \longrightarrow \text{Glucose} + \text{oxygen gas}$.

Weighed quantities of glucose were taken in two stoppered bottles and to each three grams of anhydrous sodium sulphite and 10cc of distilled water were added. Oxygen gas was then passed at an interval of five minutes through each for five minutes (and the bottles shaken). The process was continued for three days introducing one gram of sodium sulphite each day. Both solutions were then carefully worked into measuring flasks making up the volume with water. Measured volumes were then taken out, excess of sulphite eliminated and boiled on a water bath for 30 minutes with Fehling's solution. The cuprous oxide precipitated was then carefully transferred to a filter, washed, transferred to a crucible, converted into CuO, weighed and estimated as such, corresponding glucose was then taken down from table.

Glucose in gram	Na_2SO_3 in gram	Oxygen passed for	Volumes of mixt. made up to	CuO obtained on reduction of Feh. from	Glucose left in total vol. after oxidation	%Glucose oxidized
0.5070	5	3 days	100cc	20cc=.2182grCuO =.085gr glucose	.085×5 =.425	16.1
0.3424	5	3 days	200cc	50cc=.185gr CuO =.07gr glucose	=.07×7 =.28	17.6

L. In each of the following 5cc of nickel chloride solution and 5cc of 5% $FeSO_4$ soln. were used with varying quantities of NaOH, the mixture in each case was made up to 50cc. Oxygen gas was passed through the solution at the ordinary temperature for 15 min. and then each of them was treated with HCl strong and KI, and then liberated I_2 titrated with N/10 $Na_2S_2O_3$.

$$Fe(OH)_2+O_2 \longrightarrow Ni(OH)_2+O_2$$

5% $FeSO_4$	NaOH		$NiCl_2$ Sol.	Water	Oxygen gas passed for	N/10 $Na_2S_2O_3$ titration reading for the liberated I_2
5cc	5cc	.6N		40cc	15 min.	1.6cc
5cc	5cc	"	5cc	36cc	15 min.	2.8cc
5cc	10cc	"	5cc	30cc	15 min.	3.2cc
5cc	15cc	"	5cc	25cc	15 min.	3.2cc
5cc	20cc	"	5cc	20cc	15 min.	2.2cc
5cc	25cc	concentrated	10cc	10cc	30 min. +Exposure to air for 24 hrs	10.5cc
5cc	25cc	"		20cc	30 min.+ "	4.8cc
10cc	30cc	"	10cc		30 min.	8.7cc
10cc	30cc	"		10cc	30 min.	3.2cc
10cc	30cc	"	10cc		30 min.+ "	14.4cc
10cc	30cc	"		10cc	30 min.+ "	7.9cc

M. In each of the following experiments 5cc of nickel chloride and 5cc of cobalt nitrate were mixed with varying quantities of known strength of caustic soda and this volume made up with distilled water to 50cc. Oxygen gas was passed through each for 15 min. the mixtures filtered, the precipitates washed and dissolved in hydrochlorine acid. The solutions obtained were treated with potassium iodide and then liberated iodine titrated with N/10 $Na_2S_2O_3$.

10cc NaOH used=6.0cc N/2 Oxalic acid

$$Co(OH)_2+\text{Oxygen gas} \longrightarrow Ni(OH)_2+\text{Oxygen gas.}$$

$Co(NO_3)_2$	NaOH	$NiCl_2$	Water	Titration reading of N/10 $Na_2S_2O_3$ for the liberated I_2
5cc	20cc		25cc	0.4cc
5cc	1cc		44cc	0.2cc
5cc	8cc		37cc	0.3cc
5cc	1cc	5cc	39cc	0.2cc
5cc	2cc	5cc	38cc	0.2cc
5cc	4cc	5cc	36cc	0.3cc
5cc	6cc	5cc	34cc	0.3cc
5cc	8cc	5cc	32cc	0.5cc
5cc	10cc	5cc	30cc	0.7cc
5cc	12cc	5cc	28cc	0.9cc
5cc	20cc	5cc	20cc	1.2cc
5cc	22cc	5cc	18cc	2.7cc
5cc	26cc	5cc	15cc	3.0cc
5cc	30cc	5cc	10cc	3.9cc
5cc	35cc	5cc	5cc	3.6cc
5cc	40cc	5cc		3.5cc
5cc	4.0cc[1]	5cc	36cc	2.0cc
5cc	6.0cc[1]	5cc	34cc	1.4cc
5cc	10.0cc[1]	5cc	30cc	1.3cc

[1] Strength NaOH 10cc = 125cc N/2 Oxalic acid.

N. Similarly $Mn(OH)_2$+Oxygen gas $\longrightarrow$ $Ni(OH_2$+Oxygen gas. vol = 50cc and O_2 passed for 15 min.

5% $MnSO_4$	NaOH		$NiCl_2$	Water	Titration reading with N/10 $Na_2S_2O_3$ for the liberated I_2
5cc	5cc	.6N/1	——	40cc	3.0cc
5cc	10cc	6.0N/1		35cc	2.1cc
5cc	5cc	0.6N/1	5cc	35cc	1.6cc
5cc	10cc	"	5cc	30cc	3.3cc
5cc	15cc	"	5cc	25cc	4.2cc
5cc	20cc	"	5cc	20cc	4.0cc
5cc	40cc	"	5cc		3.8cc
5cc	5cc	6.0N/1	5cc	35cc	3.2cc
5cc	10cc	"	5cc	30cc	2.2cc
5cc	20cc	"	5cc	20cc	1.4cc
5cc	40cc	"	5cc		1.0cc
5cc	10cc	"	5cc		1.6cc

Induction Factor

The proportion in which the actor divides itself between the inductor and the acceptor is called the *Induction factor* thus:

$$I=\frac{\text{amount of acceptor transformed}}{\text{amount of inductor transformed}}=\frac{\text{amount of } Na_3AsO_3}{\text{amount of } Na_2SO_3}$$

The following induction factors have been obtained from the foregoing results given under A1 and 2.

1*a*.

1cc of N/1 Na$_2$SO$_3$ or 0.63 gram Na$_2$SO$_3$ induced the oxidation of .110 gram Na$_3$AsO$_3$.

2cc of N/1 Na$_2$SO$_3$ or .126 gram Na$_2$SO$_3$ induced the oxidation of .091 gram Na$_3$AsO$_3$.

3cc of N/1 Na$_2$SO$_3$ or .189 gram Na$_2$SO$_3$ induced the oxidation of .082 gram Na$_3$AsO$_3$.

4cc of N/1 Na$_2$SO$_3$ or .252 gram Na$_2$SO$_3$ induced the oxidation of .072 gram Na$_3$AsO$_3$.

5cc of N/1 Na$_2$SO$_3$ or .315 gram Na$_2$SO$_3$ induced the oxidation of .060 gram Na$_3$AsO$_3$.

Hence the induction factors are:

1.75, .725, .431, .286, .19.

1*b*.

1cc of N/1 Na$_2$SO$_3$ or .063 gram Na$_2$SO$_3$ induced the oxidation of .221 gram Na$_3$SsO$_3$.

2cc of N/1 Na$_2$SO$_3$ or .126 gram Na$_2$SO$_3$ induced the oxidation of .205 gram Na$_3$AsO$_3$.

3cc of N/1 Na$_2$SO$_3$ or .189 gram Na$_2$SO$_3$ induced the oxidation of .195 gram Na$_3$AsO$_3$.

4cc of N/1 Na$_2$SO$_3$ or .252 gram Na$_2$SO$_3$ induced the oxidation of .188 gram Na$_3$AsO$_3$.

5cc of N/1 Na$_2$SO$_3$ or .315 gram Na$_2$SO$_3$ induced the oxidation of .180 gram Na$_3$AsO$_3$.

Hence the induction factors are:

3.5, 1.6, 1.0, .75, .57.

2.

2cc	of 10% Formic acid	induces	the oxidation of	.257	gram	Na$_3$AsO$_3$
3cc	"	"	"	.257	"	"
5cc	"	"	"	.232	"	"
6cc	"	"	"	.214	"	"
10cc	"	"	"	.180	"	"

Hence the induction factors are:

1.28, .86, .46, .36, .18.

From the above induction factors no simple relation like that of Schönbein's law of autoxidation is observed in these reactions.

From the above results we find that the amount of induced oxidation increases up to a maximum value with the increase in the concentration of alkali, after this limit is reached, increase in the amount of alkali decreases the induced the oxidation. In this connection it is interesting to compare the results obtained by Gire[1] who showed that the volume of oxygen absorbed by a mixture of arsenious acid and ferrous sulphate in presence of alkali at

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[1] Compt. rend. **171**, 174 (1920).

first diminishes, as the amount of alkali increases, reaching a minimum when the alkali is slightly in excess of that required to form the arsenite $Na_2As_2O_4$. It then increases to a constant maximum when the amount of alkali present is slightly in excess of that required to form the arsenite $Na_4As_2O_5$. If the amount of alkali present is kept constant the oxygen absorbed is proportional to the amount of iron present, but is always in excess of that required to oxidize the ferrous salt to the ferric state. Apparently the excess of oxygen goes to oxidize the arsenite to arsenate and this is a typical example of induced oxidation.

In a foregoing paper[1] we have advanced the view that the experiments of Willstätter and Waldschmidt-Leitz[2] and Venkataramaiah[3] are really cases of induced reactions. Thus Willstätter and Waldschmidt-Leitz (loc. cit.) have shown that *traces of oxygen*[4] *are necessary in the hydrogenation of* substances by hydrogen in presence of palladium. We are of the opinion that the hydrogen and oxygen combine in presence of palladium and this reaction induces the hydrogenation of the other substance. Venkataramaiah (loc. cit.) has shown that when hydrogen and oxygen are exploded by passing an electric spark in presence of alkaline potassium permanganate the permanganate is converted into the manganate. In other words, the chemical change between hydrogen and oxygen, has induced the chemical change between hydrogen and potassium permanganate.

Similarly the researches of Wieland[5] and his colleagues can be readily interpreted according to these views. They have shown that when dilute aqueous solutions of carboxylic acids (acetic, pyruvic, succinic, malic, benzoic or better oxalic, lactic, malonic, fumaric, and citric) are shaken with copper powder in an atmosphere of oxygen, the latter is rapidly absorbed. With oxalic acid, 3 Cu absorbs $2O_2$ and the acids are converted into CO_2 the metal passes into solution and the action ceases when solution is complete. Neutral substances (alcohol, dextrose, etc.,) are only oxidized when acid is present, since the autoxidation of copper depends on its solution to form a salt and the metal cannot, therefore, alone activate molecular oxygen.

These reactions may be looked upon as examples of induced oxidations. At first the copper powder is oxidized to the oxide condition and this oxidation will induce the oxidation of the carboxylic acids. It is well known that finely divided copper takes up oxygen very readily forming a layer of oxide and that this oxide layer is dissolved by the acid and hence more and more oxidation of copper will take place. This is apparently a joint action of oxygen and acids on copper and thus the oxidation and solution of copper is facilitated. This oxidation of copper will induce oxidation of the organic acids, just as we have proved that the oxidation of sodium sulphite or of

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[1] Dhar: Z. anorg. Chem. **128**, 207 (1923).

[2] Ber. **54** B, 43 (1924).

[3] Nature, **106**, 46 (1920).

[4] Compare, however Hofmann: Ber. **55** B, 573 (1922).

[5] Ann. **434**, 185 (1923).

ferrous hydroxide by oxygen can induce the oxidation of all sorts of organic substances.

Instead of molecular oxygen, p-benzoquinone, methylene blue, or potassium persulphate may be used. It is well known that metals like Cu, Zn, etc, dissolve readily in persulphate solutions according to the equation $Cu + K_2S_2O_8 = CuSO_4 + K_2SO_4$. In these cases, the copper will be at first converted into the oxide and then the acid will dissolve the oxide. This reaction will induce the oxidation of the organic acids by the above oxidizing agents. We have already proved that the oxidation of sodium sulphite by mercuric chloride can induce the oxidation of sodium arsenite by mercuric chloride. Other examples of this type have also been investigated by us.

Instead of metallic copper, cuprous salts may be used with the same results and the explanation would be identical.[1] Again, palladium and charcoal have been used instead of copper. Thus Wieland and his colleagues (*loc. cit.*) have shown that in presence of palladium, H_3PO_3 which is not oxidized by ordinary air or by oxygen alone, can be oxidized to H_3PO_4. Instances of this type have been known for a long time.

Similarly with purified blood charcoal many substances have been oxidized by air or oxygen[2]. It is very likely that unstable oxides are first formed with palladium or charcoal and this oxidation induces the oxidation of the organic substances. Long ago Calvert[3] proved that charcoal saturated with oxygen can oxidize aldehyde into acetic acid, also unsaturated ethylenic compounds are partially oxidized.[4] It seems probable that unstable oxides of the type C_xO_y are formed with charcoal and oxygen and this oxidation will induce the oxidation of oxalic acid, acetic acid and other substances.

In order to explain reactions of this type Wieland[5] assumes that at first hydration of the reducing agent takes place and then loss of hydrogen from the hydrate is the next step in the process and then the hydrogen reacts with molecular oxygen. It is evident that the conception of the mechanism of the reactions advanced by Wieland is complicated and far fetched[6]. Recently Goard and Rideal[7] have oxidised glucose, galactose, lactose, laevulose, arabinose and potassium arsenite in presence of cerous hydroxide by passing air.

In the case of the oxidation of potassium arsenite the observed potentials arranged in the order of increasing "oxygen pressure" are: cerous salt (inductor)—arsenite (acceptor)—equilibrium mixture perceric salt. In the case of the catalytic oxidation of the sugar the corresponding order is: reducing sugar-cerous salt-perceric salt.

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[1] Compare Trillat: Bull. (3) 29, 35 (1903); Orloff: J. Phys. Chim. Soc. Russ, 39, 855, 1023 (1907); 40, 203, 652, 799 (1908); Fokin: 45, 286 (1913); Palmer: Proc. Roy. Soc. 98 A, 13 (1920).

[2] Compare Gompel, Mayer and Wurmser: Compt. rend. 178, 1025 (1924).

[3] Compt. rend. 64, 1246 (1867).

[4] Compare also Warburg: Pflüger Archiv, 155, 597 (1914); Freundlich and Bjercke: Z. physik. Chem. 91, 1 (1916).

[5] Ber. 46, 3327 (1913): Ann. 434, 185 (1923).

[6] Compare Warburg: Biochem. Z. 142, 578 (1923).

[7] Proc. Roy. Soc. 105 A, 135 (1924).

This oxidation was first systematically investigated by Job.[1] These cases are really examples of induced oxidations. Very recently Spoehr[2] has oxidized sugars by passing air through solutions of sugars containing ferric or ferrous salts and phosphoric acid. It is well known that in presence of excess of phosphoric acid or disodium phosphate complex ferrous and ferric salts are formed[3]. The ferrous complex can be readily oxidised to the ferric state and this oxidation induces the oxidation of sugar, starch, etc. The amount of sugar or starch oxidised will depend on the amount of ferrous salt oxidised and hence this is a typical case of induced reaction.

Glucose and other hexoses are also oxidised by air in solutions containing disodium phosphate and methylene blue with the formation of carbon dioxide. This reaction is greatly accelerated by iron salts. Not only the hexose sugars are thus oxidised, but also sucrose, trehalose, mannitol, and glycerol.

Spoehr has observed that ferric salts also are effective in the oxidation of hexoses by air, but iron in the ferrous condition is more active than iron in the ferric condition. We have already observed that complex ferrous phosphate is a very good reducing agent and that the oxidation of this substance induces the oxidation of sugar, glycerol, etc.

With complex ferric phosphate the case is different as it cannot be oxidised further. We have observed that the complex is very slowly reduced by sugar, glycerol, etc., into the ferrous complex, which in its turn is readily oxidised to the complex ferric phosphate and this oxidation induces the oxidation of glycerol, sugars, etc. As the action of sugars, glycerol, etc. on the complex ferric phosphate is very slow, the amount of induced oxidation of sugars, glycerol, etc. is much less than the amount of induced oxidation with complex ferrous phosphate. That is why Spoehr got 0.5600 gr CO_2 from 1 gram ferrous sulphate and 0.5392 gr CO_2 from an equivalent weight of ferric sulphate using the same quantities of glucose and sodium phosphate.

In foregoing papers we have come to the general conclusion that the phenomenon of negative catalysis in oxidation reactions is possible when the catalyst is a reducing agent and is liable to be readily oxidised[4]. Very recently Moureu[5] and his colleagues have obtained several negative catalysts in the oxidation of organic substances by oxygen or air. These negative catalysts are generally reducing agents (e. g. benzaldehyde sulphur, quinol, phenols, etc.

Induced Precipitation

The phenomenon of induced precipitation is of common occurrence. When any one of the phosphates of iron, aluminium, or chromium is precipitated by sodium phosphate in presence of acetic acid and calcium chloride the precipi-

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[1] Ann. Chim. Phys. (7) 20, 207 (1900); Compt. rend. 134, 1032 (1902); 136, 43 (1903).

[2] J. Am. Chem. Soc. 46, 1494 (1924).

[3] Pascal: Ann. Chim. Phys. (8) 16, 363 (1909); Dhar and Urbain: Compt. rend. 169, 1395 (1919).

[4] Dhar: Proc. Acad. Sci. Amsterdam, 29, 1023 (1921); Dhar and Mittra: Trans. Faraday Soc. 17, 676 (1922).

[5] Compt. rend. 174, 258; 175, 127 (1922); 176, 624, 797 (1923); 178, 824, 1397, 1861 (1924).

tate after being thoroughly washed with acetic acid gives test for calcium with ammonium oxalate. Similarly strontium or barium phosphate is precipitated along with ferric phosphate or aluminium phosphate or chromium phosphate even in presence of acetic acid. When any of the hydroxides of iron, aluminium, or chromium is precipitated in an excess of concentrated ammonium hydroxide in presence of copper sulphate, zinc sulphate, nickel chloride, or cadmium nitrate, the precipitates, even after being thoroughly washed with concentrated ammonia, gave test for the ion in presence of which the precipitation has been carried on.

When calcium, strontium or barium carbonate is precipitated by means of ammonium carbonate from any of their soluble salts containing a little of magnesium chloride, the precipitate after being thoroughly washed with ammonium chloride shows the presence of mangnesium. Moreover when a little of sulphuric acid is added to a solution of calcium or strontium or barium chloride containing ferric or chromium or aluminium salt the precipitated sulphates of calcium, strontium or barium contain iron or aluminium or chromium. Similarly lead sulphate is precipitated along with barium sulphate even in presence of a large excess of ammonium acetate. Magnesium oxalate is precipitated with barium or strontium or calcium oxalate in presence of an excess of ammonium chloride and ammonia.

These facts make it clear that the phenomenon of induced precipitation is of very general occurrence. On investigating these various cases of induced reactions we are naturally led to the more general conclusion that one chemical change should induce another chemical change of the same type and we tried to verify this conclusion. We found that the reduction of mercuric chloride by such different reducing reagents as formic acid, sulphurous acid, phosphorous acid, etc., induce in all cases the reducing of the same substance, e.g. mercuric chloride, by sodium arsenite.

Induced Decomposition

We also investigated other changes as for instance the decomposition of unstable substances. It is well known that ammonium dichromate decomposes readily into nitrogen, water, and chromium oxide. Also the decomposition temperature of potassium persulphate is lower than that of potassium chlorate and it has been found that in presence of decomposing ammonium dichromate or potassium persulphate the decomposition temperature of potassium chlorate is appreciably lowered. In this connection it will be of interest to investigate whether the presence of an easily decomposable explosive will lower down the decomposition temperature of a difficultly decomposable explosive, and this investigation will throw light on the velocity of decomposition of mixed explosives. Farmer[1] has recently shown that the velocity of decomposition of high explosives becomes greater in presence of another explosive which is more readily decomposed. As far as our experiments go we are inclined to the view that one chemical change will either promote or induce another chemical change of the same nature.

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[1] J. Chem. Soc. 117, 1432, 1603 (1920).

It is well known that ions are generated in several reactions. Very recently Brewer[1] has observed that ionisation will be found to accompany every chemical reaction if suitable precautions are taken. If we can prove that, in the reaction between formic acid or sodium sulphite and mercuric chloride, ions are produced and that these ions activate the molecules of sodium arsenite, which again in turn reduce mercuric chloride because of their increased energy, then the mechanism of this type of induced oxidation will become intelligible.

It is well known that ions are generated in the slow oxidation of phosphorus. It is very likely that these ions activate the molecules of oxygen which thus become reactive and induce chemical changes which are not possible with molecular oxygen.

If it can be definitely proved that ions are generated in all slow oxidations then the phenomenon of induced oxidation will be readily explained—e. g. let us take the case of the mixture of sodium sulphite and sodium arsenite. If the spontaneous oxidation of sodium sulphite by air or oxygen can liberate ions which would activate the molecules of oxygen, then these activated molecules of oxygen would react on the molecules of sodium arsenite. Consequently all the foregoing experimental results of numerous workers would be readily understood from the above point of view in which it is emphasised that slow chemical change can give out ions which would activate otherwise inactive substances.

Similarly it can be conceived that the decomposition say of ammonium dichromate can give out ions which would activate the molecules of potassium chlorate and thus the decomposition of potassium chlorate in presence of the decomposing ammonium chromate is accelerated.

Diabetes from the Viewpoint of Induced Oxidation

From our investigations on oxidation and reduction processes we have observed the following important facts: A substance which is not ordinarily oxidised by air or by oxygen can be oxidised at the ordinary temperatures when it is mixed with another substance which is capable of being readily oxidised. In the foregoing pages several cases of reactions of this type have been investigated. We have also shown that stable substances like sugar, starch, etc., can be oxidised by passing air through these substances containing reducing agents like sodium sulphite, ferrous hydroxide, manganous hydroxide, ferrous sulphate, cerous salts, etc.

There is another way of oxidising starch, sugar, etc., at the ordinary temperature, e. g. if we take starch or tartaric acid solution and add to it hydrogen peroxide we find that at the ordinary temperature, there is hardly any chemical change. But if a little ferrous or ferric salt is added to the mixture, the starch or tartaric acid is oxidised rapidly. It is very likely that ferrous or ferric salts in presence of hydrogen peroxide become converted into an iron per salt or iron peroxide which can readily oxidise starch or tartaric acid because of its unstable nature.

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[1] J. Am. Chem. Soc. 46, 1403 (1924).

In the following pages these ideas of oxidation and reduction processes have been applied to the problem of diabetes. Various carbohydrates contained in the food stuffs are believed to yield chiefly glucose in the process of digestion, absorption and assimilation. It follows therefore that the problems of carbohydrate metabolism chiefly centre round the chemical changes which glucose may undergo. The nature of the enzymes which help the oxidation of glucose by air is still unknown. Now it is also well known that by liver and muscles glucose is converted into glycogen and is stored there as such and reconverted into glucose to give a constant supply of this substance to blood and tissues. In this way a part of the carbohydrates is stored in the body for emergent purposes; whilst another part of the glucose is taken by the blood and tissues and oxidised giving us heat and energy. Moreover there is equilibrium between glycogen and glucose

$$\text{glycogen} \rightleftarrows \text{glucose}$$

The view originally advanced by Claude Bernard is still generally accepted that the blood in health always contains a certain amount of sugar, which is consumed in the capillaries in the normal metabolic processes, and is ultimately eliminated in the form of carbonic acid and water. Claude Bernard regarded the liver as a regulator of the sugar-forming and sugar-consuming processes, storing in its cells glycogen by conversion of the alimentary glucose reaching it in the blood of the portal vein and then by reconversion of this glycogen into sugar producing a fixed and constant supply of sugar to the blood and tissues.

We assume that, in normal health, the glucose which is necessary for the maintenance of health is oxidised in blood and tissues by enzymes called oxidases. Now when a person suffers from diabetes the glucose not being adequately oxidised increases in the system and comes out unchanged from the body in the urine. In diabetic patients the percentage of sugar in blood may go up to 0.4 whilst in normal human blood the percentage of glucose is 0.1. Consequently the amount of heat and energy available in normal health due to the oxidation of glucose is practically lost in diabetic patients; hence a person suffering from diabetes has to depend for heat and energy necessary for existence on the oxidation of fats and proteins and in order to get the minimum quantity of heat and energy necessary for existence one should take more protein and fat otherwise the person might lose weight. So it is reasonable that medical people prescribe abstinence from carbohydrate food in the case of diabetic patients simply because carbohydrates and their derivatives pass out of the system and load the stomach uselessly, serving very little purpose in the maintenance of health. There is possibly another aspect of the case which is this: if starch is taken in the system it must undergo hydrolysis into sugar before it can be oxidised and this process would absorb some energy from the body which will be uselessly spent because the product of hydrolysis will not be utilised for the maintenance of health. It seems very likely that in diabetes complete oxidation of fat into carbon dioxide and water is also affected because acetone, β oxybutyric acid, diacetic acid, lactic acid, etc. which are believed to be products of imperfect oxidation of fat by air are given out.

According to our conception of diabetes the disease is caused mainly by the want of oxidation of glucose in the blood and tissues and possibly the imperfect oxidation of fat is another important factor in the disease. In other words, some how or other the catalyst or enzyme necessary for the oxidation of glucose ceases to perform its function or may be absent from the blood and tissues in cases of diabetes. Similarly the enzyme which can completely oxidise fat into carbon dioxide and water does not perform its part well. This being the etiology of the disease, in order to fight it we have to activate these catalysts to perform their natural function or to supply some catalyst which can accelerate the oxidation of glucose by air or of complete oxidation of fat by air or oxygen.

It is very likely that Insulin which is a pancreas extract given to diabetic patients, activates the oxidation process of glucose by the inhaled oxygen. In other words, the pancreas extract acts as a markedly positive catalyst in the oxidation of glucose by air. Consequently the injection of Insulin is useful because it oxidises the sugar in the blood and tissues and supplies heat and energy to the body. Though there is a great deal of difference in opinion amongst physiologists and medical men with regard to the fate of the sugar in blood when Insulin is injected, we are convinced that it is certainly oxidised in the blood into carbon dioxide and water supplying heart and energy to the body.[1] Similarly the recent products obtained from yeast and other substances that have been found to decrease the amount of sugar in blood by injection in cases of diabetes are certainly positive catalysts which accelerate the chemical change between oxygen and sugar.[2]

In cases of diabetes some people prescribe the taking in of food stuffs rich in their vitamin contents and it seems plausible that these vitamins are accelerators in the oxidation of food stuffs by air. With regard to the nature of these complex substances (e. g. insulin, yeast extract, vitamins etc.) nothing is definitely known. We venture to suggest that they are either reducing agents of the type of thione compounds in complex combination with other substances and are certainly of colloidal nature. It is quite possible that these substances are good reducing agents and readily oxidised by atmospheric oxygen and the oxidation of these substances induces the oxidation of sugar in blood. It is well known that iron (and possibly manganese) exists in most animal and vegetable substances. It is quite likely that iron may be present in a very convenient form in insulin and yeast extracts and this iron is the real catalyst which helps the oxidation of sugar by air. We have already shown that iron is a very powerful catalyst in several oxidation reactions.

There is another way of looking at the problem which is this: In ordinary catalytic reactions we know that traces of a foreign substance act as promoters and can largely increase the catalytic activity of a substance in a chemical

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[1] Compare Kellaway and Hughes: Brit. Med. J. 1, 710 (1923); Dudley and Marrian: Biochem. J. 17, 435 (1923); McCormick, Macleod, O'Brien and Nobel: Am. J. Physiol. 63, 389 (1923); Dale: Lancet 1, 992 (1923); Needhan, Smith and Winter: J. Physiol. 57 lxxxii (1923); Thalhimer and Perry: J. Am. Med. Assoc. 80, 1614 (1923).

[2] Compare Collip: J. Biol. Chem. 56, 513 (1923); Hutchinson, Smith and Winter: Biochem. J. 17, 683, 764 (1923); Collip. Nature, 111, 571 (1923).

change. For example, in the Haber process of the synthesis of ammonia traces of molybdenum, tungsten, etc., largely increase the catalytic activity of iron and possibly other catalysts in the combination of hydrogen and nitrogen. We know that iron is present in blood in normal health and that the iron may be in such a complex combination and colloidal condition that it can act as a very convenient catalyst in the oxidation of foodstuffs. It seems probable that in diabetes the iron becomes powerless as far as oxidation of glucose is concerned. By the injection of insulin the normal activity of iron as a catalyst is restored or possibly increased. In other words, insulin, vitamin, yeast extracts, etc., may act as promoters of iron as a catalytic agent in the oxidation of glucose.

From our researches on oxidation we find that iron is a very important catalytic agent[1] in many oxidation reactions. Hence we would urge on medical people to treat diabetes by the internal use of iron salts or colloidal iron preparations. According to our conceptions in order to fight diabetes, somehow or other we must increase or induce the oxidation of sugar in the system by air. This is possible by some positive catalyst which may be iron or some other organic substance. As iron in very small doses is not harmful to the human body, and it is very likely it will be useful in the body by acting as a marked positive catalyst in the oxidation of sugar by air, we would request medical people to try this method of diabetes which seems theoretically sound. Either colloidal ferric hydroxide or colloidal iron in alcohol or ferrous citrate or any other convenient iron preparation may be used as injection or by mouth.

In this connection it will be interesting to note that Abderhalden and Wertheimer[2] have shown that the reducing power of muscle is increased to three or four times that of normal muscle under certain conditions and it is supposed that such increments are associated with the presence of thiol group in the muscle fibres.

That want of oxidation is the real cause of trouble in diabetes is shown by another fact. It is well known that when a diabetic patient suffers from a rise of body temperature, the amount of sugar in its urine becomes less even if he takes his usual food containing carbohydrates as well. We have already suggested that fever is an autocatalytic oxidation process and it is also well known that the amount of oxidation in the human body increases markedly with rise of temperature. Consequently a diabetic person who is passing an appreciable quantity of sugar when the body temperature is normal, will certainly pass less sugar at the fever temperature because at the higher temperature the amount of oxidation of sugar is much greater than at the ordinary temperature. Another fact in support of the view that diabetes is due to insufficient oxidation of glucose, fat, etc., is that in acute cases of diabetes, reducing substances such as diacetic acid, acetone, lactic acid, etc., have been found to come out in the urine. In normal health these substances are not found in urine and they are completely oxidised to carbon dioxide and

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[1] Compare Warburg and Meyerhof: Z. physiol. Chem. 85, 412 (1913); Warburg: 92, 231 (1914); Meyerhof: Lancet, 1, 322 (1923).

[2] Chem. Zentr. 1923 III, 1290.

water. It is well known that fat in normal health is completely oxidised to carbon dioxide and water; whereas in diabetes it is partially metabolised into acetone, diacetic acid, β oxybutyric acid, etc. The presence of these substances in cases of diabetes is considered to be serious as the diabetic coma is assigned to their presence in human body. Prof. Hugh McLean[1] and others of his thought hold that insulin when injected in diabetes does not help in oxidising the glucose of the blood and tissues but helps to convert the glucose into fat. This view seems unsound, for if oxidation processes are not activated by insulin the fat accumulated will be only partially oxidised with the result that more ketonic bodies will be formed in the system. Hence, instead of being a cure, insulin will only aggravate the disease.

Our view regarding the metabolism or glucose and carbohydrates is corroborated from the experimental observations of Knowlton and Starling[2] who hold that the sugar of the blood is burnt up in the muscles through the agency of a glycolytic substance which results from the interaction of bodies produced in the pancreas and the muslces. They proved that the consumption of sugar by the diabetic heart was much below that of the normal heart. They proved further that this loss of power to utilise sugar in the diabetic heart was due to absence of some substance normally present in the heart and circulating blood and presumably formed by the pancreas rather than to the presence of some toxic substance accumulating as a result of extirpation of the pancreas and preventing the utilisation of sugar by the tissues.

Summary

1. Mercuric chloride is not reduced by sodium arsenite under ordinary conditions; but the reduction of mercuric chloride by the same reagent can be induced by the chemical changes between mercuric chloride and reducing agents like sodium sulphite, sodium phosphite, and formic acid.

2. Sodium nitrite, potassium oxalate, sodium arsenite, nickelous hydroxide, etc., can be oxidised by air or oxygen at the ordinary temperature in presence of sodium sulphite, which in its turn is itself oxidised.

3. The oxidation of ferrous hydroxide or manganous hydroxide or cobaltous hydroxide by air or oxygen can induce oxidation of nickelous hydroxide by air of oxygen.

4. The oxidation of sodium sulphite by air can accelerate the oxidation of ferrous ammonium sulphate, cobaltous hydroxide, etc., by air.

5. The oxidation of stannous chloride by air accelerates oxidation of ferrous ammonium sulphate by air. Similarly the oxidation of sulphurous acid by air accelerates the oxidation of stannous chloride by air.

6. Quantitative experiments have shown that glucose can be oxidised more or less completely by passing air through solutions of sodium sulphite and glucose.

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[1] Nature, July 5 (1924).

[2] Lancet, Sept. 21 (1912).

7. It has been observed that in induced oxidation of nickelous hydroxide, the amount of the induced oxidation increases with the increase in the concentration of sodium hydroxide up to a maximum limit and then falls with the increase in the concentration of the alkali.

8. The literature on catalytic oxidation shows that many of these oxidations are really cases of induced oxidation which are of common occurrence.

9. Examples of induced precipitation and induced decomposition are given and it seems that induced precipitation and induced decomposition occur frequently.

10. An explanation of induced oxidation, induced decomposition etc., has been advanced on the basis of the generation of ions in chemical changes. Thus, if the spontaneous oxidation of sodium sulphite by air or oxygen can liberate ions which would activate the molecules of oxygen then these active molecules would react on sodium arsenite.

11. We have emphasised the view that diabetes is due to insufficient oxidation of glucose and fat in the human body. In other words, the disease is caused by want of catalysts or enzymes which in normal health exist in the body and help the oxidation of glucose, fats, etc. We venture to suggest that insulin, extracts of yeast, etc., activate the catalysts or the enzymes and consequently act as accelerators in the oxidation of glucose by air in the system. It may be that minute traces of iron are present in insulin, vitamin, etc., and that this iron present in a very reactive condition is the active substance which help the oxidation of glucose by air. It is also suggested that iron preparations specially of a colloidal nature would be helpful in the treatment of diabetes acting as an accelerator in the oxidation of glucose and fat etc., by oxygen.

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THE MOLECULAR ASSOCIATION OF FURFURAL

BY FREDERICK H. GETMAN

Both the physical and the chemical properties of furfural are such as to suggest that the molecules of the substance are more or less associated. A search of the literature, however, has failed to reveal the existence of trustworthy data upon which to base any calculations of the degree to which the molecules of furfural, either per se or in solution, have undergone association. In order to secure the necessary data for such calculations the following investigation was undertaken.

A number of determinations were made of the lowering of the freezing point of water and benzene produced by the addition of varying amounts of furfural to each of these two solvents. The ordinary Beckmann apparatus was used, the thermometer having recently been calibrated by the U. S. Bureau of Standards. At least three readings, agreeing to within 0.001°, were secured for each solution; the usual thermometric corrections were applied and also precautions were taken to prevent too great supercooling. Great care was exercised to maintain the temperature of the freezing bath only slightly below the freezing temperature of the solution under investigation. The freezing point of the pure solvent was determined either immediately before, or immediately after, each series of measurements, and throughout the entire investigation the thermometer was maintained at a temperature not far removed from the freezing temperature of the pure solvent. As a result of the latter precaution, the zero of the thermometer showed a maximum variation of only 0.003°, and that was observed in the early stages of the work, probably before the instrument was thoroughly "seasoned".

The furfural employed was purified in the manner described in a previous paper[1], while the benzene was prepared from a sample, known to be free from thiophene, by crystallization and subsequent distillation of the molten crystals over freshly cut sodium. The aqueous solutions were prepared with so-called "conductivity water". Each solution was made up by direct weighing and its concentration expressed in terms of mols per 1000 grams of solvent.

Biltz[2] having emphasized the importance of determining the value of molecular weights at infinite dilution by means of graphic extrapolation, where the osmotic laws are strictly valid, we have followed the procedure herewith outlined. After having determined the freezing point depressions produced by such concentrations of furfural as could be accurately measured by means of the thermometer, the values of the various depressions were plotted against the corresponding concentrations, and a smooth curve was drawn through the points thus obtained. This curve obviously passes through the origin. From this curve, the values of the freezing point depressions, at rounded

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[1] J. Phys. Chem. 28, 212 (1924)

[2] Biltz: "Practical Methods for determining Molecular Weights," p. 119.

concentrations, were read off and the corresponding values of the molecular depression, Δt/N, were calculated.

In addition to determining the freezing point depressions produced by freshly distilled furfural, it seemed of interest to make a similar series of determinations with furfural which had been exposed to the action of sunlight for about three months after distillation and, in consequence, had acquired a dark brown color.

The experimental results are recorded in the following tables (I to IV) in which N denotes the concentration in mols per 1000 grams of solvent and Δt the corrected depression of the freezing point.

TABLE I

Furfural (freshly distilled) in Water

N	Δt	Δt/N	N	Δt	Δt/N
0.01	0.0187	1.87	0.3	0.546	1.82
0.03	0.056	1.89	0.4	0.703	1.76
0.05	0.095	1.91	0.5	0.845	1.69
0.1	0.189	1.89	0.6	0.982	1.64
0.2	0.370	1.85			

TABLE II

Furfural (freshly distilled) in Benzene

N	Δt	Δt/N	N	Δt	Δt/N
0.01	0.052	5.20	0.3	1.497	4.99
0.02	0.104	5.20	0.4	1.932	4.83
0.05	0.264	5.28	0.5	2.340	4.68
0.1	0.530	5.30	0.6	2.724	4.54
0.2	1.034	5.17	0.7	3.101	4.43

TABLE III

Furfural (colored) in Water

N	Δt	Δt/N	N	Δt	Δt/N
0.01	0.019	1.90	0.3	0.542	1.81
0.02	0.039	1.95	0.4	0.690	1.73
0.05	0.101	2.00	0.5	0.828	1.65
0.1	0.198	1.98	0.6	0.962	1.60
0.2	0.380	1.90			

TABLE IV

Furfural (colored) in Benzene

N	Δt	Δt/N	N	Δt	Δt/N
0.01	0.052	5.20	0.3	1.533	5.11
0.02	0.105	5.25	0.4	1.926	4.82
0.05	0.267	5.34	0.5	2.310	4.62
0.1	0.536	5.36	0.6	2.700	4.50
0.2	1.075	5.38	0.7	3.070	4.39

It will be observed that the molecular depression of the freezing point recorded in each of the foregoing tables, increases to a maximum value and then steadily decreases as the concentration of the solutions increases. If furfural were perfectly normal in its behavior, however, the value of the molecular lowering of the freezing point should be 1.86 in aqueous solutions and 5.12 in benzene solutions. It follows, therefore, that only in extremely dilute solutions of water and benzene does furfural have an approximately normal molecular weight. The abnormal values of $\Delta t/N$, observed in the more concentrated solutions, are probably due to the tendency of furfural to undergo both solvation and association. In the more dilute solutions the tendency of the molecules of solute to become solvated predominates and, in consequence, the values of $\Delta t/N$ are greater than the normal molecular lowering. As the concentration increases, the tendency of the molecules of solute to become associated increases to such an extent that ultimately the effect of association completely masks the effect of solvation and the values of $\Delta t/N$ become less than the normal value. Hence, when the two processes of solvation and association are coexistent, it is evident that the ratio of the calculated to the normal molecular weight of the solute does not afford an accurate measure of its degree of association in solution. Nevertheless, we may regard the ratio of the normal value of $\Delta t/N$ to its abnormal value in any one of the more concentrated solutions as affording a rough approximation to the value of x, the factor of association of the solute. Thus, if we calculate the values of this ratio in 0.5 N solutions we obtain the results given in Table V.

TABLE V

	In Water	In Benzene
x for freshly distilled $C_5H_4O_2$	1.11	1.11
x for colored $C_5H_4O_2$	1.14	1.13

It will be observed that the degree of association, in solution, of the freshly distilled substance is slightly less than that of the sample of furfural which had been exposed to the action of light. A similar difference will be noted in the behavior of these two solutes in the more dilute solutions where the influence of solvation is apparent. In Tables I to IV it will be noted that freshly distilled furfural has undergone solvation to a smaller extent than has the colored modification.

As to the molecular complexity of furfural per se, there is very little available data upon which to base any calculations of the factor of association. From Trouton's well-known relation, $Ml_v/T = k$, where M denotes the molecular weight, l_v the heat of vaporization[1] and T the absolute boiling point of the substance, we find the following value for the constant, k

$$k = \frac{96.03 \times 107.91}{161.7+273} = 23.8$$

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[1] The value of l_v here used was determined by Prof. J. H. Mathews who very kindly supplied the author with his data on furfural.

The mean value of k for normal liquids being 20.7, we conclude that furfural is slightly dissociated.

From the modified form of the Trouton relation proposed by Nernst and Bingham[1],

$$Ml_v/T = 17 + 0.011\ T,$$

in which the symbols have the same significance as in the Trouton relation, we find $Ml_v/T = 23.8$ while $17 + 0.011T = 21.8$. The difference between the two sides of the equation being assumed to afford an approximate measure of the degree of association, x, it will be seen that the value of this factor is 2.

Again we may make use of Longinescu's relation[2],

$$n = \left(\frac{T}{100\ d}\right)^2$$

in which n is the number of atoms per molecule of liquid, d its density and T its absolute boiling point. Substituting in this equation we have

$$n = \left(\frac{434.7}{100 \times 1.16}\right)^2 = 14.$$

The formula, $C_5H_4O_2$, shows that a molecule of furfural contains 11 atoms, hence the degree of association is 1.3.

While the foregoing calculations cannot be regarded as more than rough approximations, the results obtained by the three different methods agree in indicating that the molecules of furfural are more or less associated in the liquid state.

The results of this investigation may be briefly summarized as follows:

(1) The depression of the freezing points of water and benzene produced by the addition of varying amounts of furfural have been studied. It has been found that only in extremely dilute solutions does furfural have a normal molecular weight. The abnormalities in the values of the molecular depression of the freezing point are ascribed to the tendency of the solute to undergo both solvation and association, the former predominating in dilute solutions and the latter in concentrated solutions.

(2) A similar series of measurements was carried out with a sample of furfural which had been exposed to the action of sunlight for about three months after distillation. While the results were similar to those obtained with the freshly distilled liquid the latter was found to be slightly less associated than that which had been exposed to the action of light.

(3) The approximate degree of association of pure liquid furfural has been calculated by three different formulae and found to be slightly greater than unity.

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Stamford, Conn.

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[1] Nernst and Bingham: J. Am. Chem. Soc., **28**, 730 (1906).

[2] Longinescu: J. Chim. phys. **1**, 296, 391 (1903).

SOME PHYSICAL PROPERTIES OF NACREOUS SULPHUR

BY H. WHITAKER

The attention of the author was drawn to a micro-crystalline form of sulphur in the course of an ultra-microscopic investigation of the properties of sulphur clouds. It was desired to repeat the experiments of Ehrenhaft on the resonance colours of sulphur particles and for this purpose the sulphur was vaporised at a low temperature in a U-tube. It was then noticed that the deposit which formed slowly above the molten sulphur underwent a change from liquid globules to a mass of tiny crystalline plates which exhibited striking colours. A microscopic examination of this deposit showed the presence of hexagonal plates, which at first were regarded as a new crystalline variety, but later proved to be the nacreous form which has been investigated by Muthmann. Nacreous sulphur was in all probability observed as far back as 1852, according to Muthmann,[1] who, in this connection refers to the work of Payen (1852), Ste. Claire-Deville (1852), Debray (1858), Geinez (1884), Bruhns (1887-8), the latter obtaining the crystals in sufficient size so that their physical constants could be determined. In 1890, Muthmann took up the detailed study of sulphur and selenium, repeated the experiments of Dr. Bruhns, and carefully measured the interfacial angles of nacreous sulphur crystals. In 1899, Salomon[2] obtained these crystals by heating a little sulphur in a watch glass, covered with a microscope slide, upon which a film of sulphur droplets was allowed to condense.

Salomon briefly refers to their crystallographic and optical properties and bases the identity of his crystals with those investigated by Bruhns and Muthmann, upon measurement of the interfacial angles.

It seemed worth while to investigate the mode of origin, stability, and optical properties of these crystals and in the following pages a short account is given of experiments on these points.

Experimental

Crystals of nacreous sulphur are conveniently obtained by growing them from a film of sulphur droplets. This can be accomplished in several ways. At first the film was condensed on the walls of a U-tube. Later, it was found more advantageous to substitute a rectangular glass cell, made up of microscopic slides, for one limb of the U-tube. The bend of the U-tube, containing a little roll sulphur, was gently heated in a bath of iron fillings, whilst a slow stream of dry air was aspirated through the cell. A fine film of sulphur droplets condensed on the walls of the cell, which was examined periodically under the microscope and photographed at intervals.

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[1] W. Muthmann: Z. Kryst. Min., 17, 336 (1890).

[2] W. Salomon: Z. Kryst. Min., 30, 605 (1899).

Plate I shows the appearance of the droplets after five days. Plate II shows the appearance of another portion of the same film after five days, under higher magnification. The solidified droplets are distinguished by a prickly appearance and by the absence of the central spot of axial light. The crystals appear first as needles, then as trapezia, and finally assume the shape of hexagonal plates, branching out from the solidified droplets. The mechanism of crystal growth seems to be as follows: sulphur vapour evaporates from the still liquid droplets and condenses upon the solidified droplets as crystalline nacreous sulphur. At least three processes are going on simultaneously, (1) differentiation in size among droplets, the larger droplets growing at the expense of the smaller, (2) crystallization of some of the droplets, the others remaining liquid for longer or shorter intervals, (3) growth at the expense of the surrounding droplets of crystals of nacreous sulphur and of octahedral sulphur. Neighbouring droplets evaporate for the most part more quickly than those more remote, and, since it is well known that small droplets evaporate more quickly than large ones, it is to be expected that after a suitable interval of time, a crystal will be surrounded by a space free from droplets.

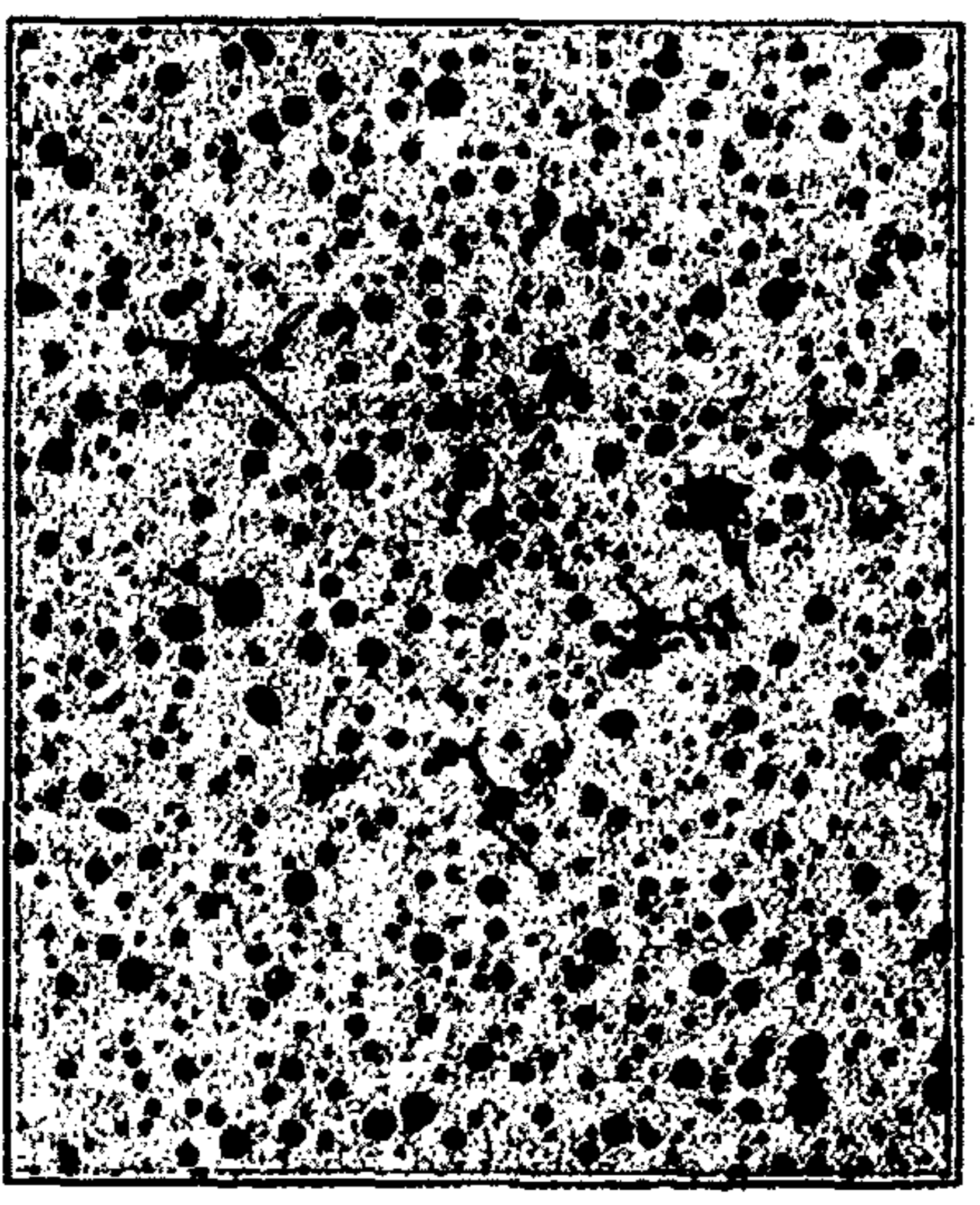

Plate I

Appearance of sulphur droplets after 5 days, × 80 diameters.

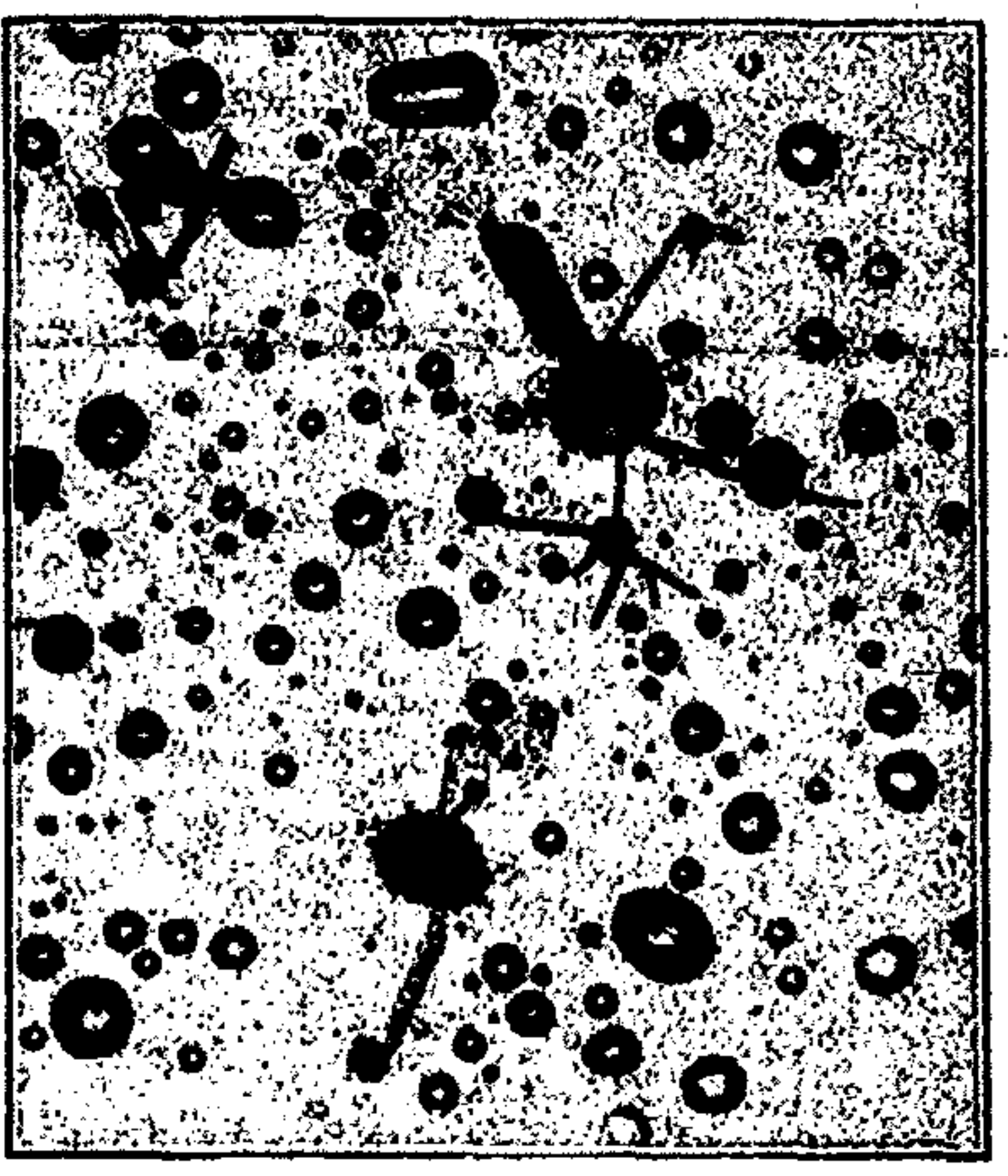

Plate II

Appearance of sulphur droplets after 5 days, × 250 diameters.

Plate III shows such a crystal surrounded by a clear space.

The ideal crystal of nacreous sulphur, obtained by growth from droplets, is hexagonal in shape, according to Salomon, having three pairs of opposite sides parallel, the three principal angles being 124° 45′, 146° 43′ and 88° 16′, measured microscopically. A single crystal was obtained from a cluster and laid flat upon a slide. In this operation one end of the crystal was unavoidably fractured and only three angles could be measured. Difficulty was found in obtaining a perfect crystal but eventually one was obtained (Plate IV) by forming a film of droplets (average diameter of a droplet = 0.1 mm.) on a microscope cover slip, which was inverted and cemented to a microscope slide, leaving a thin air film between. Measurements of the six angles gave the following mean values: 88° 8′, 146° 23′, 125° 4′, 88° 30′, 146° 36′, 124° 45′. Actual length of crystal = 0.16 mm. Between crossed Nicols, the directions of extinction were apparently parallel and perpendicular respectively to a long edge of the crystal.

Plate V shows the appearance of the crystals after eight days growth. Four types of crystals were observed: ,(1) octahedra; the plate shows one large well-developed specimen, (2) nacreous plates, imperfectly developed, (3) hexagonal plates, (4) curved hair-like crystals (estimated average thickness, 0.02 mm.). The last named do not appear on the plate.

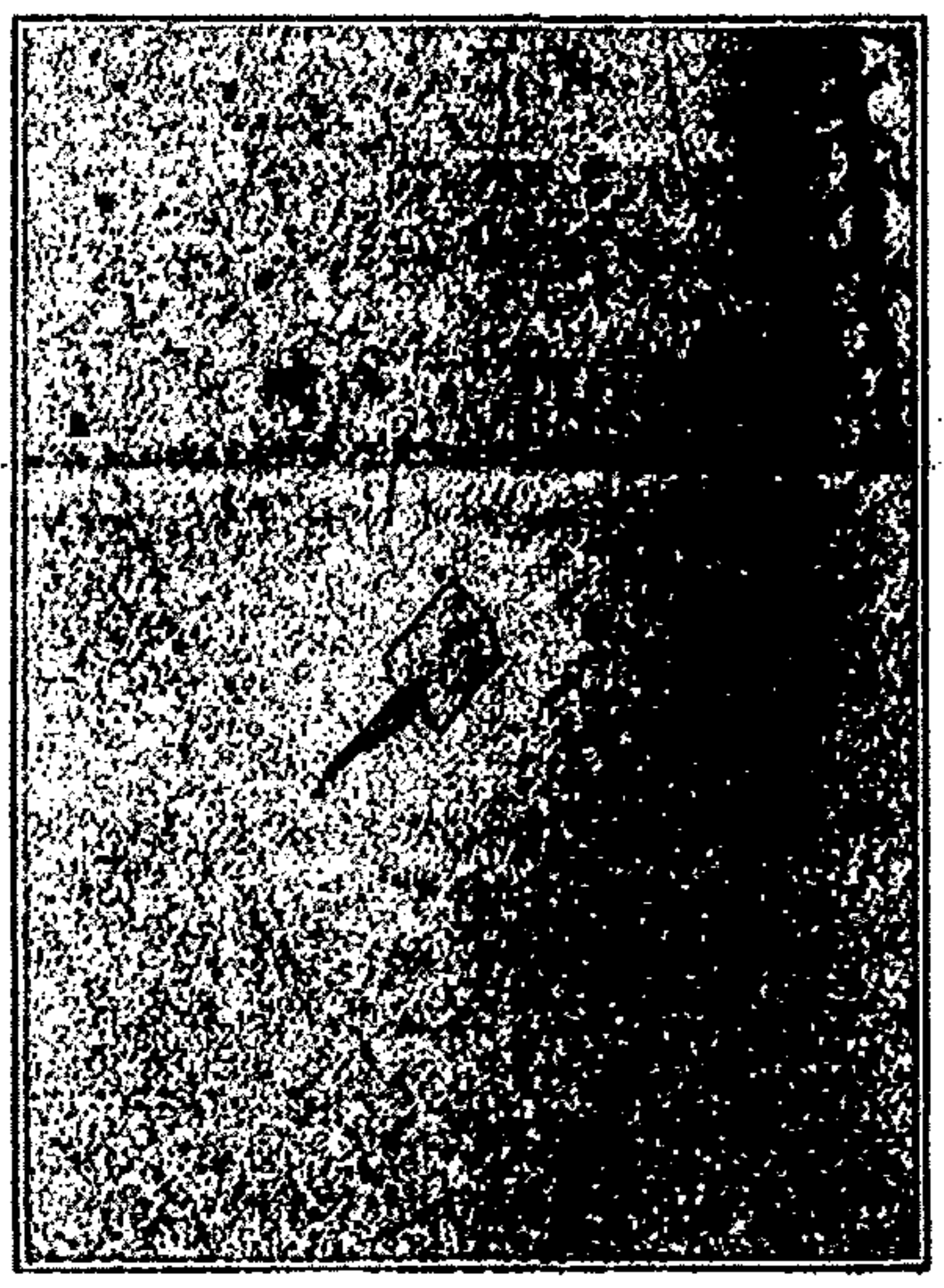

PLATE III
A single crystal of nacreous sulphur,
× 80 diameters.

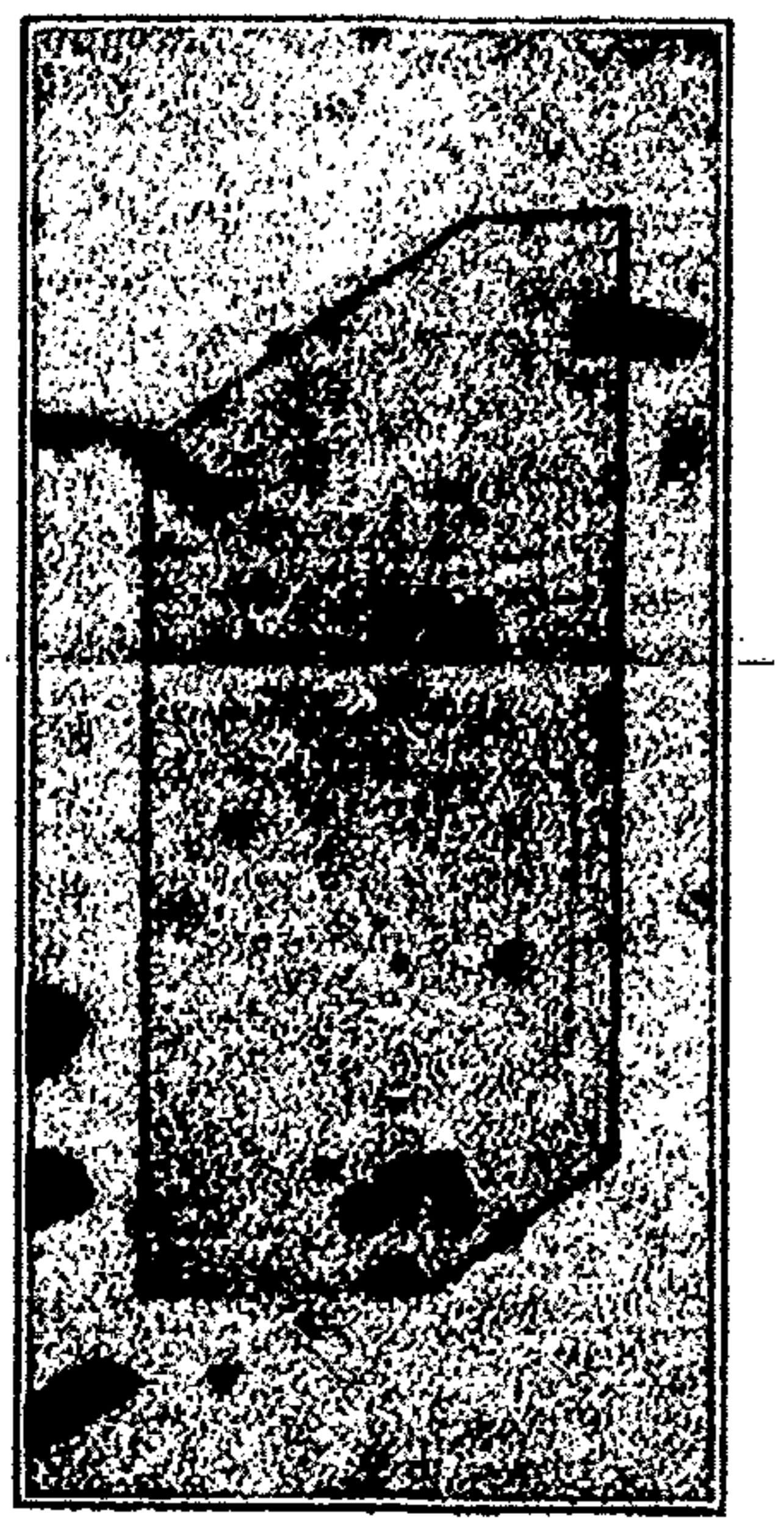

PLATE IV
A single crystal of nacreous sulphur,
with six complete sides. Age
12 days, × 330 diameters.

An edge of a hexagonal plate, after ten days growth, measured 0.024 mm. The two smaller angles measured 90°, (min. 89° 45′, max. 90°); the other four, 135° each, (min. 134° 45′, max. 135° 18′). The crystals were colourless and between crossed Nicols the directions of extinction were apparently parallel and perpendicular respectively to the long axis. The crystals are possibly rhombic or monoclinic, but they were not studied in further detail so as to determine definitely the system to which they belong. The angular measurements distinguish them from the nacreous plates and also from Muthmann's hexagonal tabular sulphur[1] (S_{iv}), the plane angles on the predominating face being 120°.

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[1] W. Muthmann: Zeit. Kryst. Min., **17**, 343 (1890).

Plate VI shows a cluster of nacreous sulphur crystals and one octahedron, two days old, its chief feature being that it shows the possibility of simultaneous growth of both crystalline forms, growing in the same way from the droplets. In this plate, the crystals shown are on the same surface as the droplets; in Plate V, the crystals are developing on the free glass surface nearest to the droplets, the hazy background being due to the droplets being out of focus.

Plate VII shows a cluster of nacreous sulphur crystals, possessing various colours by transmitted light. Their appearance under the microscope, due to the assemblage of different colours, is often very striking. The large parallelogram-shaped crystal, to the left of the centre of the plate, was grey on its outermost edge. Within this was a green band, and in the centre, a cone of colours ranging from red at the tip of the cone to greyish violet at the base. The large crystal at the bottom left hand corner was delicately coloured with alternate bands of pale red and pale green, shading into one another, resembling the pale red and green bands seen in soap films. In general, however, the tint is uniform throughout a given crystal. To the right of the centre will be seen a small crystal possessing a curious net-work appearance on its surface, which will be referred to again. The extreme thinness and transparency of these crystals is evidenced by the fact that the black dots, representing the sulphur droplets, are readily photographed *through* the crystal.

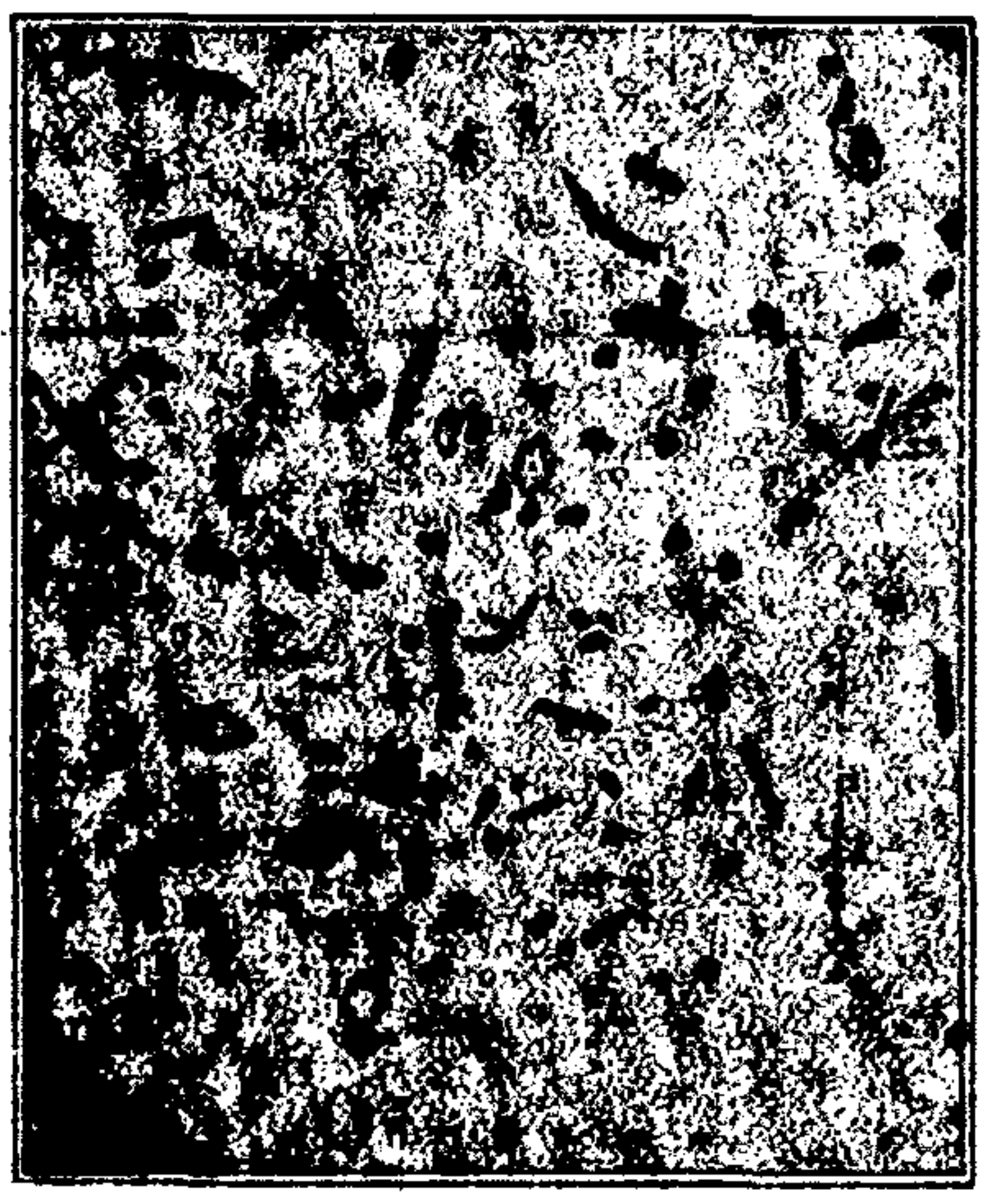


PLATE V
Sulphur crystals after 8 days growth, × 80 diameters.

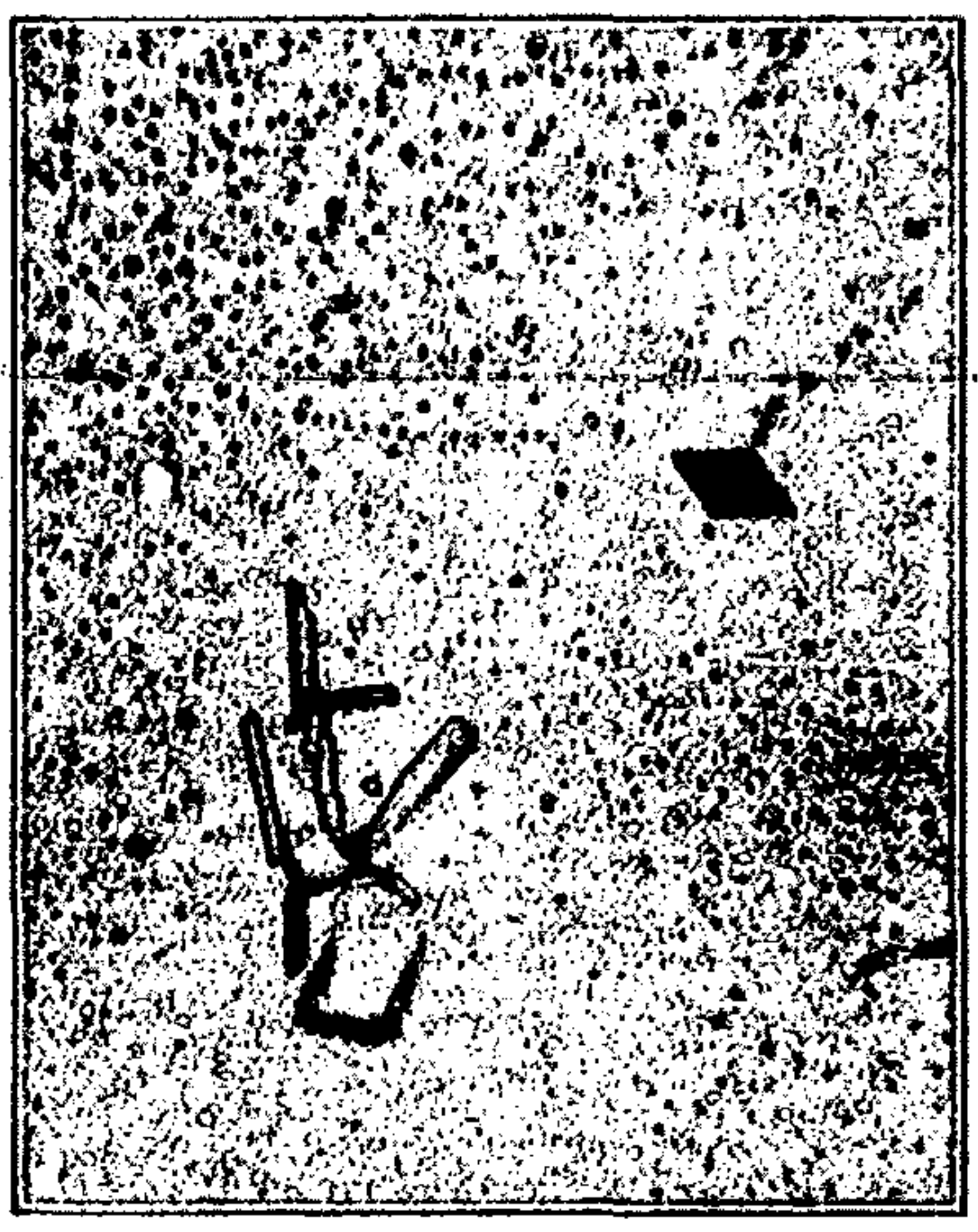


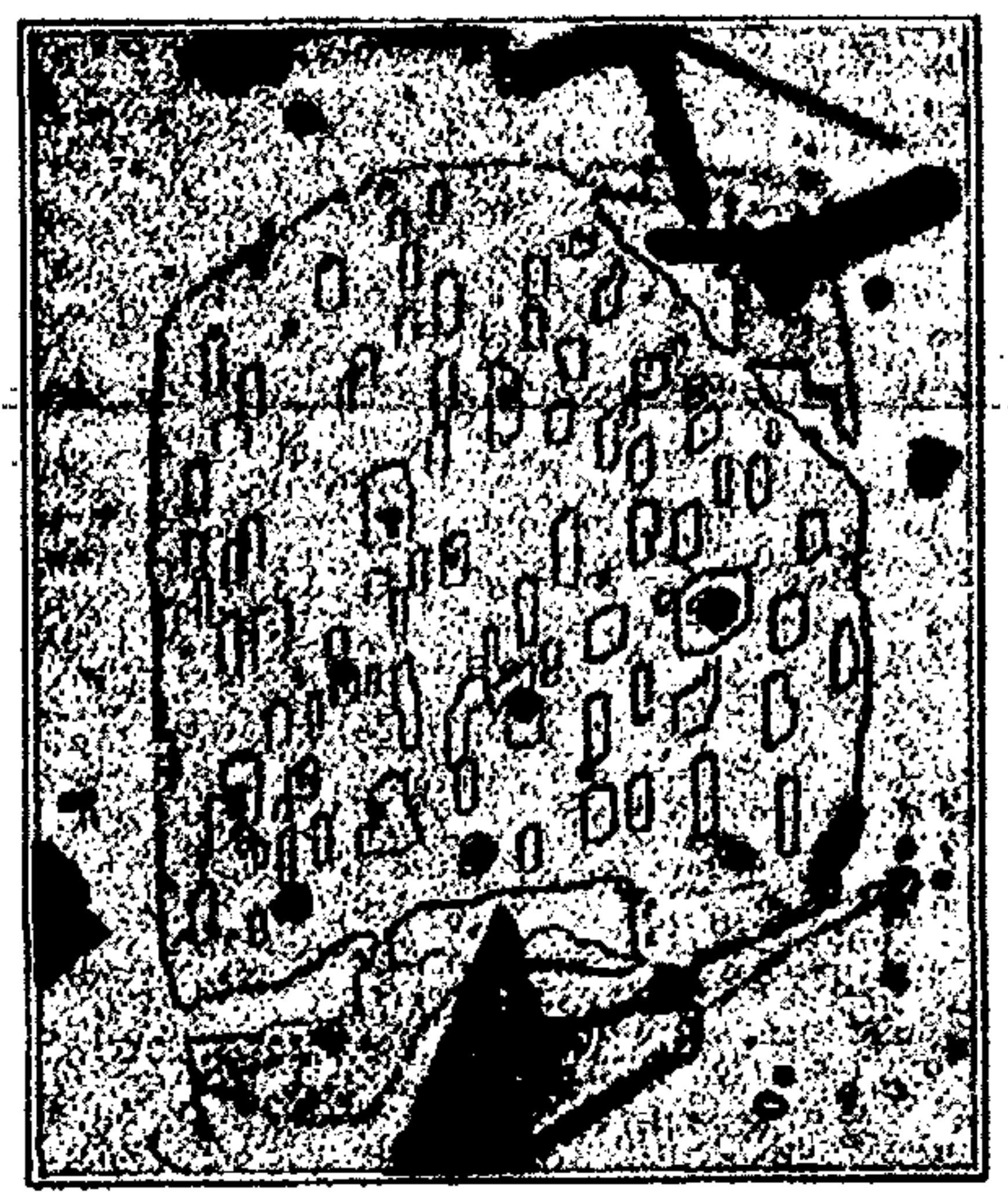
PLATE VI
Rhombic and nacreous crystals, × 360 diameters.

Thickness of crystals. This was determined in the case of some relatively thick crystals by isolating a single specimen on the end of a glass rod drawn out to a fine point, and rotating the rod until the crystal assumed a nearly vertical position. An edge was then focussed through the microscope and its thickness measured by an eye-piece micrometer. The thickness turned out to be of the order of .001 mm. In the case of the coloured crystals, attempts were made to isolate a single crystal showing an interference band in its spectrum. After many failures, a pink crystal was isolated showing a dark band in the region of 0.5μ. Its thickness was calculated to be 0.13μ. Attempts to measure directly the thickness of its edge failed; its apparent thickness, using a 1/6'' objective and a high power eye-piece, was less than the thickness of a single line of the eye-piece micrometer scale. A rough calculation from these data indicated that its thickness was below 0.4μ.

Colours of crystals. A crystal was mounted so that it could be rotated about a horizontal or vertical axis and the light reflected from its surface examined microscopically. If the colours are due to interferences, as seems to be the case, a change in tint should occur with change in the angle of incidence of light upon the crystal. To examine this question, a piece of mirror was smoked on its surface and a slide, containing some nacreous crystals, was inverted and pressed gently upon the smoked surface, leaving thereon a number of the crystals. The smoked glass was then mounted so that a given crystal could be brought into the centre of the field of the microscopic and rotated about a horizontal or a vertical axis. By using a smoked surface, reflections from the glass slide, supporting the crystals, were eliminated, and at the same time a dark background was provided, which made it possible to follow the colour changes with greater certainty. The source of illumination was diffused daylight or diffused artificial daylight from an Osram Daylight Lamp.

PLATE VII

Group of nacreous crystals showing interference colours.



PLATES VIII

Crystal showing etch figures, × 250 diameters.

To take one example, a green crystal was rotated about its long axis, with the plane containing the incident and reflected light perpendicular to the long axis. With change in the angle of incidence from roughly 15° to 75°, the colour of the crystal changed to blue, then purple and finally reddish purple. When rotated in a similar manner, about an axis perpendicular to its long axis, the colour changed to greenish blue. The greatest variation in tint occurred when the crystal was rotated about its long axis.

The pleochroism of the crystals has already been noted by Salomon. The transmitted light resolved by a Nicol consists of two components, one pale pink and the other pale green. The feeble colours may be accounted for by the extreme thinness of the crystals. The incident light is for the most part transmitted, and the pleochroic colours are to some extent masked by white light. If the reflected light be examined through a Nicol, the colour is in consequence more saturated and the change in colour on rotating the Nicol is very striking. To give only one example: light was incident upon the crystal face of a sky-blue crystal at 30° approximately. When the plane of vibration of the analysed light was parallel to the long axis of the crystal the colour was greenish-blue; when perpendicular to the long axis the colour was purple. These observations were repeated, allowing light to fall upon the crystal at different angles of incidence. In the crystals examined, the variation in tint seemed most marked when the light was incident at an oblique angle.

Strong evidence for the theory that the colours are due to interference is afforded by the presence of a dark band in the spectrum. The following observations confirm this view.

(1) Crystals 24 hours old did not show any colour. Pale colours were observed in some crystals two or three days old. Some crystals, two or three weeks old, which had evidently increased in thickness and area, showed no colour.

(2) Occassionally two similarly coloured crystals overlapped. The resulting colour was often quite different from that of either.

(3) Two or three large crystals were examined with the naked eye against a dark background and their colours, as seen by reflection noted. They were again examined against a white background when their pale complementary tints were observed.

"*Ageing*" *of crystals.* After three or four weeks, it was observed that whilst many nacreous crystals remained stable, in a few a remarkable change had taken place.

Plates VIII and IX illustrate these changes. The etch figures, which exhibit the characteristic angles of the large crystal, are in reality holes in the crystal itself. The crystal is in a process of disintegration. At the centre of each hole is a tiny speck. In the centre of some of the larger holes there are irregular masses, the details of which could not be resolved. All attempts made to resolve the detail of the tiny specks were unsuccessful. It is believed that they consist of new crystalline nuclei, of the stable octahedral variety, which are growing at the expense of the nacreous plate. Since the octahedra grow in three dimensions, whereas the nacreous crystal may be considered for practical purposes as two-dimensional, a relatively large area of plate will be required to build up a tiny octahedron. This view is supported by the observations of Gernez who found that a nacreous crystal changed into the rhombic form when touched with a rhombic crystal. Muthmann also noticed that when a rhombic crystal fell on a leaflet of nacreous sulphur which had separated from solution, a circular hole formed in the latter and the rhombic crystal continued to grow.

It is of interest to compare the relative areas presented to the eye of a nacreous crystal and of a rhombic crystal, containing the same number of molecules, i. e. equal masses of the two varieties.

Assuming that the nacreous plate has a thickness of 0.6μ, and neglecting a possible small difference in the densities between the two varieties, a rough calculation shows that a rhombic crystal will cover an area not greater than 1/10,000 (a and b axes in horizontal plane), of not greater than 1/4,500 (b and c axes in horizontal plane) of the area presented by the nacreous crystal when lying flat. This corresponds to a minimum linear shrinkage of 1 in 67.

In Plate VIII, the dimensions of one hole are 1 mm.×4 mm. Hence the area is that of a square whose side is 2 mm. But, since the magnification is 250, the actual length will be 8μ, and the corresponding linear dimension of the octahedron will be therefore $(8/67)\mu = 0.12\mu$, which is beyond the limit of microscopic resolution.

In Plate IX, the process of disintegration has gone a stage further, so that the crystal is now a mere skeleton. In the larger crystal, the acute angle is explained by the absence of one of the normal faces. Measurements of this angle gave the value 54° 46′. Calculated value 54° 54′. Some other crystals, no photographed, show signs of disintegration by the appearance of a serrated edge. The crystal in Plate VII, showing a net-work structure is no doubt breaking up in a similar way.

PLATE IX

Two crystals showing etch figures, later stage, × 120 diameters.

Summary

The growth, development and disintegration of crystals of nacreous sulphur, obtained from sulphur droplets, has been studied and the various stages illustrated by microphotographs. Colour in crystals is shown to be due to interference.

In conclusion, the author wishes to offer his sincere thanks to Professor R. Whytlaw-Gray for continual advice and encouragement throughout the work.

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THE ELECTRODE POTENTIALS AND THE FREE ENERGY OF SOLVATION

BY JAROSLAV HEYROVSKÝ

In the previous communication[1] the electrode potentials (π) of galvanic cells were deduced from physical constants, namely from the ionisation potential (I) of the electrode vapour (or, in the case of a metalloid its "electron-affinity", E), the vapour tension (P) of the electrode, the free energy (H) of solvation of the electrode-ions and the concentration of solvated ions.

Formulae

$$(2) \qquad \pi_{Me} = -\frac{RT}{F}\log P_{Me} + I - H_{Me^{\cdot}} + \frac{RT}{F}\log [Me^{\cdot}_{sol}]$$

and

$$(3) \qquad \pi_{x} = +\frac{RT}{F}\log P_{x} + E + H_{x}' - \frac{RT}{F}\log [\chi'_{sol}]$$

were obtained.

The introduction of the term H is based upon the idea of Fajans[2] of allowing the ions first to be solvated before bringing them into solution. This can proceed reversibly, if we keep the ions in the vapour phase of the solvent, letting the vapour condense upon them until they become so far solvated that they acquire the vapour pressure of the electrode solution, during this operation the free energy of solvation, H, is gained. The di-pole nature of solvent molecules explains the free energy of this physical process.[3] Although from this point of view the solvation process is regarded as a physical one, we may also, when following the modern tendency to explain chemical processes physically, look upon it chemically and apply to it—as it has been done in the previous communication—the law of mass action.

The formulae (2), (3) show us how the potential of an electrode depends upon the solvent since only the solvation term H changes in various solvents. Born[4] has physically deduced this quantity $H\left[=\frac{Ne^2n^2}{2r}\left(1-\frac{1}{D}\right)\right]$, where r is the ionic radius and n the valency showing how it should depend upon the dielectric constant. From his formula it appears that the difference of electrolytic potentials of one and the same metal in water and alcohol is only about a third of a volt.

The Effect of Solvation

For solutions in the same solvent H will depend upon their vapour-tensions, i. e., on the total concentration of the solution, whereas $\frac{RT}{F}\log c$ only

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[1] J. Phys. Chem. 29, 344 (1925).

[2] Ber. physik. Ges. 21, 249, 709 (1919).

[3] See Born: Z. Physik. 45 (1920); Herzfeld: Jahrb. Rad. Elektr. 19 (1923).

[4] Loc. cit. p. 45.

changes with the partial concentration of the electrode ions, *c*; thus in concentration cells both the factors H and log c, determine the E. M. F.

In Nernst's formula the solvation energy does not appear; however its importance becomes obvious from recent measurements of cells with very concentrated solutions.

From Formulae (2) and (3) we obtain, on subtracting, the E. M. F. of a cell consisting of a metallic electrode reversible in cations, $Me^{\cdot}$, and a metalloid electrode reversible in anions, $X'_{\perp}$, as equal to

$$\pi_x - \pi_{Me} = K + H_{Me} + H_x' - \frac{RT}{F} \log [Me^{\cdot}_{sol}] [X'_{sol}]$$

In strongly concentrated solutions, where the vapour pressure of the solvent becomes considerably lowered and the amount of solvent molecules available for the solvation of ions is limited, the energies $H_{Me^{\cdot}}$ and H_x' decrease and consequently the observed E. M. F. is much smaller than that expected from the mere ionic concentration relationship[1]. This is usually ascribed to the increase of ionic activities in most concentrated solutions. Using for the activity coefficient the symbol *f*, we can write the potential of a reversible electrode as:

$$\pi = K + \frac{RT}{F} \log c.\, f.$$

and comparing this with formula (2), which can be written as

$$\pi = K + \frac{RT}{F} \log c.\, \alpha.\, e^{-\frac{H.F}{RT}}$$

we derive *for the activity coefficient*

$$f = \alpha.\, e^{-\frac{H.F}{RT}}$$

where α denotes the dissociation degree. To see to what extent the energy of solvation varies with the vapour pressure of the solution let us return to the originally derived formula (1) (in the previous communication) writing

$$\frac{RT}{F} \log K_{sol}.\, P^{n}_{sol}$$

as free energy of ionic solvation. Here K_{sol} denotes the equilibrium constant of the process $Me^{\cdot} + n$ solvent mol. $\longrightarrow Me^{\cdot}_{sol}$

Then we obtain

$$\pi = K + \frac{RT}{F} \log c - \frac{RT}{F} \log K_{sol}.\, P^{n}_{sol}$$

Let us now substitute from the Raoult's relation

$$\log \frac{p}{p'} = \frac{M}{\rho} \cdot \frac{C}{1000}$$

where *p* is the pressure of the pure solvent, p′ that of the solution, M the molecular weight of the solvent vapour, ρ the density and C the total concentration of particles per litre.

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[1] Noyes and Mac Innes: J. Am. Chem. Soc. 42, 239 (1920).

Substituting for P_{sol} ($=p'$) we obtain:

$$\pi = K' + \frac{RT}{F}[\log Me'_{sol}] + n.\frac{RT}{F}\cdot\frac{M}{\rho}\cdot\frac{C}{1000} - \frac{RT}{F}\log K_{sol}.$$

Let us now calculate the effect due to the free energy change of ionic hydration when concentrating a normal aqueous solution of a binary electrolyte to a three times normal, assuming that K_{sol} and n remain—within this concentration range—constant

$$\text{Then } \rho = 1,\ M = 18,\ \frac{RT}{F} = 0.025 \text{ volt},$$

$$C_1 = 2,\ C_2 = 6.$$

Considering that there is hardly more room round an ion than for six water molecules (the co-ordination number), we can take $n = 6$ and obtain then an activity increase of *ca.* 10 millivolts corresponding to a 1.5 times larger ionic activity than that in the normal concentration. This order of the activity increase is indeed observable (e. g. in the work of Noyes and McInnes). We cannot, however, make precise calculations in this respect before the problem of mutual ionic attraction is solved. According to Debye[1] this attraction should become considerable in most concentrated solutions and would work in the opposite way, lowering the activities.

For ethyl-alcoholic solutions, where $M = 46$ and $\rho = 0.78$ the "activity" effect, which is due to solvation, should be about three times larger; as a matter of fact, the great anomalous increase of activity of sodium ions in most concentrated sodium ethoxide solutions, observed by M. Shikata[2] is more than three times that observable in aqueous solutions. Moreover, in iso-amyl alcohol ($M = 88$) recent measurements on sodium and potassium alcoholates carried out by M. Shikata and Z. Koutniková (hitherto unpublished) show again twice as large abnormal activity increases as in ethyl-alcohol of the same molarity.

Thus the incomplete hydration makes the ions more easily to be deposited at electrodes and this accounts for their increase in "activity"; the less completely solvated the ions are, the more numerous they appear to be when calculating their concentration from the simple Nernst formula. However, the electrolytic potential depends not only on the quantity of ions, but also on their quality, i. e., upon their degree of solvation. Electrochemically inactive electrolytes or non-electrolytes when present in large concentrations influence the electrode potentials, making them more positive,[3] no doubt since the degree of solvation of the electrode-ions is reduced.

The catalytic activity of ions must, of course, be parallel to their electrochemical activities, because a less firmly solvated ion is desolvated more easily, when entering the molecule, with which it makes an intermediate

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[1] Physik. Z. **24**, 191 (1923).

[2] Trans. Faraday Soc. "Electrode Reactions and Equilibria." **19**, p. 721 (1924).

[3] G. Scatchard: J. Am. Chem. Soc. **45**, 1716 (1923); W. A. Arkadjev: Z. physik. Chem. **104**, 192 (1923); J. Irzeborowski: **107**, 270 (1923); G. Poma: **107**, 329 (1923).

compound. The well-known catalytic neutral salt action is thus easily interpreted, explaining the activity increase of the acid as due to the dehydrating influence of the neutral salts on the hydrions.[1]

In the same way the decrease in solubility of nonelectrolytes caused by salt additions can be understood, since the large desolvating power of the latter deprives the dissolved nonelectrolyte molecules of their hydrate-water necessary to keep them in solution.

It might be pointed out, that the size of the solvated ion (which includes a large number of more or less firmly bound solvent molecules) has little to do with the energy of solvation, i. e., with the intensity with which especially the first layer of molecules sticks to the ion. The smallest of ions, the hydrion, which according to Fajans and Born should exhibit the greatest energy of solvation, might keep its little first shell of solvent molecules extremely firmly and yet be in size the smallest of all ions, with the greatest velocity of migration.

Thus the transference phenomena influenced by the size of solvated ions cannot interfer with this idea of solvation energies.

Summary

It is shown, that the electrode potential depends not only on the number of ions in solution, but also on their degree of solvation and therefore on the vapour pressure of solution.

This view allows to express the "activity coefficient" by means of the free energy of solvation and is shown to be in accordance with experimental facts.

The Charles University,
Prague

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[1] F. O. Rice: J. Am. Chem. Soc. **45**, 2808 (1923); N. Bjerrum: Z. physik. Chem. **108**, 97 (1924).

THE SECOND "ISOELECTRIC POINT" OF GELATIN.

ELMER O. KRAEMER*

The recent observations of discontinuities in the swelling[1], light absorption[2], and gel strength[3] of gelatin-containing systems at a pH approximately 7.8 have raised a number of interesting questions concerning the colloid-chemical behavior of gelatin in particular and of proteins in general. The principal attempts to explain this behavior are due to Wilson and Kern. They say in their paper on "The Two Forms of Gelatin"[4], that "the discovery of two points of minimum . . . for the swelling of gelatin, although unexpected, actually correlates and explains a number of puzzling data in the literature. Experiments upon mutarotation of gelatin led Smith[5] to suggest that gelatin exists in two forms, a sol form stable at temperatures above 35°, and a gel form . . . stable under 15°, a condition of equilibrium existing between the two forms at intermediate temperatures. The terms gel form and sol form, as used in this paper, merely indicate the form of gelatin which is capable of setting to a jelly, and the form which is not. . . . Loeb[6] has shown that the isoelectric point of the gel form of gelatin lies at pH = 4.7. . . . The work of Davis and Oakes[7] (on viscosities of 1% gelatin solutions at 40° at different concentrations of hydrogen ion) indicates an isoelectric point for the sol form of gelatin at about pH 8. . . . Lloyd[8] found that gelatin in alkaline solution changes from the gel to sol form. . . . Lloyd suggested that gelatin changes from a keto form to an enol form in alkaline solution. . . . When HCl was added to gelatin dissolved in hot solution of NaOH until Sörensen value . . . was reduced to 4.7 and the solution then cooled, it set to a firm jelly, indicating that the change is reversible. . . . The work of Smith and Lloyd suggests that the change from the gel to the sol form takes place both with rise of temperature and with rise of Sörenson value."

The hypothesis of Wilson and Kern may therefore be expressed in the form

$$\begin{matrix}\text{Sol form A}\\ \text{isoelectric point}\\ \text{about pH} = 7.8\end{matrix} \;\; \underset{\begin{matrix}\text{Temp.} > 40^\circ \text{ or}\\ \text{increasing pH}\end{matrix}}{\overset{\begin{matrix}\text{Temp.} < 15^\circ \text{ or}\\ \text{decreasing pH}\end{matrix}}{\rightleftarrows}} \;\; \begin{matrix}\text{Gel form B}\\ \text{isoelectric point}\\ \text{pH} = 4.7\end{matrix}$$

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*National Research Council Fellow in Chemistry.

[1] Wilson and Kern: J. Am. Chem. Soc., **44**, 2633 (1922), and more recently confirmed for de-ashed gelatin, ibid. **45**, 3139 (1923).

[2] Higley and Mathews: J. Am. Chem. Soc., **46**, 852 (1924).

[3] Sheppard and Sweet: Ind. Eng. Chem., **16**, 593 (1924).

[4] Wilson and Kern: loc. cit.

[5] Smith: J. Am. Chem. Soc., **41**, 135 (1919); J. Ind. Eng. Chem., **12**, 878 (1920).

[6] Loeb: "Proteins and the Theory of Colloidal Behavior" (1922).

[7] Davis and Oakes: J. Am. Chem. Soc., **44**, 464 (1922).

[8] Lloyd: Biochem. J., **14**, 147 (1920).

Reexamination of the argument of Wilson and Kern and the consideration of other experimental data show that the hypothesis is untenable in the absence of further data in its favor.

In view of the inability to establish the chemical individuality of any one form of gelatin, the assumption of a keto-enol rearrangement in explaining the so-called second isoelectric point of gelatin can be only speculative. Wilson[1] quotes incorrectly the experiments of Lloyd in favor of a gel→sol change upon changing the Sörensen value from 4.7 to 7.8. But according to the titration curve of Loeb[2] the quantity of NaOH used by Miss Lloyd to bring about the supposed transformation was *thirty-three times as great* as necessary to change the pH of the same volume of solution containing *ten times as much gelatin* from 4.7 to 7.8. It is therefore scarcely legitimate to claim that the observations of Lloyd referred to by Wilson have any special bearing upon the properties of gelatin sols at a pH 7.8.

Furthermore, the assumption that increase in pH causes a change from a *gel* form (supposed isoelectric point at pH 4.7) to a *sol* form (supposed isoelectric point at pH 7.8) is inconsistent with the observation by Sheppard and Sweet[3] of a *maximum gel strength* at a pH about 8.

Northrop[4] found that the velocity of hydrolysis of gelatin at 40° is practically constant over the range pH 3.5 to 8.5.

There thus appears to be no substantial independent evidence that alkali causes any such deep-seated changes in gelatin at such a low OH′ concentration as that existing at the assumed second isoelectric point (one millionth normal OH′). The assumption of Wilson and Kern of an equilibrium between a sol form and a gel form of gelatin (with isoelectric points at pH 7.8 and 4.7 respectively) which is displaced by changes in pH is inconsistent with experimental data, and therefore can not be accepted.

Likewise the influence of temperature[5] upon the behavior of gelatin sols and gels has not been explained successfully by Wilson and Kern upon the basis of the postulated equilibrium between two forms of gelatin with different isoelectric points.

In the first place, the swelling experiments of Wilson and Kern were made at 7° (for 4 days) under which conditions, according to Smith and Davis and Oakes, the transformation to the gel form B is supposed to be complete. And yet minima were observed at both pH 4.7 and 7.8. In the second place, the discontinuity at a pH of 4.7 in the relationship between pH and the interfacial

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[1] Wilson: "The Chemistry of Leather Manufacture", p. 110. Instead of two grams of gelatin, Lloyd used only 0.2 grams, according to the paper in Biochem. J.

[2] Loeb: "Proteins and the Theory of Colloidal Behavior", p. 62, (1922).

[3] Sheppard and Sweet: Ind. Eng. Chem., **16**, 593 (1924).

[4] Northrop: J. Gen. Physiol., **3**, 715 (1920).

[5] Since this paper was written there has appeared in J. Gen. Physiol., **6**, 457 (1924) a paper on the "Isoelectric Point of Gelatin at 40°C", in which David Hitchcock criticises the theory of Wilson and Kern. Hitchcock shows that the minimum in the osmotic pressure of one per cent gelatin solutions at a pH of 4.7 persists at 40°C. Furthermore, at a pH 7.7–8.0, an inflection point was found in the curve showing the relationship between osmotic pressure and pH at 40°C.

tension of gelatin sols against toluene at 40° C and 50°C (after 6 hours)[1] is contrary to the assumption of Wilson and Kern that above 40°C, the *gel* form (with isoelectric point at pH 4.7) is transformed to a *sol* form (with isoelectric point at pH 7.8). According to the work of Smith and Davis and Oakes, their hypothetical gelation B should be absent under the conditions of the experiments of Sheppard and Sweet.

The assumption of two forms of gelatin with different isoelectric points and in equilibrium with each other is also inconsistent with the present state of knowledge concerning the cataphoretic behavior of gelatin. Thus if in a gelatin system at a pH between 4.7 and 7.8, there exists a mixture of two dependent or independent compounds with different isoelectric points, one should expect to find one pH at which the opposite charges of the two substances exactly neutralize each other, causing a zero cataphoresis. Such has not thus far been observed. Or if neutralization does not take place and if the two compounds with different isoelectric points can migrate independently in an electric field, there must be at a pH 4.7 a pronounced cataphoresis of the form with the 7.8 isoelectric point. This behavior likewise has not been observed.

In other words, there is insufficient reason for supposing that the hypothetical gelatins A and B (of Smith and Davis and Oakes) are in any direct way related to the discontinuities in the physical properties of gelatin systems at pH's 4.7 and 7.8, or to the "isoelectric points" of Wilson and Kern. Furthermore, there appears to be at the present time no foundation in fact for the assumption of an equilibrium between two forms of gelatin (with different isoelectric points) dependent upon both pH and temperature.

The question next arises as to the possibility of some other useful hypothesis. A point of view which may prove useful in elucidating the nature of the so-called second isoelectric point is that furnished by the "irregular series" and the phenomenon of the reversal of charge of colloid particles and surfaces. In illustration[2], if to a positive ferric oxide sol are added increasing amounts of NaOH, the positive charge (on the basis of mobility in an electric field) is first decreased to an "isoelectric point", changed in sign, rising to a maximum negative value, and again decreased to a second "isoelectric point". As a result, there are two regions of stability and two regions of instability (at the two "isoelectric points"). Similar effects have been studied for the case of oil drops, sols of gold and silver, glass surfaces, etc., in contact with various solutions. The effect is ordinarily explained upon the basis of what may be called selective ionic adsorption to form at the surface in question a Gouy double layer, and therefore an electrokinetic difference of potential. The magnitude and sign of the potential difference is presumably dependent upon

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[1] Sheppard and Sweet: J. Am. Chem. Soc., **44**, 2797 (1922).

[2] Kruyt and van der Spek: Kolloid-Z., **25**, 17 (1919). Another excellent example is given in a paper, which appeared after this paper was written, by Winslow and Shaughnessy: J. Gen. Physiol., **6**, 697 (1924). It was found on the basis of actual cataphoresis experiments that suspensions of Bact. coli and B. cereus possess two "isoelectric points", one at a pH about 3., and the other at a pH about 13.5. Between pH's 3 and 13.5, the organisms carry a negative charge, while below and above these pH's respectively, the charge is positive.

the total ionic environment of the surface[1]. That such electrokinetic phenomena occur in protein sols is shown by the recent work of Loeb[2]. Reasoning by analogy, the second "isoelectric point" of gelatin[3] at a pH 7.8 should be due to a neutralization of the electrokinetic potential difference, with a reversal in sign at a pH greater than 7.8. The discontinuity in swelling and other physical properties at this point would therefore reflect the influence of the electrokinetic potential upon these properties. Unfortunately, the cataphoresis studies of Loeb mentioned above are insufficient to confirm or deny the possibility of this suggestion. The question must therefore remain open until more experimental data are available.

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University of Wisconsin.

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[1] For a detailed discussion, consult Freundlich: "Kapillarchemie", 3rd edition, 325 ff., 572 ff. (1924).

[2] J. Gen. Physiol., **5**, 505 (1923), **6**, 307 (1924).

[3] The author does not desire to discuss the possible nature of the isoelectric point at PH 4.7.

Note added at Time of Reading Proof

In a very recent paper by W. R. Atkin and G. W. Douglas: (J. Am. Leather Chemists Assoc., **19**, 528 (1924)) a carefully determined titration curve of gelatin has been published. This curve, showing a point of inflection at a pH of 7.7, is a further example of the influence upon the properties of gelatin systems of some important change in the system at this pH.

THE REACTION BETWEEN POTASSIUM PERSULPHATE AND POTASSIUM IODIDE IN GELATIN SOLS*

BY SIDNEY OWEN RAWLING AND JOHN WILLIAM GLASSETT.

In aqueous solutions, persulphates and iodides react according to the equation

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$$

The reaction is comparatively slow and its velocity under various conditions has been investigated quantitatively by Slater Price[1]. Friend and Vallance[2] record that with N/16 solutions of potassium iodide and ammonium persulphate no change of reaction velocity is caused by the addition of gelatin up to a concentration amounting to 0.1 per cent. The method adopted by Price was to titrate the iodine set free from the reaction mixture after various intervals of time. This when used for a system containing gelatin does not give a true record of the main reaction because the iodine liberated is slowly removed by the gelatin. In spite of this, it has been shown by the experiments which will now be described that the initial rate at which the iodine is liberated is greater in the presence of gelatin than in pure aqueous solutions. This rate diminishes quickly and the general type of curve representing the velocity of liberation of iodine is shown in Fig. 1, in which the volume of this sulphate solution (N/100) required by 25 cc of the reaction mixture is plotted against time.

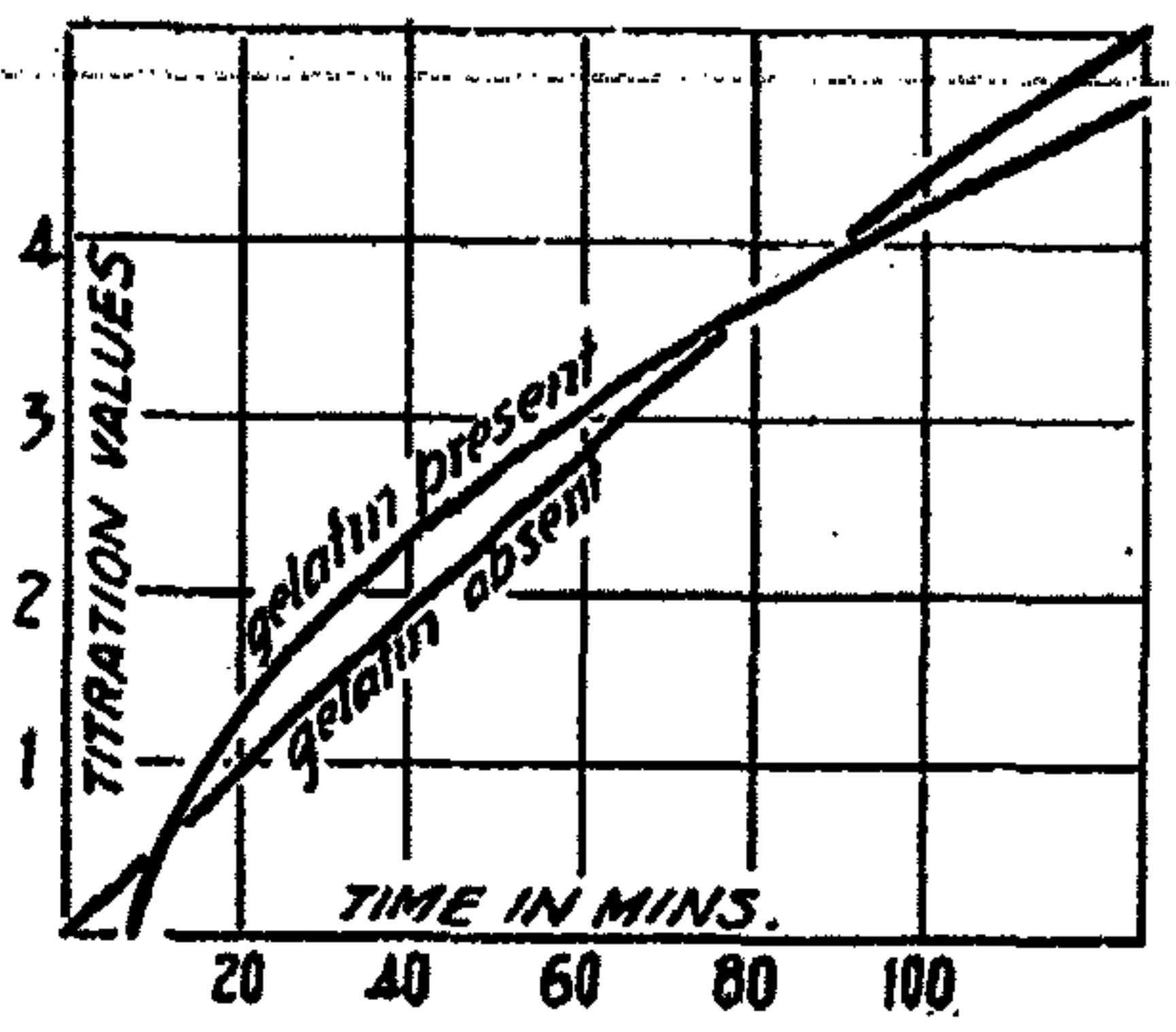

FIG. 1

Experimental

Gelatin sols were made up by dispersing 5 grams of gelatin in 250 ccs. of distilled water. In carrying out the experiments the sol to be tested was brought to 25° and 100 ccs. of it were mixed with 50 ccs. of a solution of potassium iodide (N/20) at 25°. At a noted time 50 ccs. of potassium persulphate solution (N/20) were quickly added. 25 ccs. of the mixture were withdrawn from time to time and titrated—in a large volume of cold water—with a solution of sodium thiosulphate N/100. In preliminary experiments it was found that the addition of acid caused a very marked increase in the apparent rate of

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*Communication No. 38 from the British Photographic Research Association Laboratories.

[1] J. Chem. Soc. 121, 473 (1922).

[2] Z. physik. Chem. 27, 474-512 (1898).

reaction, though Price found (*loc. cit.*, 490) that in the absence of catalysers, acids have very little effect. On account of this the experiment was repeated several times with sols containing varying amounts of acid. This was done with two kinds of gelatin and for one of these both hydrochloric and sulphuric acids were tried. The results of the experiments are recorded in Table I as titration values after allowing the reaction to run for 40 minutes.

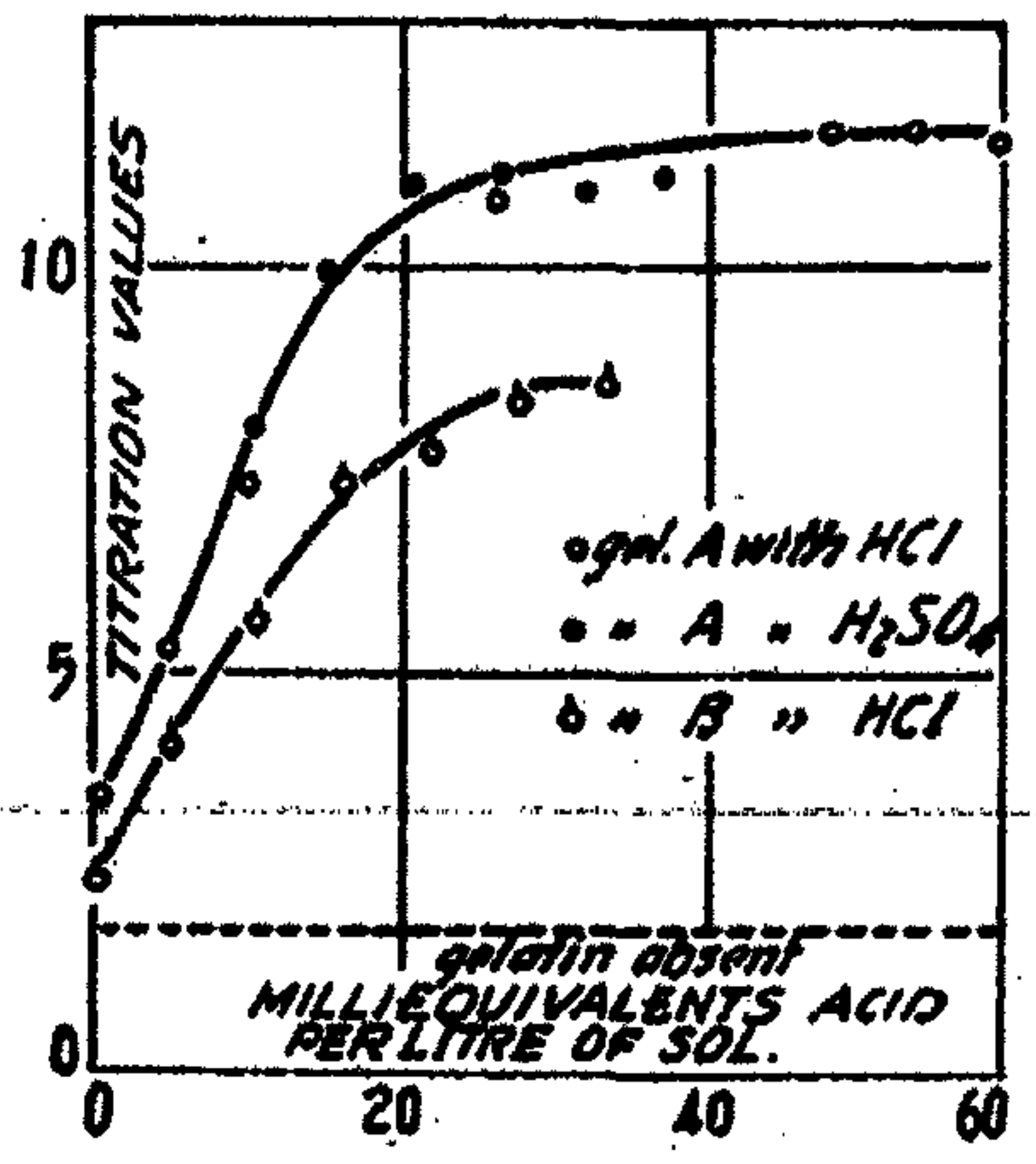

FIG. 2

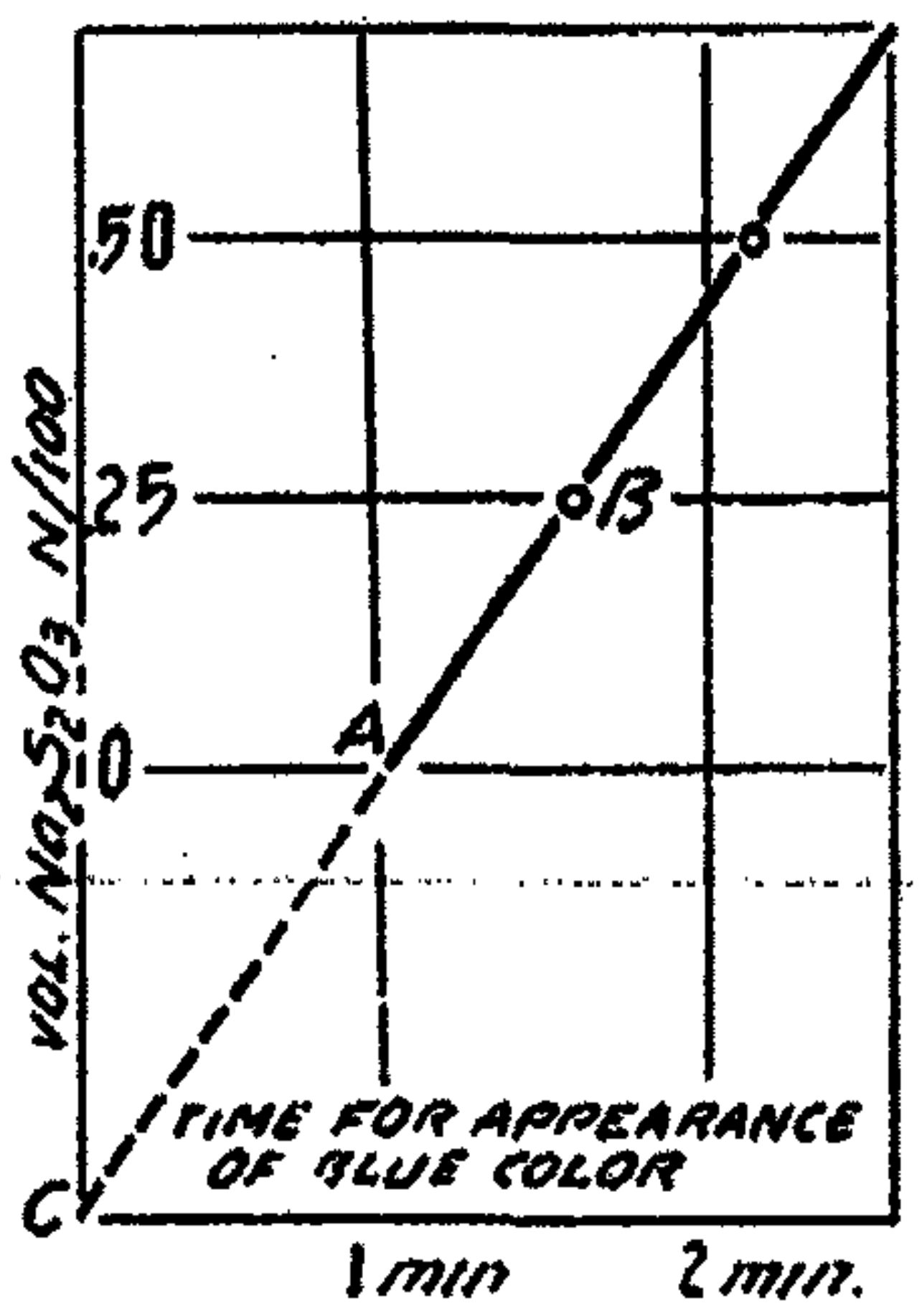

FIG. 3

TABLE I

Gelatin A.	Hydrochloric Acid.		25°
Acid present per litre of sol.	Titration value for 25 ccs. mixture.	Acid present per litre of sol.	Titration value per 25 ccs. mixture.
milli. eqts.	ccs.	milli. eqts.	ccs.
0.0	3.45	47.7	11.65
5.3	5.2	53.0	11.70
10.6	7.25	58.2	11.50
26.5	10.8		
Gelatin A.	Sulphuric Acid.		
10.7	8.0	31.8	10.9
15.9	9.9	37.2	11.1
21.3	11.0		
26.8	11.1		
Gelatin B.	Hydrochloric Acid.		
0.0	2.3	22.4	7.7
5.6	4.0	28.0	8.3
11.2	5.6	33.6	8.5
16.8	7.3		

These results are plotted in Fig. 2.

It will be noted that in Fig. 1 the curve representing the reaction in presence of gelatin does not pass through the origin. This was thought to be due to the presence of substances in the gelatin which react almost instantaneously with iodine and so cause an apparent induction period. In order to examine more closely the course of the reaction during the first few minutes the following method was devised: into a Nessler glass held in the thermostat were placed 20 ccs. of the 2 per cent gelatin sol to be tested; to this were added 10 ccs. of potassium iodide solution (N/20) and 1 cc of starch solution. The mixture was well stirred and then 10 ccs. of the persulphate solution N/20 were quickly added. The time required for the blue colour of iodo-starch to appear was noted. The procedure was repeated, but with the addition of 0.25 cc. of thiosulphate solution (N/100) and again with 0 50 cc. of thiosulphate. By plotting the volume of thiosulphate against the time for the blue colour to occur a straight line was obtained as shown in Fig. 3. In examining a great number of commercial and other samples of gelatin it was found that only in a few cases did the line pass through the origin, and that as a rule the gelatins which gave this result had been treated so as to remove the inorganic or "ash" constituents. Most of the gelatins contained sulphite and it was at first thought that the length of the intercept OC on the thiosulphate axis would give a measure of the sulphite content. Analysis showed however that this was not the case, but that the amount of sulphite present was greater than that indicated by the length of OC.

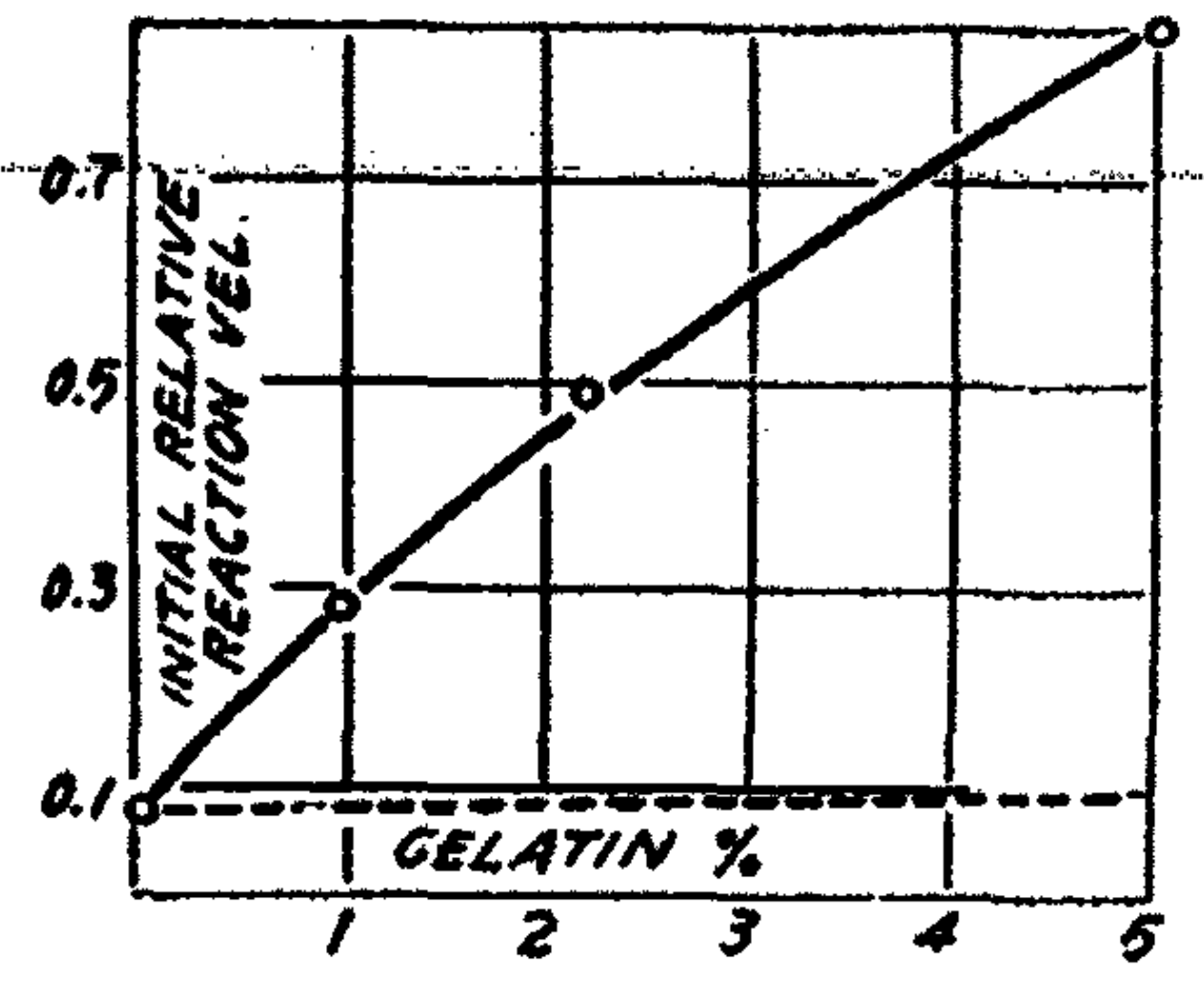

FIG. 4

This method was, however, used for a few further experiments. As may be seen from Fig. 3 the slope of the line AB really indicates the initial rate of liberation of iodine since it gives the amount of iodine liberated per minute from 40 ccs. of the reaction mixture. In this way it was found that the increase in initial rate of liberation of iodine is almost proportional to the concentration of gelatin up to about 3 per cent. This may be seen from Fig. 4 and Table II.

TABLE II

Gelatin A.

Concentration of gelatin per cent.	Apparent Relative Initial Reaction Velocity. Given by slope of line A B.
5.0	0.85
2.2	0.49
1.0	0.28
0.83	0.22
0.00 (water)	0.08

According to Davies and Oakes[1], C. R. Smith[2], and others, there is no tendency to gel formation in gelatin sols at about 40°. It was found, however, that at 39° the rate of reaction with gelatin present to the extent of 1 per cent increased the rate of reaction about 4 or 5 times at this temperature, so that the presence of the gel form is not responsible for the accelerating effect. It was also shown repeatedly that the velocity of reaction measured in a sol which had been freshly cooled to 25° was the same as that in a sol which had been allowed to stand for two hours at this temperature. Thus the accelerating effect seems to be independent of the age of the sol.

Discussion

The effect of the presence of gelatin upon the salt reaction here described may be considered in relation to four factors: (1) the reaction between the iodine liberated, and the gelatin, (2) the influence of catalysts present as impurities in the gelatin (3) the formation of gelatin salts of persulphuric and hydriodic acids and (4) the adsorption of the reacting ions by gelatin.

(1) The first factor causes the apparent velocity curve Fig. 1 as determined by the rate of liberation of iodine to be very different from what the real velocity curve would be. The actual amount of iodine measured at any time is never as great as it would be if there were no reaction between gelatin and iodine. A further complication occurs on this account if gelatin itself is the accelerator, for the actual amount of gelatin is diminished as more and more iodogelatin is formed.

(2) The accelerating effect might be ascribed to the presence of catalysers contained as impurities in the gelatin. The most likely impurities of this kind are to be looked for in the inorganic of "ash" content. Analysis showed that the ash in each case consisted of the following ingredients present in varying amounts:—

$$Fe_2O_3, CaO, MgO, Al_2O_3, Cl', SO''_4 \text{ and } PO'''_4$$

The one constituent of the ash which is known to produce acceleration of the reaction under consideration is iron. This was shown by Slater Price (*loc. cit.*) who also showed that the reaction velocity in pure aqueous solutions is almost independent of hydrion concentration unless iron or some other such catalyser be present. It seemed therefore that a possible explanation of the phenomena described here could be found by taking the iron content of the gelatins into consideration. The B gelatin was a powdered sample and contained 0.013 per cent of iron, which is present to some extent as finely divided particles of metal. The addition of acid would cause this to dissolve and so to become active. The iron content of the A gelatin was only 0.0023 per cent. Thus the reaction mixture in the case of the B gelatin would contain 0.000023 gram atoms of iron per litre. Whilst in the case of the A gelatin the concentration would be 0.000004 gram atoms of iron per litre.

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[1] J. Am. Chem. Soc. 41, 135—150 (1919).

[2] J. Am. Chem. Soc. 44, 464—479 (1922).

Slater Price found that with N/90 persulphate and N/40 iodide in N/200 sulphuric acid the acceleration due to a concentration of 0.000024 of iron was about 81 per cent. In the particular experiment described here the maximum reaction velocity attained with the B gelatin was about 400 per cent above that obtained without gelatin present. This indicated that the iron in the gelatin could not be responsible for the whole of the acceleration. This conclusion was confirmed when it was found that the A gelatin containing only one sixth as much iron as the B sample gave the higher maximum reaction velocity.

When the second experimental method described here was applied to gelatins which had been treated so as to remove almost all the inorganic constituents, it was found that the accelerating effect was still present, in fact one such gelatin, kindly supplied by Dr. Mees and Sheppard of the Kodak laboratories, containing only 0.035 per cent of ash gave one of the highest values for initial reaction velocity yet recorded for any of the samples of gelatin examined. From these results it was concluded that if the acceleration is due to catalysts present as impurities, these impurities are of an organic nature and must be present in all gelatins, for none of the twenty or thirty samples of gelatin examined failed to give the effect.

(3) As already pointed out the velocity of reaction in the asbence of gelatin is almost independent of the hydrion concentration and since the considerable effect of acids cannot readily be explained as being due to iron, etc., it seemed that the modern theories of colloidal behavior of gelatin might provide an explanation. From the work of C. R. Smith[1], Davies and Oakes[2], and Bogue[3], it seems that at 40° a gelatin sol is far simpler than at temperature below 30°. J. Loeb[4] puts forward a theory of the conditions prevailing in protein sols. He supposes that "although gelatin solutions may be, and probably are, as a rule true solutions, consisting of isolated protein ions and molecules distributed equally through the water, they contain under certain conditions submicroscopic, solid particles of gelatin." The solid particles referred to are presumably formed in the neighbourhood of the "transition temperature" of Davies and Oakes (*loc. cit.*), and have the properties of small particles of jelly. They must therefore be subject to the laws of membrane equilibria enunciated by Donnan, and applied by Procter[5] to the explanation of the swelling of gelatin jellies when surrounded by aqueous solutions of acids.

If we accept Loeb's theory we must consider a gelatin sol at 25° as consisting of two phases: the continuous phase being a solution of gelatin ions and molecules, and the disperse phase being particles of jelly. In an acid sol there will be a distribution of hydrogen ions and the acid anions between the two phases which may be expressed by the equation

$$x_1 y_1 = x_2 y_2$$

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[1] J. Am. Chem. Soc. **41**, 135–150 (1919).

[2] J. Am. Chem. Soc. **44**, 464–479 (1922).

[3] J. Am. Chem. Soc. **44**, 1313–1322 (1922).

[4] "Proteins and the Theory of Colloidal Behaviour" (1922).

[5] J. Chem. Soc. **105**, 313 (1914).

where x_1 is the concentration of hydrogen ions in the continuous phase, y_1 is the concentration of acid anions in the continuous phase, x_2 and y_2 are the corresponding concentrations in the jelly phase. Loeb (*op. cit.* Chapter 12) found that when hydrochloric acid is added to a sol of gelatin at 25° the viscosity increases. This was explained as being due to an increase in concentration of diffusible ions within the jelly particles over that in the continuous phase resulting in the swelling of the particles. The hydrion concentration itself is higher in the continuous phase so that the effect is mainly due to an increase of chloride ion concentration in the disperse phase. According to this idea, in the case of the reaction mixture of persulphate and iodide in acid gelatin sols there is a higher concentration of persulphate and iodide ions in the jelly phase which would result in an increase in the reaction velocity in that phase, and a diminution of velocity in the continuous phase. The reaction velocity actually measured would then lie between the velocities in the two phases and would depend upon the difference between the concentration of the reacting ions in the two phases and upon the relative volume occupied by the disperse phase.

Suppose now that a gelatin sol containing persulphate and iodide may be considered as corresponding with the two-phased system discussed. According to Loeb there is no chemical combination between gelatin and acid radicles in this condition and thus according to this theory we should expect no catalytic action at the isoelectric point. Experiment showed however that even at the isoelectric point there is still a fairly marked effect and the addition of alkali appears to make this less. Work with alkali is rendered difficult, however, owing to the reaction between iodine and free alkalies.

It may further be noted that the maximum concentration of diffusible ions within the jelly phase occurs—according to Loeb's experiments on viscosity—at a Sörensen value of 3.0. We should therefore expect a maximum reaction velocity to occur about pH 3.0 and that further addition of acid would cause a decreased velocity. The experiments showed however that although the maximum acceleration occurred about pH 2.8, further addition of acid did not produce any diminution in the effect.

Thus the theory of colloidal behaviour of gelatin as developed by Loeb cannot explain all the facts, and this is emphasized by the observations that gelatins giving practically isoelectric sols exert a considerable accelerating effect, and that above the temperature of gel formation the effect still occurs.

(4) From what has been said already we are left to consider the possibility of adsorption of the reacting ions on the surface micelles of gelatin. These simpler particles may be supposed to exist at temperatures at which the gel form cannot exist. By assuming adsorption of the ions upon these the accelerating effect of gelatin at 39° may be explained.

It may be pointed out that much work has been done concerning the laws governing the combination of acids with gelatin in which the amount of acid combined has been calculated from the difference between the hydrogen ion concentration in an aqueous solution of the acid that and in a corresponding solution of the acid containing a definite quantity of gelatin. These measurements when made at temperatures at which the gel form exists may be erroneous since they do not take into account the different hydrogen ion concentrations in the different phases of the sol, nor do they consider a higher concentration—or perhaps a different chemical condition of gelatin—in the gel particles from that which exists in the surrounding liquid, a state of affairs which must necessarily exist if membrane equilibria are to exert any influence at all. Indeed, for quantitative purposes it seems as if the expression "hydrogen ion concentration of a gelatin sol" has little meaning except at temperatures at which the gelatin is entirely in the sol form or the gel form, for in other cases the pH value must be different in the different phases.

Luther[1] describes a method for finding the copper ion concentration in dilute solutions. This depends on the observation of reaction velocity between persulphate and thiosulphate and iodide in the presence of iron and copper salts as catalysts. It may be pointed out that the presence of gelatin would interfere with this method.

Summary

The reaction in solution between iodides and persulphates is accelerated by the presence of gelatin. The acceleration is increased up to a maximum by the addition of acids. Alkalies reduce the effect. Even with sols at the isoelectric point considerable acceleration occurs. The presence of the "gel" form of gelatin is not necessary for the effect to occur since the same phenomena may be observed above the so-called "transition temperature" of gelatin. The presence of inorganic catalysts such as iron have been shown not to be the cause of the acceleration, nor does Loeb's theory offer a satisfactory explanation of the facts. The effect may be due either to an organic catalyst in the gelatin or to adsorption of the reacting ions on gelatin particles which are different from the "submicroscopic particles of jelly" postulated by Loeb.

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[1] Trans. Faraday Soc. 19, 394 (1923).

A STUDY OF ADSORPTION PHENOMENA IN THE VICINITY OF THE CRITICAL TEMPERATURE[1]

BY W. A. PATRICK, W. C. PRESTON, AND A. E. OWENS

The present investigation is a continuation of the study of the adsorption of gases by silica gel that has been in progress in this laboratory for some years.[2] The results of such studies have led to the adoption of the idea that the forces involved are largely capillary in nature and can be expressed by the empiric relationship $V = K\left(\frac{P\sigma}{P_o}\right)^{1/n}$ in the case of adsorption from the gaseous state,—where V is the volume of liquefied gas adsorbed per gram gel, P is the equilibrium pressure, P_o the ordinary saturation pressure at the temperature, σ the surface tension of the liquefied gas, and K and $1/n$ constants dependent entirely upon the structure of the gel. It will be noticed that the equation, unlike the ordinary empiric equation of Freundlich, is applicable in any temperature; and it has been shown that, for the same gel samples, the constants K and $1/n$ are the same for all temperatures. In fact, as shown by Patrick and Long,[3] these constants vary very slightly for the adsorption of different substances (SO_2, NH_3, butane, etc.), and furthermore they retain practically the same values for gels of very different water content. The slight variation for different substances is due, as will be shown later, to the great difficulty in preparing gel samples of similar structure.

Since the above view involves condensation of a gas to the liquid state, it becomes of interest to study the case of adsorption in the neighborhood of temperatures at which, under ordinary conditions, no condensation could occur;—that is, near the critical temperature. Inasmuch as adsorption does occur even above the critical temperature, it is obvious that the capillary theory of adsorption must undergo modification in order to account for such results. By this statement we do not mean to imply that all cases of adsorption are due to capillary forces, but rather that it is possible to extend the temperature range of capillary adsorption above the critical temperature in certain cases. The purpose of the following investigation is, therefore, to modify the present theory of capillary adsorption so as to extend its range above the critical temperature.

Of the gases previously studied, sulfur dioxide has a critical temperature of 157.2°, ammonia of 132.3° and butane of 153.2°,—all temperatures so high as to render difficult a study of adsorption in their vicinity. Carbon dioxide and

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

[2] Patrick and McGavack: J. Am. Chem. Soc., 42, 946 (1920); Patrick and Davidheiser, 44, 1 (1922); Patrick and Long: J. Phys. Chem. 29, 336 (1925); L. H. Opdycke: Dissertation John Hopkins University (1922); Patrick and Jones: J. Phys. Chem. 29, 1 (1925); Patrick and Eberman: J. Phys. Chem. 29, 220 (1925).

[3] Loc. cit.

nitrous oxide, however, with critical temperatures of 31.1° and 38.8° C respectively, seemed ideal for this study, inasmuch as they are both easily obtained, stable, not excessively soluble in water and possess physical constants which have been well worked out.

Materials and Procedure

Great care was exercised to obtain samples of gel as pure and uniform as possible. Sodium silicate from Muth Bros. & Co. was mixed with C. P. hydrochloric acid from the J. T. Baker Chemical Co. according to the method described by Patrick and McGavack.[1] The sol set to a gel within a few hours and in the gel form was washed continuously for about two weeks, using running tap water. No trace of electrolyte could be found in the wash-water at the end of this time—or for many days before the washing was discontinued. The thoroughly washed gel was air-dried on a frame for eleven days, and then refluxed with aqua regia for fifteen hours. It was then washed by decantation with distilled water for ten days changing the water three times a day, the water appearing pure when tested again for the chloride ion. After drying in air, it was subjected to drying in an electric furnace in a current of air dried by P_2O_5, the temperature being raised but slowly. After thirty-five hours at a maximum temperature of 400° C., the gel was ground in a mortar and only that portion used which passed thru a #10 mesh sieve and not thru a #30 mesh. It was then reheated for twelve hours at 550°, after which time duplicate analyses showed a water content of 3.63% and 3.64%. The sample of this water content was designated Gel A_1. Gel A_2 was heated for two weeks longer at a temperature of 700° to 750°, and subsequent analysis, after treatment in the adsorption apparatus, showed a much lower water content—1.28%. Another sample of gel, (A_3), to be used in the case of nitrous oxide, was prepared having a water content of 1.38%. An analysis of Gel A_1 was also made for acid content by heating the gel in a hard glass tube over Bunsen burners to the softening point of the glass, while drawing over the gel a slow current of air, which was then bubbled through two wash-bottles containing standardized NaOH. Titration then showed that no acid had been driven off, and the gel was therefore considered acid-free.

The CO_2 was generated as needed in a Kipp generator which was rendered as nearly air-free as possible. The marble used was completely covered with water and boiled for one hour, then rapidly introduced into the generator and the latter filled with a solution of one part C. P. HCl and two parts of distilled water. A small amount of cupric chloride was added to prevent the evolution of H_2S from any pyrite in the marble. The gas generated was then passed through water to remove acid fumes, through a mercury trap, and then through drying tubes of $CaCl_2$ and P_2O_5.

The nitrous oxide used was that of commerce, and contained nitrogen as an impurity. This was greatly eliminated by allowing large quantities of gas to escape from the cylinder. The gas was finally passed through tubes containing P_2O_5 before introduction into the adsorption apparatus.

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[1] Loc. cit.

The method of making a run has been fully described by previous workers in this field,[1] and their procedure has been largely followed in this investigation. Due to the small solubility of both carbon dioxide and nitrous oxide in water[2] (unlike the case of ammonia) it was unnecessary to take into account the small amount of gas which dissolved in the gel water.

Experimental Results

A number of preliminary runs were made at 30° with carbon dioxide both with Gel A_1 and with Gel A_2 without success. Smooth adsorption curves were obtained, but the curves did not coincide, although all lay very close together. The smoothness of the curves, their regularity and similarity seemed to indicate that the experimental technique was not at fault, and that the failure to check was due to non-uniformity of the gel samples used, despite the uniformity of the treatment to which they had all been subjected. A close examination of Gel A_2 bore out this view. Most of the gel particles appeared perfectly clear, like glass, but an occasional particle could be seen which was opaque, like china. This might well be explained when we consider the drying of the gel in the electric furnace, where the gel was contained in a quartz tube of nearly one inch diameter. Under a current of air it is readily conceivable that the temperature of the gel near one end might not be the same as that at the center where the thermocouple junction was placed, or near the other end; and also, the gel along the central axis would not be so hot as that actually touching the heated walls of the quartz tube. This latter condition we take to be the chief cause of the non-homogeneity of the gel samples, for high temperatures always cause transparent silica gel granules to become opaque.

To avoid this trouble it was decided to use the same sample throughout the investigation, rather than to change it for each run. In this way we know that we have an absolutely definite adsorbent, and so avoid the uncertainty which often beclouds adsorption experiments. After the adoption of this method no difficulty was experienced in making almost perfect duplicate runs, the points obtained in two different runs at the same temperature lying on a single smooth curve with only very few and negligible deviations.

The experimental results of the adsorption experiments at 0°, 20°, 30° and 40° are given in Tables I and II. The value of the water content of the gel in each case is that which actually existed after the heating and evacuating in the adsorption bulb previous to making an adsorption run. The analyses were carried out by noting the loss of weight of the gel samples after blasting in a platinum crucible. X/M represents the volume of gas in cubic centimeters (reduced to standard conditions) adsorbed per gram gel, and P the equilibrium pressure in millimeters of mercury.

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[1] Patrick and McGavack: loc. cit.

[2] Patrick and Davidheiser: loc. cit.

Discussion of Results

The results given in Tables I and II are represented graphically in Figs. 1 and 2, which show the applicability of the Freundlich equation $\frac{X}{M} = aP^{1/n}$. It will be noted, however, that these curves differ from the parabolic curves usually obtained, in that these approximate straight lines. In Fig. 3, where log X/M is plotted against log P, straight lines result. Here, it is important to note that 1/n, which expresses the slope of the curves, is practically the same for all four temperatures in the case of each gas; while K (or *a* in the Freundlich equation), as indicated by the intercepts on the log X/M axis, increases as the temperature falls.

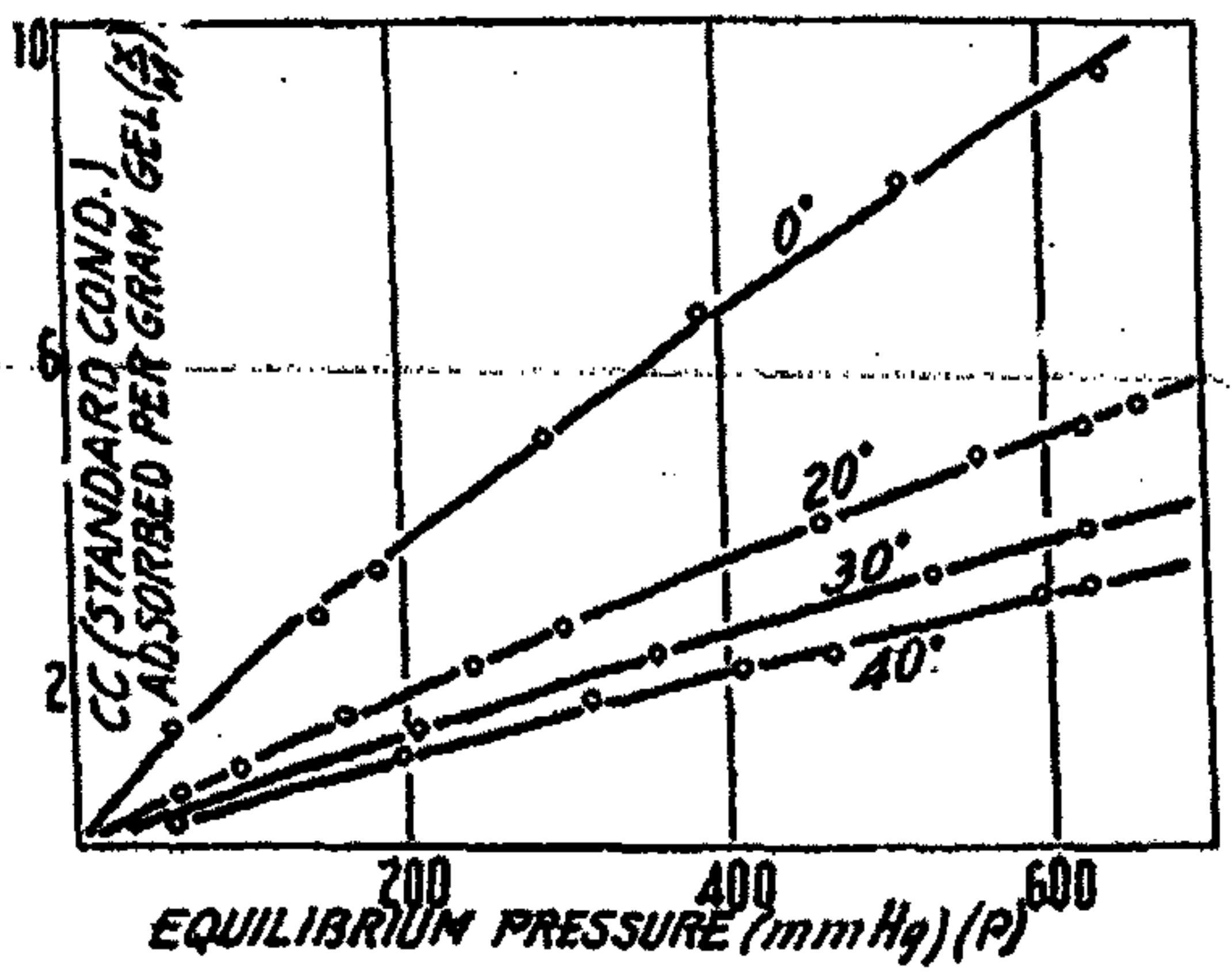

FIG. 1
Adsorption of CO_2 by Silica Gel

In order to apply our ideas of capillary effects, it is necessary to test out the above results according to the equation $V = K\left(\frac{P\sigma}{P_o}\right)^{1/n}$ the terms of which have already been defined.

In the case of carbon dioxide, V and σ are found as follows. Lord Rayleigh's (Landolt-Börnstein) value of the density of gaseous CO_2 (1.9652 g. per litre at 0° & 760 mm.) and Amagat's values for the density of liquid CO_2 are taken. Then $\frac{0.0019652\ X}{M}$ divided by Amagat's values of the density (D) of the liquid at various temperatures (Landolt-Börnstein's Tables) gives us V. P is the pressure measured, P_o is the saturation pressure taken from Regnault's values in Landolt-Börnstein, and σ is read from a curve based upon the data of Verschaffelt, also given in Landolt-Börnstein. From Verschaffelt's values of σ at —24.3°, 8.9°, 15.2°, and 20.9°, a curve is drawn, and the values of σ at 0° and 20° are read from this. This seems preferable to making use of such a relationship as that of Ramsay - Eötvös - Shields, since the temperature is so near the critical point. Even this graph becomes valueless at 30°, so no attempt was made to draw a curve at that temperature. At 40°, above the critical temperature, the equation, in its present form, obviously becomes inapplicable.

In the case of nitrous oxide, V was calculated from the density of the gas (.001966) given in Landolt-Börnstein, and from the dentisy of the liquified gas given by the equation of Andreff,[1] $S = .93684 - .0038647T + .0000022647T^2 - .0000003985T^3$. P_o, the saturation pressure at the temperature concerned, is taken from Regnault, and values of σ were calculated from the Ramsey-Eötvos-Shields equation, using the value of σ at -89.3° C ($= 26\frac{\text{dynes}}{\text{cm}}$) given by Grünmach,[2] and the density values of Andreff. Tables III and IV give the values of log V and log $\left(\frac{P\sigma}{P_o}\right)$ at different temperatures calculated as outlined

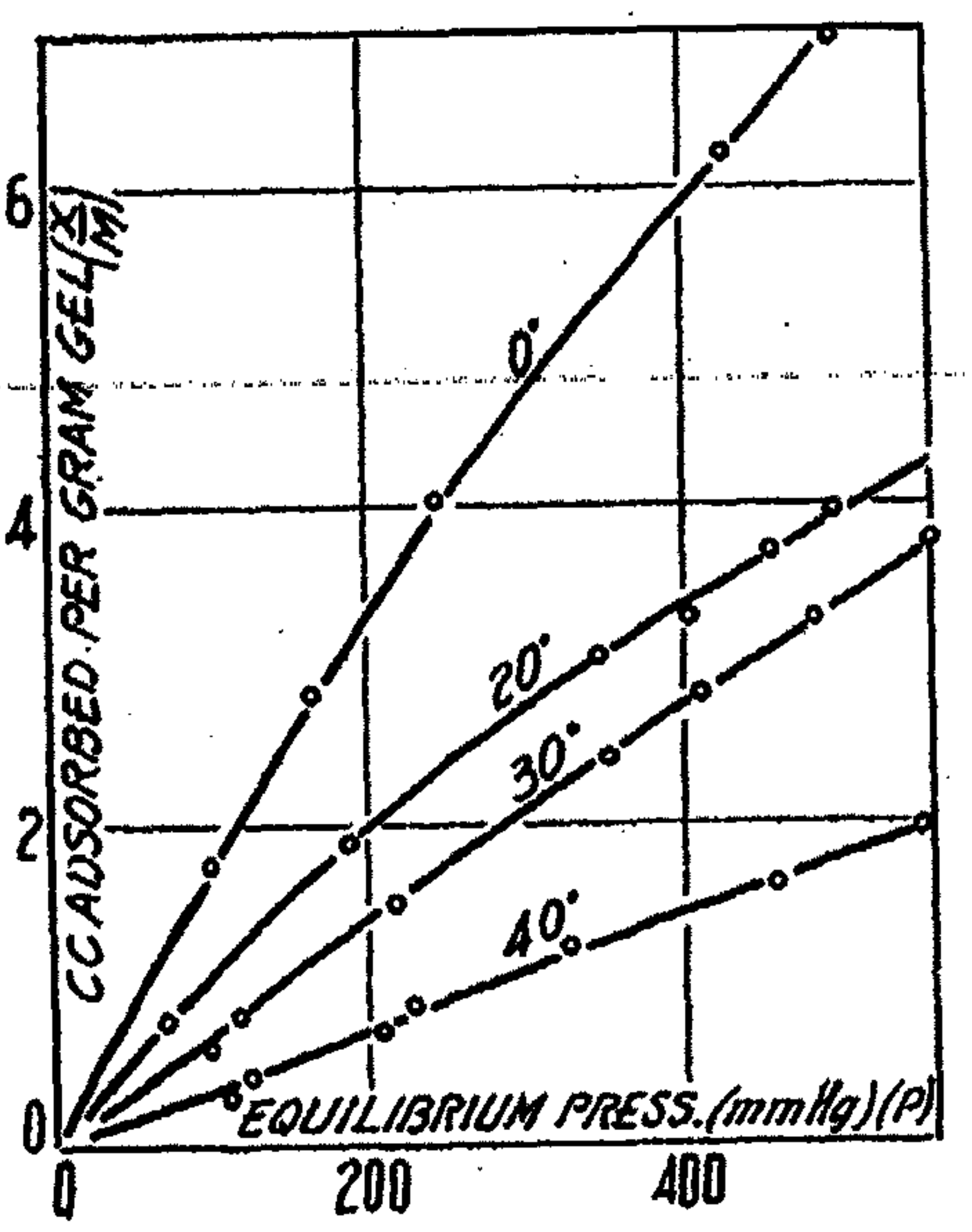

FIG. 2
Adsorption of N_2O by Silica Gel

In Fig. 4 are plotted the values of log V and log $\left(\frac{P\sigma}{P_o}\right)$ from Tables III and IV. Here we note a feature characteristic of the gases under present consideration and at marked variance with the conduct of SO_2, NH_3 and butane. In each of these latter cases, it was found that, when log V was plotted against log $\left(\frac{P\sigma}{P_o}\right)$, the curves for all temperatures became identical, while in the present case, this is not at all true; the curves run practically parallel,—indicating that $1/n$ for all temperatures is the same, but that K increases with decreasing

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[1] Ann. **110**, 10 (1859).

[2] Ann. Physik (4), **15**, 401 (1904).

temperature. For example, evaluating the constants in the case of CO_2, either by solving simultaneously the equations for pairs of points or by direct readings from a graph plotted on uniform scale, gives a value for $1/n$ at 0° of 0.866 and at 20° of 0.898, corresponding to a variation of only one degree in the slope,—while K at 0° is 0.145 and at 20° is 0.558.

Table I

Adsorption of CO_2

Run No. 11; Temp. 0°; Wt. gel sample 1.1380 gm; H_2O-1.28%

X/M	P
3.37	182.11
4.98	285.14
6.54	387.19
8.10	506.63
9.44	640.01

Run No. 12; as No. 11

1.45	68.82
2.79	149.88
4.60	259.78
6.75	403.60
8.69	550.69
9.60	614.84

Run No. 13; Temp. 20°; Wt. sample 1.1380 gm; H_2O-1.28%

0.62	61.28
1.57	162.81
2.69	297.32
3.88	456.64
5.08	624.23

Run No. 14; as No. 13

.92	100.24
2.17	240.23
3.62	418.28
4.76	567.44
5.36	658.91

Run No. 10; Temp. 30°; Wt. sample 1.0526 gm; H_2O-1.28%

X/M	P
0.57	69.32
1.44	208.36
3.27	525.13
3.91	625.93

Run No. 8; Temp. 40°; Wt. sample 1.0526 g; H_2O-1.28%

0.28	59.86
1.11	194.68
1.79	311.13
2.39	461.34
3.03	593.77

Run No. 9; as No. 8

0.62	97.29
1.40	257.12
2.15	408.82
2.71	549.99
3.16	625.44

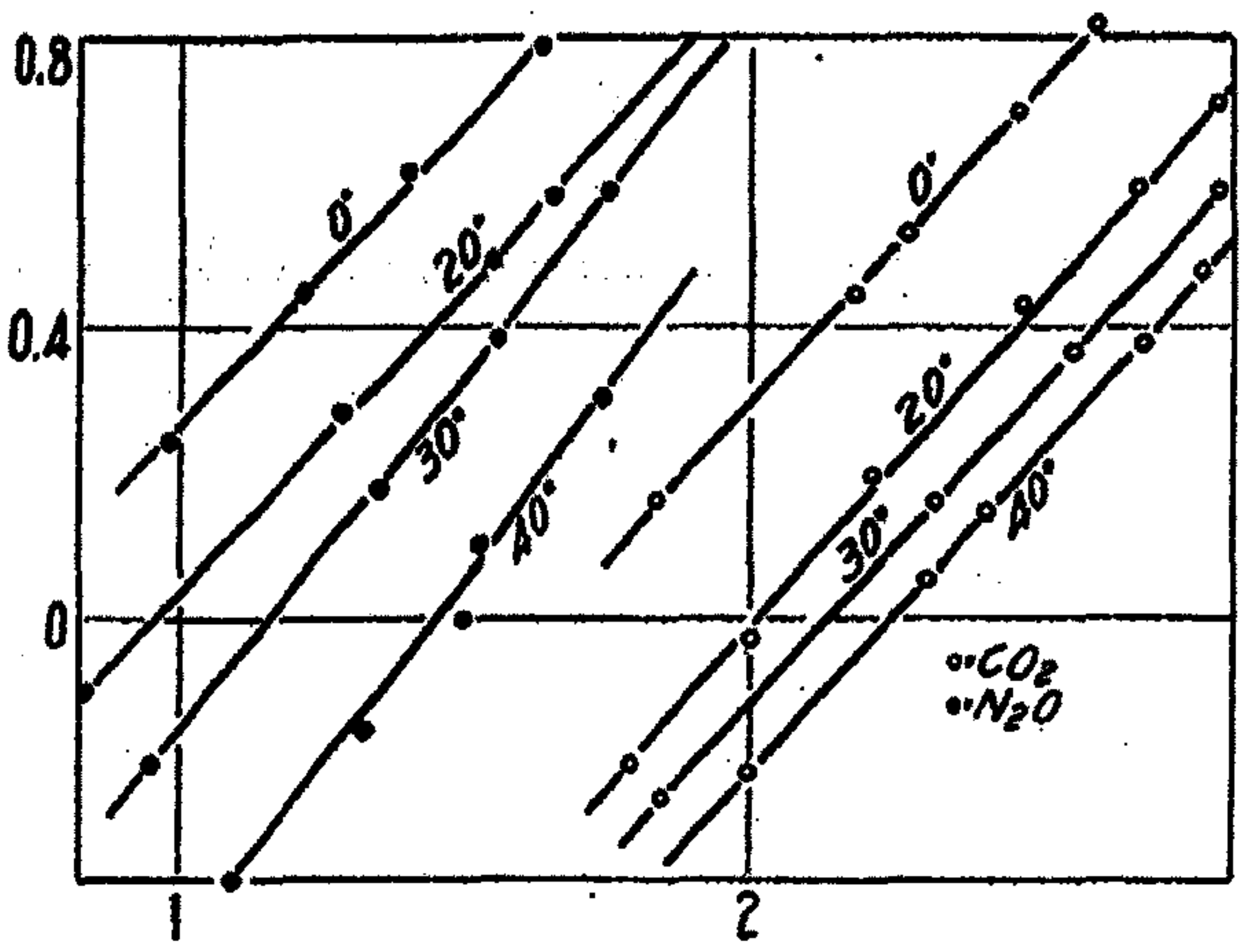

Fig. 3

Table II

Adsorption of N_2O

Run No. 2; Temp. 30°; Wt. gel 0.9754 g; H_2O-1.38%

X/M	P
0.635	99.12
1.517	219.66
2.84	412.10
3.36	484.06
3.83	560.20

Run No. 3; as No. 2

X/M	P
0.83	119.05
1.57	227.66
2.41	353.38
3.26	490.92

Run No. 4; Temp. 20°; Wt. gel .9625 g; H_2O-1.38%

X/M	P
0.769	68.90
1.91	189.31
3.09	344.05
3.74	453.46
3.97	496.46

Run No. 5, as No. 4

X/M	P
0.71	81.70
1.39	155.04
2.03	233.25
3.30	404.23
3.83	476.07

Run No. 8; Temp. 0°: Wt. gel .9625 g; H_2O-1.38%

X/M	P
1.75	97.27
2.83	165.90
4.04	243.97
6.23	424.28
6.98	494.60

Run No. 13; Temp. 40°; Wt. gel .9625 g; H_2O-1.38%

X/M	P
0.30	108.41
0.71	207.19
0.99	308.55
1.62	457.07
1.98	550.68

Run No. 14; as No. 13

X/M	P
0.44	124.00
0.87	228.23
1.26	324.73
1.77	435.23

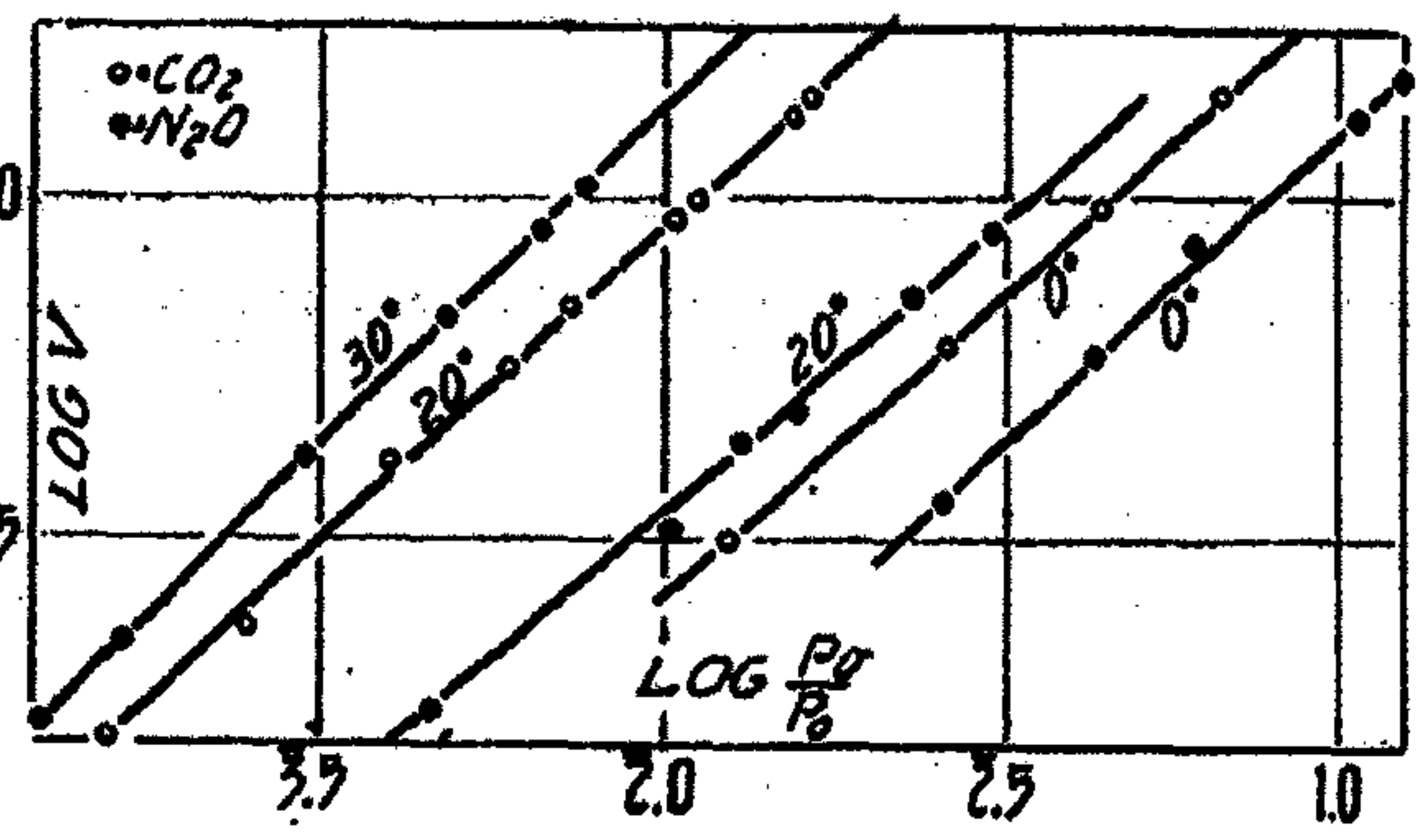

Fig. 4

Table III
CO_2

Run No. 11; Temp. 0°;
P_0 = 26904 mm.; σ = 4.6;
D (liq) = 0.914

log V	$\log\left(\frac{P\sigma}{P_0}\right)$
$\bar{3}$.860	$\bar{2}$.493
$\bar{2}$.029	$\bar{2}$.688
$\bar{2}$.147	$\bar{2}$.820
$\bar{2}$.241	$\bar{2}$.937
$\bar{2}$.329	$\bar{1}$.039

Run No. 12; as No. 11

$\bar{3}$.493	$\bar{2}$.076
$\bar{3}$.777	$\bar{2}$.408
$\bar{3}$.994	$\bar{2}$.647
$\bar{2}$.161	$\bar{2}$.838
$\bar{2}$.271	$\bar{2}$.973
$\bar{2}$.314	$\bar{1}$.021

Run No. 13; Temp. 20°;
P_0 = 44718 mm.; σ = 1.10;
D (liq) = .766

$\bar{3}$.204	$\bar{3}$.178
$\bar{3}$.605	$\bar{3}$.602
$\bar{3}$.838	$\bar{3}$.864
$\bar{3}$.998	$\bar{2}$.050
$\bar{2}$.114	$\bar{2}$.186

Run No. 14; as No. 13

log V	$\log\left(\frac{P\sigma}{P_0}\right)$
$\bar{3}$.374	$\bar{3}$.391
$\bar{3}$.745	$\bar{3}$.771
$\bar{3}$.967	$\bar{2}$.013
$\bar{2}$.087	$\bar{2}$.144
$\bar{2}$.138	$\bar{2}$.209

Run No. 10; Temp. 30°,
P_0 = 56118 mm.; σ = unknown;
D (liq) = .598

$\bar{3}$.272	———
$\bar{3}$.676	———
$\bar{3}$.880	———
$\bar{2}$.030	———
$\bar{2}$.109	———

TABLE IV
N_2O

Run No. 3; Temp. 30°;
$P_0 = 51708.5$ mm.; $\sigma = 0.7$;
D (liq) = .7337

log V	$\log\left(\frac{P\sigma}{P_0}\right)$
$\bar{3}.347$	$\bar{3}.207$
$\bar{3}.623$	$\bar{3}.488$
$\bar{3}.810$	$\bar{3}.679$
$\bar{3}.941$	$\bar{3}.822$

Run No. 5; as No. 4

log V	$\log\left(\frac{P\sigma}{P_0}\right)$
$\bar{3}.252$	$\bar{3}.735$
$\bar{3}.514$	$\bar{2}.014$
$\bar{3}.678$	$\bar{2}.191$
$\bar{3}.889$	$\bar{2}.430$
$\bar{3}.954$	$\bar{2}.501$

Run No. 2; as No. 3

$\bar{3}.230$	$\bar{3}.081$
$\bar{3}.609$	$\bar{3}.743$
$\bar{3}.881$	$\bar{3}.746$
$\bar{3}.954$	$\bar{3}.816$
$\bar{2}.011$	$\bar{3}.879$

Run No. 8; Temp. 0°;
$P_0 = 27421.0$ mm.; $\sigma = 7.0$;
D (liq) = .9369

$\bar{3}.564$	$\bar{2}.395$
$\bar{3}.773$	$\bar{2}.626$
$\bar{3}.928$	$\bar{2}.794$
$\bar{2}.116$	$\bar{1}.034$
$\bar{2}.165$	$\bar{1}.101$

Run No. 4; Temp. 20°;
$P_0 = 42027.9$ mm.; $\sigma = 2.8$;
D (liq) = .83695

$\bar{3}.256$	$\bar{3}.661$
$\bar{3}.652$	$\bar{2}.100$
$\bar{3}.860$	$\bar{2}.360$
3.943	$\bar{2}.480$
$\bar{3}.969$	$\bar{2}.519$

This behavior of K can be accounted for if we consider the evaluation of the term $\left(\frac{P\sigma}{P_0}\right)$. It is evident that too low values of surface tension at higher temperatures would produce the above effect,—likewise, would too high values at low temperatures; but the latter view is untenable, since it cannot be conceived, according to the laws of capillarity, curvature, etc., as will be shown later, that a liquid with a concave surface (in the pore) could, under any circumstances, have a *smaller* surface tension than it would have existing with a plane surface. In all applications of capillarity, hitherto noted, the surface tension has been regarded as varying only with the temperature; but there is considerable evidence to show that the surface tension is subject to many other influences. For instance, Freundlich[1] makes the statement that "in the case of very small drops, one has no right to assume that the ordinary value of surface tension applies" and "one must consider that with such small drops

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[1] "Kapillarchemie", pp. 1068, 63.

(10^{-6} cm) the surface tension has a *smaller* value than in the case of larger drops." In the present case, the liquid surface is highly concave (in the pores) and therefore the liquid itself must possess a larger surface tension than in the case of a plane surface. Furthermore, Patrick and Eberman,[1] by other considerations, have arrived at the same conclusion; that is, that the surface tension changes with the curvature of the liquid in question,—which in turn depends, in the present adsorption experiments, upon the concentration (pressure) of the vapor phase above the liquid. Now it is reasonable to suppose that the surface tension is a function of the composition of the vapor phase. In the case of a plane liquid surface, the vapor pressure can only be varied by a change of temperature, but with a liquid in a capillary tube of varying diameter (conical), it is possible to change over a wide range the composition of the vapor in equilibrium with the liquid. For example, it is not probable that liquid CO_2 at 20° under a vapor pressure of 4472 cm. possesses the same surface tension as does liquid CO_2 in a capillary tube of such dimensions that the equilibrium pressure is only 10 cm. at the same temperature.

In the case of sulfur dioxide, ammonia and butane it was found, as mentioned above, that the value of K was constant over the temperature range studied; but it is to be noted that in no case were the measurements extended higher than 30° below the critical temperature. From these facts it becomes apparent that the change in surface tension with the composition of vapor phase (i.e. with the curvature) becomes a most important factor in the neighborhood of the critical temperature. This is in agreement with the well known instability of the meniscus near this point, in which vicinity it becomes impossible to measure surface tension by the customary methods. Very slight changes in conditions then, produce very large changes in its value; it becomes an excessively sensitive quantity; the temperature coefficients of both surface tension and density become unusually high in this region.

A rough qualitative idea of the change in surface tension with the curvature may be obtained by the use of the values of K and $1/n$ for CO_2 at 0°. The variation in these constants at the higher temperatures is a result of the fact that the surface tension increases more rapidly at the higher temperature; or, in other words $\frac{d\sigma}{dr}$ *increases with the temperature.* The direction of this variation is in agreement with calculations made by Patrick and Eberman,[2] who find indications to warrant the belief that the surface tension, per same volume of liquid adsorbed (i. e. per same curvature) has a much greater value than the ordinary value for a plane surface at high temperatures than at low. By substituting values of K and $1/N$ obtained at 0° for CO_2 in the formula $V = K \left(\frac{P\sigma}{P_o}\right)^{1/n}$, it is possible to evaluate σ at 30°. Proceeding in this manner, the value $5.29 \frac{\text{dynes}}{\text{cm}}$ is obtained. This result can only be considered as a rough ap-

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[1] Loc. cit.

[2] Loc. cit.

proximation, which is given merely to indicate that there is an increase in the surface tension of the liquid in the small capillaries. At 30°, only 1° below the critical temperature, a *plane* surface of liquid CO_2 would exhibit no surface tension.

Let us now calculate, by a more exact method, the variation in surface tension as above explained, in order to test out our adsorption measurements with the thus corrected empirical formula before used.

The lowering of vapor pressure in a capillary tube has been related to other quantities by the well known formula[1] in which M is the molecular weight of

$$\ln \frac{P_0}{P} = \frac{2\sigma M}{rD_1RT}$$

the substance in the capillary, D_1 the density of the liquid, r the capillary radius, σ the surface tension, P_0 the saturation pressure at temperature T, P the equilibrium vapor pressure above the liquid, and R the gas constant expressed in dynes per sq. cm.—cc. Using this formula it is possible to obtain values of r at the measured pressure, P, of a gas at temperatures sufficiently far below the critical temperature for the effect of capillarity upon surface tension to be very small or negligible. Having done this, the values of V (from Tables III and IV) corresponding to the pressure P (from Tables I and II) can be plotted against r in the form of a curve. This has been done in Fig. 5, using the 0° runs with CO_2 and N_2O. The temperature of these runs is not as low as could be desired, as even at 0° it is possible that the value of σ as taken from measurements made by the ordinary methods may be lower than the value actually existing in the capillaries; but an increase in σ at 0° would *increase* the effect which is to be brought out later, and would thus strengthen rather than weaken the reasoning upon which our conclusions are based. We therefore assume, for purposes of calculation, that the surface tension at 0° remains unchanged or but inappreciably changed in the capillaries, and calculate r for the pressures measured in the experiments. The curves in Fig. 5, then, relate the radius of the pore to the volume of liquid held up to that point for which the value of the radius applies. By recalling the fact that the pores are conical in shape, it is clear how there can be this variation in r as V changes.

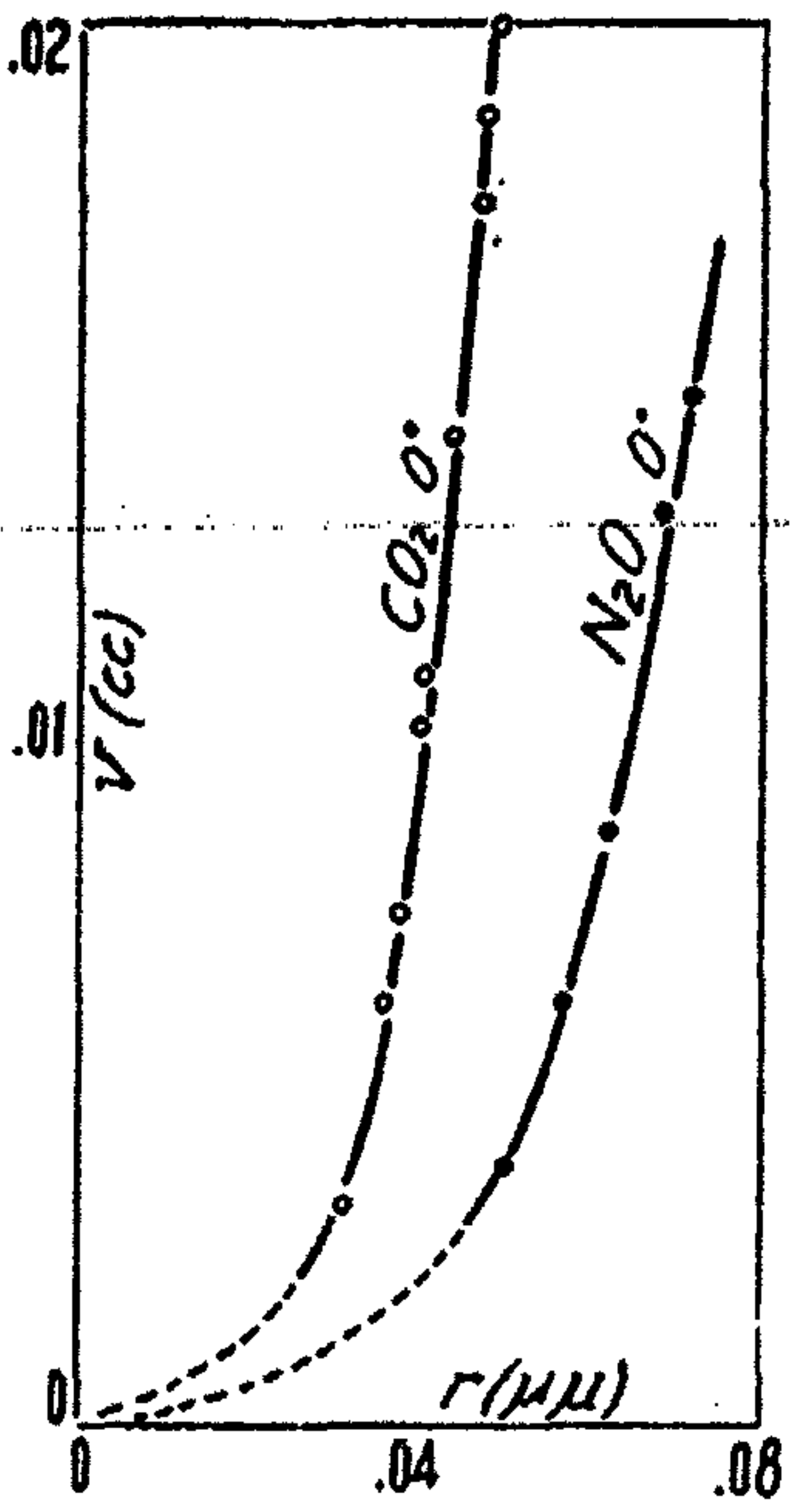

Fig. 5

The next step is to take the values of V for all temperatures other than 0°, read from the curve of Fig. 5, the values of r corresponding, and substitute

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[1] Anderson: Z. physik. Chem. 88, 191, (1914).

these latter values in the same equation given above. In this case, however, σ is the unknown, and can be solved for. In this manner, for CO_2, σ comes out $3.45 \frac{\text{dynes}}{\text{cm}}$ for 30° and 4.08 for 20°; and for N_2O, σ attains the value at 30° of 5.93, and at 20° of 6.29. The 40° run for N_2O could not, obviously, be calculated according to the above method, since the critical temperature of N_2O is 38.8°. It will be remembered at this point that the rough calculation for σ at 30° for CO_2 made above by means of values of K and 1/n found at 0° yielded a value of $5.29 \frac{\text{dynes}}{\text{cm}}$. It is not surprising, however, that this value should not agree with that found by the more rigorous method just outlined; but the important feature is the fact that both lines of reasoning lead to the same conclusion qualitatively. From these new values, it becomes apparent that, as above stated, $\frac{d\sigma}{dr}$ is positive and varies directly with the temperature.

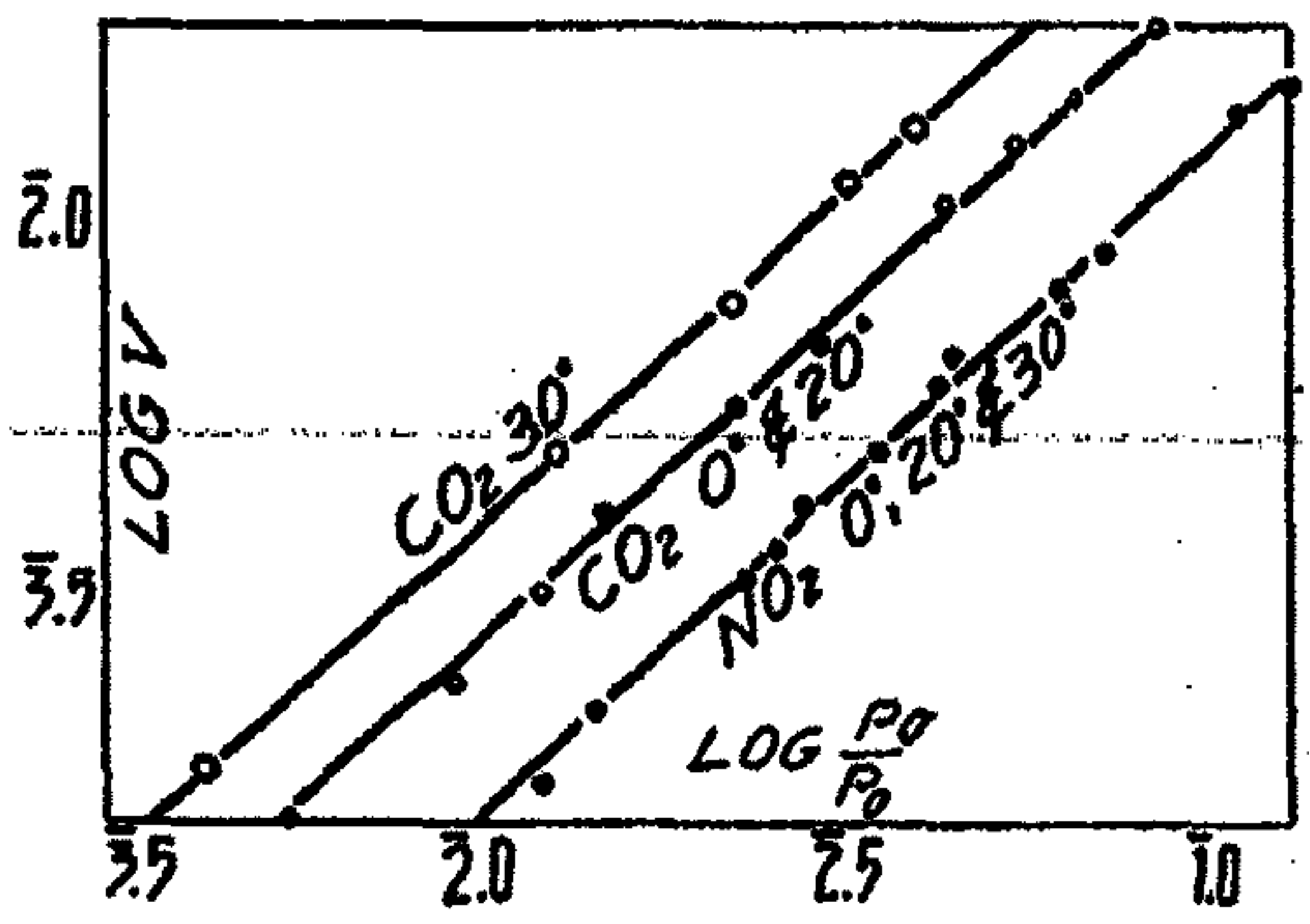

FIG. 6

These conclusions are entirely in harmony with the view discussed above,—namely, that menisci and surface tension phenomena actually exist at (relatively) high temperatures, that great concave curvature is effective in raising the surface tension, and that this rise is more noticeable in the case of liquids near their critical temperature,—in which condition the surface tension is far more sensitive to changes in conditions. The assumption that the surface tension at 0° is unchanged or negligibly changed by capillary forces may be ultra-conservative; but if the surface tension at 0° is actually increased, one should obtain yet higher values for it at 20° and 30°, showing that the capillary effect is even greater than indicated by the figures given above.

If now, the above corrected values for σ are substituted in the formula $V = K\left(\frac{P\sigma}{P_0}\right)^{1/n}$, curves for almost all temperatures for the same substance (different samples of gel were used for different substances) coincide. These curves are represented in Fig. 6. It is noted that the 30° curve for CO_2 does not coincide with the other two. Although the difference is appreciable, it must be pointed out that the sample of gel used for the 30° work was different from that used in the 0° and 20° runs. This fact alone would account for the non-coincidence of the 30° curve; but there is also the uncertainty as to the true density of the liquid in the pores at this temperature (very near C.T.), due to the dilation effect discussed by Patrick and McGavack,[1] and the conservative assumption that at 0° the gas is far enough below its critical temperature to permit taking the 0° curve as a reference. We can therefore say that the proposed capillary effect on surface tension near the critical temperature explains (in the case of CO_2) quantitatively the variation of the 20° runs from those at 0° and brings the 30° run very nearly into accord. In the case of N_2O where the same gel sample was used, it will be noted that the 0°, 20°, and 30° curves coincide.

In other words, after applying corrections, K, in our equation, as well as $1/n$, is the same for all temperatures as demanded by theory. This means that with CO_2, N_2O, SO_2, NH_3 and butane, the same volume (V) is taken up at "corresponding pressures" $\left(\frac{P\sigma}{P_o}\right)$.

Since, then, capillarity lowers the vapor pressure of a liquid within the capillary system, and increases the surface tension, and since there is no perceptible break in the adsorption phenomena between 30° and 40°, we think there is justification for extending the capillary condensation theory of adsorption to temperatures above the ordinary critical temperature, and propose the idea that in the pores of the gel the critical temperature is raised, and that condensation and surface tension exist even at 40°. The view that the critical temperature in capillaries is raised is also in entire agreement with the conclusions of Patrick and Jones,[2] based on a study of adsorption from solution. No attempt has been made to calculate the surface tensions in the capillaries at 40°, nor to subject the results of the 40° runs to the same mathematical treatment as the others, since neither the density nor the saturation pressure (P_o) of the condensed phases of this temperature is known.

Summary

1. Accurate measurements have been made of the adsorption of carbon dioxide and nitrous oxide by silica gel at 0°, 20°, 30°, and 40° at pressures below one atmosphere.

2. When the equation $V = K\left(\frac{P\sigma}{P_o}\right)^{1/n}$ was applied to the experimental results, it was found that K at 0° was not equal to K at higher temperatures, as has been true of K at different temperatures in the case of other gases to which the capillary theory of adsorption had been applied. The explanation is offered that this is due to an increase in surface tension of the liquid in the

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[1] Loc. cit.

[2] J. Phys. Chem. 29, 1 (1925).

capillaries at temperatures near the critical temperature, brought about by capillary forces. A method is given by which the surface tension can be corrected. These corrected values for surface tension, when applied to the above equation, bring about results entirely in accord with theory,—making K and 1/n dependent *only* upon the structure of the gel.

3. The capillary theory of adsorption has been extended to temperatures above the critical temperature, and evidence is brought forth to indicate that the critical temperature is raised in the pores of the adsorbent.

STUDIES IN ADSORPTION, PART X.

Influence of ions carrying the same charge on (a) coagulation of diluted sols (b) coagulation by a mixture of electrolytes and (c) acclimatization

BY S. GHOSH AND N. R. DHAR

In the foregoing papers of this series[1] we studied the influence of the change of concentration of a sol on its coagulation by electrolytes. We enunciated the general dilution rule that the greater the concentration of a sol, the greater is the amount of electrolyte necessary for coagulation irrespective of the valency of the precipitating ion. Sulphides of arsenic and antimony are exceptions to the above rule when precipitated with univalent electrolytes. It has been observed that the coagulation of these sulphide sols by bivalent and trivalent cations practically follow the general rule that the greater the concentration of the sol the greater is the amount of electrolyte necessary for coagulation. This general dilution rule has been found applicable to manganese dioxide sol, positively and negatively charged ferric hydröoxide, positive and negative chromium hydroxide, prussian blue, $Al(OH)_3$ suspended in organic acids, etc. In this paper it will be reported that this rule is also valid with negative stannic hydroxide. In our attempt to explain the abnormal behaviour of As_2S_3, Sb_2S_3 sols on dilution in their coagulation by univalent salts, we have established the following facts:—

(1) We have proved that it is impossible to prepare a pure arsenious sulphide sol. Arsenious sulphide is readily hydrolysed according to the following equation $As_2S_3+3H_2O \rightleftarrows As_2O_3+3H_2S$. As soon as the sol of arsenious sulphide is freed from H_2S by passing hydrogen, some arsenious acid is immediately set free; hence it is not practicable to prepare a pure sol of arsenious sulphide. It has been repeatedly observed that when all free H_2S is removed from a sol of As_2S_3, an appreciable amount of arsenious acid is always present along with the arsenious sulphide: the free arsenious acid can be detected by coagulating the colloid and testing for arsenious acid in the clear filtrate. The amount of arsenious acid increases with the time during which hydrogen is passed. The amount of arsenious acid also goes on increasing if the sol is kept at the ordinary temperature. If hydrogen is bubbled for about three or four hours in freshly coagulated, well-washed arsenious sulphide suspended in water, an appreciable amount of arsenious acid appears in the filtrate. Hence the sol of arsenious sulphide always contains free arsenious acid.

(2) We have also proved that free arsenious acid has a coagulating effect, whilst free H_2S has a stabilising effect on arsenious sulphide sol in its coagulation by univalent cations. We have also proved that in equivalent concentrations, H_2S exerts more influence as a peptising agent than arsenious acid as a coagulating agent, towards arsenious sulphide sol when it is coagulated by potassium chloride. When arsenious sulphide sol is diluted, more and more

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[1] J. Phys. Chem. 26, 701 (1922); 28, 313 (1924); Kolloid-Z. 34, 262 (1924).

free H_2S and arsenious acid are formed. As will be seen in the equation, the amount of H_2S set free by hydrolysis of As_2S_3 is greater than the amount of arsenious acid liberated, when the concentrations of both H_2S and arsenious acid are expressed iodometrically. The H_2S set free tries to peptise the unhydrolysed arsenious sulphide whilst the arsenious acid tries to coagulate the sol. The net effect of these opposing influences is that the sol is really stabilised on dilution towards KCl, NaCl etc. because the influence of H_2S which is a product of the hydrolysis more than counterbalances the coagulating influence of arsenious acid. Hence dilution according to these results should stabilise arsenious sulphide sol towards potassium chloride and the experimental results are in support of this conclusion. On the other hand, from our experimental results we find that arsenious sulphide sol is not stabilised but becomes unstable by the presence of H_2S when coagulated by bivalent and trivalent electrolytes. Consequently when the sol is diluted and is hydrolysed more and more, it becomes more unstable than the concentrated sol towards bivalent and trivalent cations. Hence the dilute sol would require less bivalent and trivalent electrolytes for coagulation than the concentrated one and experimental results are in favour of this conclusion.

(3) We have proved that negatively charged hydrated manganese dioxide not only adsorbs cations but it also adsorbs appreciable quantities of anions and of hydroxide ions. We have also proved that barium sulphate in the course of its precipitation mainly adsorbs the negative portion of an electrolyte, leaving the basic part free, but it also adsorbs the positive ions as the experimental results in Table I will show:—

TABLE I

Electrolyte	Original concentration of positive ion.	Final concentration of positive ion.	Percentage of adsorption.
KCl	0.1038 M	0.1032 M	0.1%
$K_2C_2O_4$	0.06894 M	0.06753 M	2.0%
$KBrO_3$	0.09400 M	0.09336 M	0.6%
Na_3AsO_3	0.08833 M	0.08532 M	3.7%

In the foregoing paper[1] it has been observed that Cl′, SO''_4, C_2O_4'' ions etc., are adsorbed by arsenious sulphide when it is coagulated by KCl, K_2SO_4, $K_2C_2O_4$, etc. In another paper[2] the following quantitative experiment has been made with KCl and As_2S_3 sol.

TABLE II

Adsorption of potassium and chlorine ions

Amount of As_2S_3 = 0.4508 grm and volume = 100 cc

Original concentration	Final concentration	Adsorption
0.05997 Cl′	0.05900 Cl′	1.6%
0.05997 K·	0.05790 K·	3.3%

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[1] Sen and Dhar: Kolloid-Z. 34, 264 (1924).

[2] Ghosh and Dhar: Kolloid-Z. (1924).

Hence the ratio of adsorption of potassium ion to that of chloride ion is 2.06.

(4) In a foregoing paper[1] it has been proved that the real interpretation of the Schulze-Hardy Law is that the greater the valency of an ion, the less is the adsorption and this is also corroborated by the experimental results obtained by us as well as by other workers. The exceptional cases have been explained on the view that the neutralised particles can adsorb the precipitating electrolyte.

There is another plausible view which also can explain the exceptional cases. Let us consider the coagulation[2] of positively charged $Fe(OH)_3$ by $K_2C_2O_4$ and $K_2Cr_2O_7$. It is observed that the precipitation value and the amount of adsorption of the oxalate ion are much greater than those of the dichromate ion. It is likely that the sol will adsorb more of the positive ion in one case than in the other.

Experiments on the precipitation of barium sulphate already noted in presence of potassium chloride and of oxalate show that the adsorption of oxalate ion is much greater than that of chloride ion (12% with oxalate and 2% with chloride at the same molecular concentration) though according to the Schulze-Hardy Law it should be otherwise. We have found out that along with the adsorption of oxalate ion by barium sulphate, appreciable quantities of potassium ion are also adsorbed. The positively charged substance barium sulphate can adsorb potassium ions and hence more of the oxalate ion would be necessary for its charge neutralisation and precipitation.

(5) When KCl is added to As_2S_3 sol it will attract and adsorb the positive ion. It may also adsorb the negative ion and molecular KCl. Now when the charge on the sol is neutralised by the adsorption of positive ions, the neutralised particles can easily adsorb Cl' ions because of the chemical attraction of the sol for Cl' ions. It is quite probable that when the charge on the sol becomes sufficiently small due to the adsorption of potassium ions, they might attract the chloride ions because of the chemical attraction which counterbalances the repulsive force due to the sameness of the electric charge.

The adsorption of negative ions like Cl', SO_4'', C_2O_4'', etc., will certainly stabilise the sols of As_2S_3, Sb_2S_3, etc., and the stability of a sol in respect to its coagulation by a certain electrolyte will depend on the ratio of the amounts of adsorption of the two ions of the electrolyte. For example, when KCl is added to As_2S_3 sol, it will adsorb both the ions, as has been shown experimentally but the potassium ion is adsorbed more than the chloride ion and hence the sol is adsorbed more than the chloride ion and hence the sol is actually coagulated by the electrolyte.

In the case of bivalent salts like $BaCl_2$, $SrCl_2$, etc., and trivalents salts like $AlCl_3$, $FeCl_3$, etc., the ratio of the amounts of adsorption of the positive to the negative ion is undoubtedly much greater than unity in all concentrations of the sol. This is the reason why the rule that the greater the concentration of

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[1] Dhar, Sen and Ghosh: J. Phys. Chem. 28, 457 (1924).

[2] Compare Weiser: J. Phys. Chem. 25, 399 (1921).

the sol, the greater is the concentration of the electrolyte necessary for coagulation is applicable in all these cases.

In the case of univalent salts like KCl, LiCl, etc., with negatively charged sols As_2S_3, Sb_2S_3, etc., the ratio of the amounts of adsorption of positive ions to the negative ions is usually greater than unity. It seems probable that when the concentration of these sols becomes small this ratio tends to decrease and may approach unity. That is why more and more of KCl or LiCl is necessary to coagulate a dilute sol of As_2S_3 or Sb_2S_3 than concentrated sols of the same substance.

We are trying to show experimentally that the ratios of the amounts of adsorption of positive ions to the negative ions decrease with dilution of the sols in their coagulation with KCl.

In cases of positively charged ferric hydroxide, chromium hydroxide, etc., the adsorption of the positive ion is very small in comparison with that of the negative ion. The ratio of the amounts of adsorption of the negative ion to that of the positive ion is always greater than unity and does not much change with the concentration of the sol. For this reason, the general rule that the greater the concentration of the sol, the greater is the amount of electrolyte necessary for coagulation, is applicable in all dilutions of these sols with all electrolytes.

(6) From a critical summary of the existing data on the coagulation of sols by electrolytes we have observed that the effect of positive ions on positively charged sols like $Fe(OH)_3$, $Cr(OH)_3$, etc., is not so marked as that of negative ions in the case of negatively charged sols like As_2S_3, Sb_2S_3 etc. Thus from Linder and Picton's results[1] with chlorine as the precipitating ion, the average precipitation value of different univalent sols becomes 283 in the case of ferric hydroxide sol, and the average precipitation value with bivalent sols is about 305, the difference is 7%. On the other hand, the precipitation value with univalent salts on arsenious sulphide sol is 99.4, and that of the salts containing bivalent negative ions is 130 showing a difference of 30%. These results can be satisfactorily explained on the assumption that negatively charged arsenious sulphide can adsorb appreciable quantities of the ions carrying the same charge as the sol, whilst positively charged ferric hydroxide can hardly adsorb an ion carrying a positive charge.

In this connection it should be noted that the influence of the ion carrying the same charge as the sol on its coagulation has been emphasised by Bancroft[2], Burton and Bishop[3], Ostwald[4], Weiser[5], and others. Weiser has given this idea great prominence in explaining many facts in the coagulation of sols by electrolytes. But as far as we know, we were the first to observe experimentally (qualitatively and quantitatively) that ions carrying the same charge as the sols are actually adsorbed by sols and we have co-ordinated diverse facts on coagulation and adsorption from this point of view.

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[1] J. Chem. Soc. 67, 65 (1895); 87, 1926 (1905).

[2] Second Report on Colloid Chemistry, Brit. Ass. p. 2, (1919).

[3] J. Phys. Chem. 24, 701, (1920).

[4] Kolloid-Z. 26, 28, 69, (1920).

[5] J. Phys. Chem. 25, 665, 742 (1921); 28, 232 (1924).

In the foregoing paper of this series[1], we have reported that the presence of free sulphur in colloidal arsenious sulphide can be detected by treating the coagulated mass of arsenious sulphide by carbon disulphide. It seems likely that the presence of this negatively charged sulphur sol adds to the stability of arsenious sulphide sol, which is also negatively charged. Consequently a boiled sol of arsenious sulphide is more stable towards all electrolytes, because it contains free sulphur in the colloidal condition.

Recently Murphy and Matthews[2] have proved that arsenious sulphide sol does not contain a simple compound such, for example, as the molecule As_2S_3. It is very likely that most sulphide sols would be contaminated with negatively charged sulphur sol. Hence antimony sulphide or mercuric sulphide sol does not contain simple compounds, such as, Sb_2S_3 or HgS, but really is a mixture of two or more sols or of different molecular species. In the case of mastic, which is a naturally occurring resinous matter, we are probably dealing with a mixture of different substances. It is interesting to note that these very substances, e.g. arsenious sulphide, antimony sulphide, mastic, etc., show abnormal dilution effect towards univalent cations.

The sulphide sols are partially decomposed on boiling or on keeping for a long time at the ordinary temperature. Moreover, these sols undergo hydrolysis readily and are also oxidized easily. It appears, therefore, that sols which are liable to be hydrolysed or to undergo other chemical changes readily are likely to show complications in their coagulation with electrolytes.

In Part VII of this series[3] the following observations were made:

"The adsorption of negative ions like Cl′, SO_4'', C_2O_4'', etc., by negatively charged sols explain some interesting observations of Linder and Picton[4] and of Weiser[5].

They have found out that if small quantities of KCl, NaCl, LiCl, etc., are added at the beginning, the sol of arsenious sulphide, becomes more stable towards electrolytes like $BaCl_2$, $SnCl_2$ etc., whilst ferric hydroxide sol is not stabilised towards K_2SO_4, $K_2C_2O_4$, etc., by the previous addition of KCl, $KBrO_3$, KNO_3, etc."

Very little work has been done on the precipitation of colloids by mixtures of electrolytes. Linder and Picton (*loc.cit*), Freundlich[6] and coworkers, Blake[7], and Weiser (*loc. cit.*) have investigated the coagulation of some sols by a mixture of electrolytes. The important facts observed are:

(1) With positive ferric hydroxide, positive chromic hydroxide, and negative stannic hydroxide, the precipitating values of mixtures of pairs of electrolytes of widely varying precipitating power (uni-and bivalent ions) are slightly less than the additive values. Thus mixtures of KCl and either K_2SO_4 or

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[1] Ghosh and Dhar: Kolloid-Z. (1924).
[2] J. Am. Chem. Soc. 45, 16 (1923).
[3] Sen and Dhar: Kolloid-Z. 34, 262 (1924).
[4] J. Chem. Soc. 67, 67 (1895).
[5] J. Phys. Chem. 25, 665 (1921).
[6] Z. physik. Chem. 44, 145 (1903), Kolloidchem. Beihefte 16, 267 (1922).
[7] Am. Chem. J. 16, 438 (1903).

$K_2C_2O_4$ precipitate ferric hydroxide and chromic hydroxide at concentrations less than the additive values, and the same is true for mixtures of LiCl and either $BaCl_2$ or $MgCl_2$ with negative stannic hydroxide. The maximum difference between the observed and the calculated values is less than 20%.

(2) With the above sols an approximately additive relationship is obtained with a mixture of bivalent precipitating ions.

(3) With As_2S_3 the same is true for mixtures of (a) NH_4Cl and HCl, (b) $Ca(NO_3)_2$ and $BaCl_2$, and (c) $BaCl_2$ and $MgCl_2$.

(4) With As_2S_3, the precipitating values of mixtures of electrolytes of widely varying precipitating powers are always much greater than the additive values. This was observed with (a) LiCl and $MgCl_2$ (b) LiCl and $BaCl_2$, (c) HCl and $MgCl_2$, (d) KCl and $SrCl_2$, (e) KCl and $BaCl_2$.
The difference between the observed and the calculated values is as high as 120% in certain cases.

In explaining the behaviour of a mixture of electrolytes in the precipitation of colloids, Weiser has emphasised two factors—

1. The effect of the presence of each precipitating ion on the adsorption of the others.

2. The stabilising action of the ions having the same charge as the colloid.

If the influence of both these factors be small the precipitation value of mixtures would be additive, whilst if the influence of both these factors be large the precipitation value of mixtures will be greater than that expected from the values for the two different salts. Recently he has shown that a relatively large amount of chloride ion has no appreciable effect on the adsorption of oxalate ions by chromium hydroxide. The same is true, as Weiser has shown, in the case of ferric hydroxide and that is why no ionic antagonism is observed in the precipitation of chromium hydroxide or ferric hydroxide by a mixture of potassium chloride and oxalate. On the other hand, Weiser has shown that the adsorption of barium ion is decreased to a marked extent by the presence of lithium ion in the coagulation of arsenious sulphide. Freundlich and Scholz are of the opinion that the extent of hydration of a colloid is the most important factor in causing the ionic antagonism which results in precipitation values for certain mixtures of electrolytes that are considerably above the additive values. It is very difficult to understand how the hydration of the sol or the precipitating ion can explain ionic antagonism. Moreover it is so difficult to ascertain the amount of hydration of a sol or an ion[1].

Experimental Results

A. *Stannic Hydroxide Sol.*

In this paper we have studied the coagulation of negatively charged stannic by droxide sol by different electrolytes and at various dilutions. The sol was prepared by slowly adding stannic chloride solution to a dilute caustic soda solution till the mixture was practically neutral. The sol was dialysed for

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[1] Compare Dhar: Z. Elektrochem. **20**, 57 (1914).

about 3 days, when it was free from alkali. The sol was practically optically clear and is very stable. It will be seen from the following tables that this sol follows the Schulze-Hardy Law in general and the rule that the greater the concentration of the sol, the greater is the amount of electrolyte necessary for the coagulation of the sol irrespective of the valency of the precipitating ion.

TABLE III

Concentration of sol = 2.71 grms SnO_2 per litre
Volume of sol taken each time = 4 cc
Volume after mixing electrolyte = 6 cc
Time = ½ hour

Electrolyte	Concentration.	Amount added in c. c.	Precipitating Concentration
KCl	N/2	1.30	0.1083
K_2SO_4	N/2	1.40	0.1167
$K_4Fe(CN)_6$	N/2	<2.0	———
$BaCl_2$	N/125	0.9	0.0012
$MgCl_2$	N/100	1.2	0.0020
$Al_2(SO_4)_3$	N/250	1.45	0.0009
$Th(NO_3)_4$	N/200	1.25	0.0012

An examination of the above table gives the following order for the precipitation values, beginning with the highest one—

$K_4Fe(CN)_6 > K_2SO_4 > KCl > MgCl_2 > BaCl_2, Th(NO_3)_4 > Al_2(SO_4)_3$.

From the experimental results, it appears that the Schulze-Hardy Law is applicable in this sol with the exception of thorium, which has been found to behave abnormally in other cases, such as As_2S_3, Sb_2S_3, negatively charged $Cr(OH)_3$, etc.[1]

Since the colloid is negatively charged it is obvious that the cation is the coagulating agent. It appears, however, that the anions also have appreciable influence as shown in Table IV.

TABLE IV

Electrolyte	Concentration	Amount added c. c.
KCl	N/2	1.3
K_2SO_4	N/2	1.4
$K_4Fe(CN)_6$	N/2	< 2

The precipitation values of different salts with the same cation are in the order $Fe(CN)_6'''' > SO_4'' > Cl'$.

It is interesting to observe that salts like potassium citrate, potassium ferrocyanide, etc., precipitate negatively charged stannic hydroxide with great difficulty. Exactly similar results were obtained with negatively charged ferric hydroxide and chromium hydroxide due to the great peptising influence of polyvalent negative ions.

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[1] Sen and Dhar: Kolloid-Z. 34, 262 (1924).

TABLE V

Effect of dilution

Electrolyte	Sol (A)	Sol (A/2)	Sol (A/4)
KCl N/2	1.3 cc	1.2 cc	1.1 cc
$BaCl_2$ N/125	0.9 cc	0.6 cc	0.35 cc
$MgCl_2$ N/100	1.2 cc	0.7 cc	0.4 cc
$Al_2(SO_4)_3$ N/250	1.45 cc	0.8 cc	0.4 cc

Mixed Electrolytes Sol (A)

KCl N/2	$BaCl_2$ N/125 added	$BaCl_2$ N/125 Calculated	Difference
0.6 cc	0.45 cc	0.5 cc	0.05

Hence this sol follows the general dilution rule that the greater the concentration of the sol the greater is the amount of electrolyte necessary to coagulate the sol irrespective of the valency of the precipitating ion. Moreover this sol behaves more or less normally with a mixture of electrolytes.

B. *Negatively charged ferric hydroxide.*

This sol was prepared by the method already described[1].

TABLE VI

Concentration of sol = 5.54 grms Fe_2O_3 per litre
2 cc sol : Volume = 10 cc

N KCl c. c.	N/25 $BaCl_2$ c. c.	N KCl c. c.	N/25 $BaCl_2$ c. c.
—	0.65	2.0	0.62
0.5	0.65	3.0	0.60
1.0	0.65	5.0	0.55

The sol was very stable and could not be coagulated by N KCl, it could only be coagulated by a saturated solution of KCl, but it is readily coagulated by $BaCl_2$ and $AlCl_3$.

C. *Negatively charged chromium hydroxide.*

This sol was prepared by the method described in Part VII of this series[2].

TABLE VII

Concentration of sol = 3.62 grms Cr_2O_3 per litre
2 cc sol : Volume = 10 cc

N KCl c. c.	N/25 $BaCl_2$ cc
—	1.15
1.0	1.10
3.0	1.05
5.0	1.00

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[1] J. Phys. Chem. 28, 313 (1924).

[2] Kolloid-Z. 34, 262 (1924).

This sol was also very stable and could not be coagulated by N KCl. Strong solutions of KCl coagulate it, whilst it was readily coagulated by $BNaCl_2$ and $AlCl_3$.

From the foregoing results which are of a preliminary nature we find that the sols are not stabilised towards $BaCl_2$ by the previous addition of KCl, and that additive relationship is obtained when negatively charged ferric hydroxide and chromium hydroxide are coagulated by a mixture of KCl and $BaCl_2$. In

TABLE VIII

Concentration of undialysed Sb_2S_3 sol = 1.986 grs. per litre
Volume of sol taken each time = 4 cc
Volume on mixing electrolyte = 8 cc
Time = ½ hr.

KCl N/4 cc	$BaCl_2$ N/125 added cc	$BaCl_2$ N/125 Calculated cc	Difference cc
1.20	——	——	——
——	0.95	——	——
0.2	0.90	0.79	+ 0.11
0.4	0.85	0.64	+ 0.21
0.6	0.55	0.48	+ 0.07
0.8	0.35	0.32	+ 0.03

$MgCl_2$ N/100 cc	$BaCl_2$ N/125 added cc	$BaCl_2$ N/125 calculated cc	Difference cc.
1.0	——	——	——
0.2	0.75	0.76	− 0.01
0.4	0.55	0.57	− 0.02
0.6	0.45	0.38	+ 0.07
0.8	0.20	0.19	+ 0.01
——	0.95	——	——

KCl N/4 cc	$Al_2(SO_4)_3$ N/166.7 added cc	$Al_2(SO_4)_3$ N/166.7 Calculated. cc.	Difference cc.
1.15	——	——	——
——	1.15	——	——
0.2	1.10	0.95	+ 0.15
0.4	0.95	0.75	+ 0.20
0.6	0.70	0.55	+ 0.15
0.8	0.50	0.35	+ 0.15

$MgCl_2$ N/100	$Al_2(SO_4)_3$ N/166.7 added	$Al_2(SO_4)_3$ N/166.7 calculated.	Difference
——	1.10	——	——
1.0	——	——	——
0.1	1.0	1.0	0.0
0.4	0.75	0.66	+0.09
0.7	0.40	0.33	+0.07

other words, the behaviour of these two sols when coagulated by a mixture of electrolytes is normal.

We have shown in other papers that these two sols follow the general dilution rule that the greater the concentration of the sol, the greater is the amount of electrolyte necessary for coagulation irrespective of the valency of the coagulating ion.

D. *Antimony Sulphide.*

In the foregoing papers of this series[1] we have investigated the coagulation of negatively charged antimony sulphide sol by electrolytes under different conditions. In this paper we have investigated the coagulation of the above sol by mixtures of electrolytes and from the following results it will be observed that ionic antagonism is noticeable in the coagulation of this sol by electrolytes. In other words, previous addition of small quantities of potassium salts makes this sol stable towards bi-valent and trivalent electrolytes.

We have also determined the adsorption of both barium and potassium ions when antimony sulphide is coagulated by a mixture of barium chloride,

TABLE IX

Adsorption by Sb_2S_3.

Amount of sol taken = 75 c c, containing 0.1490 grm Sb_2S_3.

Volume = 100 cc; Amount of potassium ion already present as K_2SO_4 due to the presence of potassium tartrate = 0.0795 grm

Mixture added to 75 cc sol.			Amount of cations present as sulphates.	Amount remaining as sulphates	Adsorption of cations as sulphates.	Adsorption in Milli-equivalent
cc N/125 $BaCl_2$	cc N/4 KCl	cc H_2O				
15	—	10	0.0140 grm. of $BaSO_4$	0.0062 grm. of $BaSO_4$	0.0078 grm. of $BaSO_4$	0.0668Ba
—	16	9	0.4279 grm. of K_2SO_4	0.4055 grm. of K_2SO_4	0.0224 grm. of K_2SO_4	0.2571 K
10	8	7	0.0095 grm. of $BaSO_4$	0.0060 grm. of $BaSO_4$	0.0035 grm. of $BaSO_4$	0.0299 Ba
			0.2537 grm. of K_2SO_4	0.2438 grm. of K_2SO_4	0.0099 grm. of K_2SO_4	0.1137 K

From the above experiments on Sb_2S_3 sol we find that the adsorption of barium ion is decreased to the extent of 55% by the presence of potassium ion below the precipitation concentration of potassium chloride. We have also observed that adsorption of potassium ion by antimony sulphide is also decreased by the presence of barium ion. A very interesting fact will be noticed that the sum of the adsorption of potassium and barium ions expressed as

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[1] J. Phys. Chem. 28, 313 (1924); Kolloid-Z. (1924).

equivalents by Sb_2S_3 is greater than the adsorption of barium ion by Sb_2S_3 when coagulated by $BaCl_2$ alone but less than the adsorption of K ion when coagulated by only KCl.

These results are in entire agreement with the interpretation of the Schulze-Hardy Law from the adsorption point of view already advanced[1]. It was enunciated that an ion which has high precipitation value (a small coagulating power) for a colloid is more adsorbed than an ion with a high coagulating power. In other words univalent ions are more adsorbed than bivalent ones. In this case when Sb_2S_3 is coagulated by electrolytes potassium ion is more adsorbed than barium ion and from a mixture of potassium and barium chlorides the sum of the adsorption of barium and potassium expressed in equivalents is less than the adsorption of potassium when coagulated by KCl alone and greater than that of barium when coagulated by only $BaCl_2$.

E. *Mastic Sol.*

The sol was prepared by dissolving a known amount of mastic in alcohol and then dropping the alcoholic solution in a measured volume of water. It has been observed that small quantities of alcohol do not appreciably affect the coagulation of the sol by electrolytes.

TABLE X

Concentration of mastic sol = 1.2528 grms. per litre
Sol = 4 cc; Total volume after mixing electrolyte = 8 cc
Time = ½ hour

KCl N/8 cc	$BaCl_2$ N/25 added cc	$BaCl_2$ N/25 calculated cc	Difference cc
1.70	—	—	—
—	1.55	—	—
0.5	1.15	1.10	+0.05
0.7	1.00	0.91	+0.09
0.9	0.85	0.73	+0.12
1.2	0.50	0.45	+0.05
1.70	—	—	—

KCl N/8 cc.	$Al_2(SO_4)_3$ N/2000 added cc.	$Al_2(SO_4)_3$ N/2000 calculated cc	Difference cc.
—	1.50	—	—
0.1	1.45	1.40	0.05
0.7	0.95	0.85	0.10
0.9	0.75	0.68	0.07
1.2	0.50	0.45	0.05

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[1] Dhar, Sen and Ghosh: J. Phys. Chem. 28, 457 (1924).

Effect of dilution.

TABLE XI

Sol A = 4 cc. Original sol made to 8 cc on mixing electrolytes.

Electrolyte	Sol A Amount added cc	Sol A/4 Amount added cc
KCl N/8	1.70	2.50
$BaCl_2$ N/25	1.55	1.85
$Al_2(SO_4)_3$ N/2000	1.50	1.05

From the experimental results on mastic sol, which is negatively charged, it will be observed that the sol is abnormal with a mixture of electrolytes and does not follow the dilution rule that the greater the concentration of the sol the greater the amount of electrolyte necessary for coagulation with monovalent and bivalent cations[1].

It will be evident from the foregoing tables on the coagulation of mastic by $BaCl_2$ that the coagulating power of $BaCl_2$ is not preponderantly greater than that of KCl. The coagulating power of $BaCl_2$ on mastic is about seven times greater than that of KCl. In the case of other negatively charged sols the coagulating power of $BaCl_2$ is about fifty times greater than that of KCl. Consequently the sol is likely to adsorb appreciable quantities of chlorine ions from KCl or from $BaCl_2$. Therefore it seems reasonable to expect that in the coagulation of this sol by KCl or $BaCl_2$, the ratio of the adsorption of positive to negative ion is not much greater than unity and the ratio is likely to decrease as the sol is diluted, that is why more KCl or $BaCl_2$ is necessary to coagulate a dilute sol than a concentrated one.

We have proved that negatively charged stannic hydroxide, ferric hydroxide, and chromium hydroxide follow the general rule that the greater the concentration of a sol, the greater the amount of electrolyte necessary for its coagulation. We have also shown that when these sols are coagulated by a mixture of electrolytes, the coagulative power of the mixed electrolytes is an additive function of the coagulative powers of the individual electrolytes. In other words, towards mixed electrolytes the behaviour of negatively charged stannic hydroxide, ferric hydroxide, and chromium hydroxide may be said to be normal. Similar results have been obtained by Weiser (*loc. cit.*) with a mixture of electrolytes towards $Sn(OH)_4$. Recently Freundlich and Scholz (*loc. cit.*) have shown that with colloidal gold and Weimarn's sulphur sol the action of the precipitating cations showed an additive relationship, while the precipitating action was not additive with arsenious sulphide sol and Odèn's sulphur sol particularly with mixtures of ions having widely varying precipitating powers. Very recently Weiser has shown that the behaviour with a mixture of electrolytes of positively charged chromium hydroxide sol is normal; in other words, an additive relationship is observed in the coagulation of positively charged chromium hydroxide sol by mixtures of ions having widely different precipitating powers. Similarly, more or less additive relationship was observed with

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[1] Compare Neisser and Friedemann: Münchener Med. Wochenschrift, **51**, 827 (1904).

ferric hydroxide by Weiser. Our results with mastic sol show that this sol is abnormal. Consequently sols can be divided into two distinct classes, one of which is normal whilst the other class is abnormal as far as their behaviour with mixed electrolyte is concerned, thus:—

TABLE XII

Normal	Abnormal
$Cr(OH)_3$ positive	As_2S_3
$Fe(OH)_3$ negative	Sb_2S_3
$Cr(OH)_3$ negative	Mastic
$Fe(OH)_3$ positive	Sulphur(Odèn)
$Sn(OH)_4$ negative	
Gold (Donau)	
Sulphur(Weimarn)	

From Table XII it will be seen that $Cr(OH)_3$ both positive and negative, $Fe(OH)_3$ both positive and negative, negatively charged $Sn(OH)_4$, Weimarn's S sol and gold sol show additive relationship when coagulated with electrolytes having widely varying coagulating powers. It must be observed that $Fe(OH)_3$ and $Cr(OH)_3$ both positive and negative, and $Sn(OH)_4$ negative follow the general dilution rule that the greater the concentration of the sol the greater the amount of electrolyte necessary for coagulation. As_2S_3, Sb_2S_3, mastic, sulphur (Odèn) *do not show additive relationship* in their coagulation by a mixture of electrolytes and these very sols do not follow the general dilution rule that the greater the concentration of a sol the greater the amount of electrolyte necessary for coagulation. Consequently we were led to the conclusion that those sols which follow the general dilution rule that the greater the concentration of the sol the greater is the amount of electrolyte necessary for coagulation, should behave normally with a mixture of electrolytes in their coagulation. In other words, there is an intimate connection between the dilution effects of sols and their behaviour with mixture of electrolytes.

Weiser and Nicholas[1] have shown that prussian blue on dilution takes less electrolyte for coagulation; in other words, this sol follows the general dilution rule.

We expected that prussian blue will also behave normally when coagulated by a mixture of electrolytes.

F. *Prussian Blue.*

In order to verify this conclusion we made some preliminary experiments on the coagulation of prussian blue by mixture of electrolytes. The sol was prepared by washing the precipitate of prussian blue obtained by treating a solution of $FeCl_3$ with $K_4Fe(CN)_6$. The sol was dialysed till it showed no tests for either $Fe^{\cdots}$ or $Fe(CN)_6''''$ ions. We find that prussian blue does not behave normally as experimental results in Table VIII show:

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[1] J. Phys. Chem. 25, 742 (1921).

TABLE XIII

Concentration of the sol = 7.54 grs per litre
Sol taken = 1 cc; Volume = 10 cc

KCl N/4 added	$BaCl_2$ N/125 added	$BaCl_2$ N/125 Calculated
1.75 cc coagulated in ½ hour	——	——
——	2.80 cc coagulated in ½ hour	——
0.4 cc	Did not coagulate with 2.1 cc in ½ hour, but showed coagulation with 2.30 cc)	2.15 cc to coagulate in ½ hour.
0.8 cc	Did not coagulate with 1.70 cc. On adding 0.2 cc more after ½ hour it coagulated.)	1.52 cc to coagulate in ½ hour.

Having observed this anomaly we were led to study the effect of dilution on the coagulation of prussian blue by potassium and barium chlorides. From the results of Weiser and Nicholas (*loc. cit.*) we find that the amount of KCl necessary to coagulate a sol of prussian blue which is diluted ten times is only 14% less than the amount of KCl necessary to coagulate the sol which is ten times stronger. Whilst in the coagulation of chromium hydroxide sol the amount of KCNS required to coagulate a sol which is ten times diluted is only 1/3 of the amount of KCNS required to coagulate the stronger sol.

From our preliminary experiments we find that a dilute sol of prussian blue takes more of KCl and less of $BaCl_2$ than the concentrated sol for its coagulation as the preliminary experiments in Table XIV show:

TABLE XIV

Sol A = 1 cc of the original sol containing 7.54 grs of prussian blue made to 10 cc by mixing electrolytes
Volume = 10 cc

Concentration of the sol	KCl N/4	$BaCl_2$ N/125
A	Coagulated with 1.75 cc in ½ hour	Coagulated with 2.80 cc in ½ hour
A/10	Did not coagulate with 2.1 cc in ½ hour	Coagulated with 2.80 cc before ½ hour

Hence it appears that the behaviour of prussian blue is not normal as shown by Weiser and Nicholas but is abnormal towards its coagulation both by KCl and by a mixture of electrolytes. These experimental results on the coagulation of prussian blue strengthen the view that the abnormal dilution effect and abnormal coagulation by mixed electrolytes go hand in hand.

Similarly colloidal gold (Donau's method) and Weimarn's sulphur which are found to behave normally with mixtures of electrolytes should follow the general dilution rule. This is practically all the literature available on the subject. We are trying to extend observations on other sols.

It seems certain that the deviations of the sols from the general dilution rule and from additive relationships towards mixtures of electrolytes are based on the same phenomenon. Substances like As_2S_3, Sb_2S_3, etc., adsorb appreciable quantities of ions carrying the same charge as that on the sol and hence they are stabilised on the addition of univalent electrolytes and thus they require greater quantities of bivalent ions for charge neutralisation and coagulation; that is why these sols do not show additive relationship when coagulated by a mixture of electrolytes.

"Acclimatization" of Sols

It is an interesting fact that the amount of an electrolyte necessary to coagulate a sol completely is influenced by the rate at which the electrolyte is added. Since an amount of the electrolyte necessary for complete coagulation when the addition is slow, the colloid is said to become acclimatized to the presence of the electrolyte and the phenomenon is called acclimatization.

It should be emphasised that the phenomenon of acclimatization of sols first observed by Freundlich[1] can be satisfactorily explained from the point of view of the adsorption of the ion carrying the same charge as the sol. Freundlich observed "the amount of barium chloride solution containing 9.55 millimoles of $BaCl_2$ per litre, necessary to precipitate completely in two hours an arsenious sulphide colloid containing 5.752 millimoles of As_2S_3 per litre. The same amount of electrolyte, 2 cc, was next added drop-wise to the same amount of colloid 20 cc in 18 hours, 27 days, and 45 days respectively. After the addition of each drop the solution was shaken once. Two hours after the addition of the last drop the solutions were filtered and it was found that the filtrate was still quite cloudy—the cloudiest solution being the one to which the electrolyte was added slowest. In order to precipitate the remainder of the first solution completely 1.5 cc of the same barium chloride solution was added and after two hours it was clear.

"To 20 cc of a colloid containing 20.45 millimoles of $Fd(OH)_3$ per litre was added 2 cc of magnesium sulphate solution containing 4.82 millimoles per litre. The addition was made drop-wise in the course of eight days, after each addition the flask was shaken once. Although a salt solution of this concentration precipitated the colloid completely after two hours, by this slow addition the solution was not entirely clear two hohrs after the last drop was added and the filtrate still contained ferric hydroxide. The addition of three drops (0.13 cc) more of magnesium sulphate solution was sufficient to coagulate the remainder within an hour."

From the foregoing quotation it is evident that with As_2S_3 the phenomenon of acclimatisation is more pronounced than with ferric hydroxide.

Similar results are obtained by Weiser[2] who observed that "whereas 1.8 cc N/50 $K_2C_2O_4$ will certainly cause a complete precipitation in one hour when added all at once, the precipitation was not complete one hour after the

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[1] Z. Physik. Chem. 44, 143 (1903).

[2] J. Phys. Chem. 25, 397 (1921).

addition of the electrolyte by the slow method. By adding 0.1 cc more and allowing to stand one hour more a filtrate clear from colloidal ferric hydroxide was obtained." With arsenious sulphide Weiser obtained the following results. "Precipitation values were determined for strontium chloride and potassium chloride. On rapid addition, 2.05 cc of N/50 $SrCl_2$ and 2.50 cc N/2 KCl were necessary to precipitate completely 20 cc of colloid. The slow addition of the electrolyte in 0.1 cc portions over a period of approximately 36 hours required 2.50 cc of $SrCl_2$ and 2.70 cc of KCl solutions."

Moreover, according to the above observations of Freundlich, partial precipitation of the sols took place in arsenious sulphide as well as with ferric hydroxide. It has been already noted that As_2S_3, Sb_2S_3, etc., markedly adsorb the ion carrying the same charge as the sol; consequently when drops of $BaCl_2$ are added to a sol of As_2S_3 as has been done by Freundlich, the sol is appreciably stabilised by the adsorption of chloride ions and so greater quantities of $BaCl_2$ are now necessary to coagulate the sol completely. On the other hand, ferric hydroxide does not appreciably adsorb the ion carrying the same charge and that is why they are not appreciably stabilised by the addition of a few drops, say of magnesium sulphate; consequently very slow addition of an electrolyte to ferric hydroxide sol produces only a slight increment in the amount necessary for coagulation.

We venture to suggest that sols like As_2S_3, Sb_2S_3, mastic, etc., which show abnormal dilution effect and are abnormal in their behavious towards mixed electrolytes should show this phenomenon of acclimatization more markedly than sols like $Fe(OH)_3$, $Cr(OH)_3$, etc., which follow the general dilution law and are normal towards mixed electrolytes. We are strongly of the opinion that the three phenomena, viz. (1) the abnormality of sols to follow the general dilution rule (2) the abnormality towards mixed electrolytes and (3) the phenomenon of acclimatization are essentially connected and are mainly due to the adsorption of the ion carrying the same charge as the sol.

Weiser has tried to explain the phenomenon of acclimatization from the point of view of the adsorption of ions by the coagulated mass. There is no doubt that the coagulated mass adsorbs electrolytes. Freundlich has observed in his experiments that partial coagulation takes place not only with As_2S_3 but also with $Fe(OH)_3$ and as a matter of fact a little of the precipitating electrolyte is adsorbed by the coagulated As_2S_3 or $Fe(OH)_3$. From our experiments on the adsorption of electrolytes by coagulated substances we find that $Fe(OH)_3$ can adsorb ions appreciably from solutions and Freundlich[1] has shown that coagulated As_2S_3 adsorbs slightly several ions. From our preliminary experiments we are of the opinion that freshly precipitated $Fe(OH)_3$ is a better adsorbent than As_2S_3. Consequently the explanation of the phenomenon of acclimatization advanced by Weiser is certainly incomplete because it cannot explain the occurrence of the phenomenon of acclimatization more markedly with As_2S_3 than with $Fe(OH)_3$. In this respect our explanation stands on a better footing than that of Weiser.

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[1] Z. physik. Chem. 73, 385 (1916).

We have made preliminary experiments on the acclimatization of mastic sol towards KCl and of negatively charged ferric hydroxide sol with $BaCl_2$. With mastic the following results are obtained:—When KCl is added very rapidly (the addition of the total volume of electrolyte necessary for coagulation is finished in a few seconds) to 4 cc of mastic sol containing 1.2528 grams per litre, the sol requires 1.9 cc N/8 KCl for complete coagulation and settling in 18 hours. When 0.3 cc of N/8 KCl is added at the interval of 45 minutes, and the addition is completed in about 6 hours, the sol takes 2.35 cc N/8 KCl for complete coagulation and settling in 24 hours.

With negatively charged ferric hydroxide sol the following results are obtained:—When $BaCl_2$ is added very rapidly to 2 cc of the negatively charged $Fe(OH)_3$ sol and the total volume is made to 10 cc the sol requires 0.5 cc N/25 $BaCl_2$ for complete coagulation and settling in 48 hours. When N/25 $BaCl_2$ is added drop by drop to the same volume of the sol and the addition was carried on for 24 hours, complete coagulation and settling of the sol did not take place in 48 hours, till 0.55 cc of N/15 $BaCl_2$ was added.

Accordingly our experiments prove that acclimatization is more pronounced with mastic than with negatively charged ferric hydroxide, although both these sols show the phenomenon of partial precipitation.

Ageing of Sols

In previous papers (*loc. cit.*) we have investigated the effect of ageing on sols like Sb_2S_3, As_2S_3, etc. We have observed that 5 cc of a sol of Sb_2S_3 containing 2 grs. of pot. antimony tartrate per litre when freshly prepared takes 0.85 cc N/25 NaCl for complete precipitation, whilst the same amount of the sol kept for 33 days can be precipitated by only 0.70 cc NaCl.

Similarly we have obtained the following results with As_2S_3:—

TABLE XV

Concentration of the sol = 0.922 grm. per litre; Vol. = 10 cc

Time = ½ hour

Electrolyte	cc to coagulate	cc to coagulate after one month
KCl N/2	2.0 cc	1.80
K_2SO_4 N/1	1.25	1.15
$BaCl_2$ N/50	1.30	1.25

Moreover in this paper we have repeatedly observed that the effect of ageing is more pronounced when Sb_2S_3 sol is coagulated by KCl, NaCl, etc., than when the same sol is coagulated by bivalent and trivalent ions.

Consequently we are of the opinion that the effect of ageing will be more noticeable when sols like Sb_2S_3, As_2S_3, mastic, etc., are precipitated by univalent cations than when the above sols are coagulated by bivalent and trivalent cations and this phenomenon should be more pronounced with the above sols than with sols like $Fe(OH)_3$, $Cr(OH)_3$, etc., which hardly adsorb ions carrying the same charge as the sol. It appears that on ageing the electric charge on colloidal particles decreases very little, whilst the capacity for the adsorption of ions carrying the same charge is decreased appreciably and hence the ageing effect is pronounced with Sb_2S_3, As_2S_3, etc., when coagulated by KCl, NaCl, etc.

We have frequently observed that the adsorptive power of freshly precipitated $Fe(OH)_3$, $Cr(OH)_3$, etc., for negative ions is greatly reduced on ageing. Moreover, we have noted that precipitated $Fe(OH)_3$, $Cr(OH)_3$, etc., prepared about a year ago and kept in contact with water change colour; the deep brown ferric hydroxide becomes deep red and the green $Cr(OH)_3$ becomes grayish, and their chemical activity is greatly decreased. The "aged" precipitates do not dissolve in concentrated HCl at the ordinary temperature, whilst the freshly precipitated substances dissolve very readily in HCl. We are carrying on experiments on ageing with different substances under various conditions.

Discussion

Let us try to visualise what takes place when positively charged ferric hydroxide sol is coagulated by a mixture of KCl and $K_2C_2O_4$. When a few drops of potassium chloride solution are added to ferric hydroxide sol the chloride ion is attracted by the positively charged sol and at the same time a very small quantity of potassium ion can also be taken up by the sol. In this case the ratio of the adsorption of chlorine ion to that of potassium ion is always greater than unity, as the sol is likely to adsorb a little potassium ion also and hence it should be very slightly stabilised. Apparently the effect of the adsorption of potassium ion by ferric hydroxide would have been that a slight excess to that of the calculated amount of potassium oxalate would have been necessary to coagulate the sol completely. But from experimental results we find that a slightly less amount of potassium oxalate is sufficient to coagulate a sol of ferric hydroxide to which KCl has already been added. This is because, as Weiser has pointed out, more adsorption takes place from dilute solutions than from concentrated ones of the electrolytes. The adsorption of chlorine ion or of oxalate ion is relatively greater at concentrations below their precipitation values. As the sol is precipitated by a mixture of KCl and $K_2C_2O_4$ the concentration of each electrolyte in the mixture will be less than its precipitation concentration and hence the percentage of adsorption of chlorine ion or of oxalate ion will be greater in the mixture than when the sol is coagulated by KCl or by $K_2C_2O_4$ separately[1]. So that relatively less oxalate is necessary to bring the combined adsorption of chloride and oxalate above the critical value necessary for neutralisation and coagulation. This second factor is certainly more predominating and more than counterbalances this very slight stabilisation of the sol due to the slight adsorption of potassium ion, consequently the precipitation values for a mixture of KCl and $K_2C_2O_4$ towards ferric hydroxide are slightly less than additive. An exactly similar explanation can be given in the coagulation of chromium hydroxide, negative stannic hydroxide, negative ferric hydroxide, etc. It must be stated clearly that in some cases the precipitation

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[1] Compare Chatterji and Dhar: Kolloid-Z. 33, 18 (1923).

values with a mixture of electrolytes with widely varying precipitation powers may be exactly additive provided there is no complication, or the opposing factors mutually annul each other.

On the other hand, with sols like arsenic sulphide, antimony sulphide, mastic, etc., we observe certain complications. Weiser has shown with arsenic sulphide and we have shown with antimony sulphide that in presence of monovalent ions like $K^{\cdot}$, $Li^{\cdot}$, etc., the adsorption of Ba ions by the sulphide sols is greatly decreased. We have also proved experimentally that the adsorption of K ion is also decreased by the presence of $Ba^{\cdot\cdot}$, consequently the precipitating action of a mixture of electrolytes (KCl and $BaCl_2$) towards Sb_2S_3 sol is not additive; but a relatively higher concentration of the bivalent ion is necessary to secure neutralisation of the sulphide sol by adsorption in the presence of K or Li ion.

From our experiments on the adsorption by Sb_2S_3 from a mixture of KCl and $BaCl_2$ at the precipitating value we find that the presence of KCl decreases the adsorption of $Ba^{\cdot\cdot}$ to the extent of 55% and the adsorption of potassium ion is also depressed to the extent of 56%. Weiser has shown that at the precipitation concentration of a mixture containing 1/8 the precipitation value of LiCl alone the adsorption of Ba is lowered more than 25 per cent; whilst from a mixture containing 1/2 the precipitation value of LiCl alone the adsorption of $Ba^{\cdot\cdot}$ is decreased 53%. Weiser has made no experiments on the adsorption of Li ion is presence of Ba ion.

It must be observed that the decrease of adsorption of a bivalent ion in presence of monovalent electrolytes need not be a general phenomenon; certain cases are actually known for example in the coagulation of $Fe(OH)_3$, $Cr(OH)_3$, etc., in which the presence of an excess of chlorine ions does not affect the adsorption of bivalent ions (SO_4'', C_2O_4'') appreciably.

There is another important factor in the precipitation of sols like antimony sulphide, mastic, etc., by mixtures of electrolytes. When a few drops of KCl are added to the sol of antimony sulphide the K ions are adsorbed and at the same time the adsorption of Cl ions also takes place. If we now precipitate the sol with say $BaCl_2$ we find that the amount of $BaCl_2$ necessary for the complete coagulation of the sol is greater than the amount of $BaCl_2$ necessary in absence of KCl; consequently we cannot escape from the conclusion that in presence of small quantities of KCl the sol of antimony sulphide is made more stable than in its absence and this can only happen by the adsorption of a greater quantity of Cl ion than that of potassium ion. In other words, when a few drops of KCl are added to a sol of Sb_2S_3 we have to assume that the ratio of adsorption of potassium ion to chlorine ion is less than unity. Now because the sol of Sb_2S_3 can actually be precipitated by KCl we are also forced to the conclusion that at the precipitating concentrations or at higher ones of the electrolyte the ratio of adsorption of K to Cl must be greater than unity. In other words, the ratio of adsorption of K to that of Cl goes on increasing as the concentration of the electrolyte becomes greater and greater. From this point of view it seems pretty clear that certain ionic antagonisms would also be noticeable in the coagulation of these sulphides or mastic sols even when they are precipitated by a mixture of say KCl and NH_4Cl. We have assumed that the addition of a few drops of KCl makes the sol of As_2S_3 more stable owing to amount of adsorption of Cl ions being greater than that of potassium ions, consequently this stabilised sol should require more of say NH_4Cl for its coagulation than in the absence of KCl. Unfortunately there is very little experimental work in this line. The only data available are those of Linder and Picton on the coagulation of As_2S_3 by a mixture of HCl and NH_4 or HCl and HNO_3, or HNO_3 and K_2SO_4. In all these cases instead of adding only a few drops of the stabilising electrolyte they have at first added 2 cc or more of the electrolyte in question whilst about 4 cc is necessary for complete coagulation. We have already pointed out that the ratio of adsorption by say As_2S_3 of positive ions and negative ions goes on increasing and becomes greater than unity at the precipitating concentration. Consequently when 2 cc or more of the stabilising electrolyte is first added the ratio of the adsorption of positive ions to the negative ions may be unity or greater and hence the sol is not at all stabilised by its addition and approximately the calculated amount of the second electrolyte is actually needed for complete coagulation. In order to find out the stabilising influence of the first electrolyte on the sol it is necessary to add only a few drops of the electrolyte and then only the ratio of the adsorption of positive to negative ions woold be less than unity and hence the sol would be actually stabilised.

It has been already observed that in presence of Ba ions the adsorption of K ions by antimony sulphide is appreciably decreased. Consequently in presence of Ba ion the ratio of the adsorption of K to that of Cl can be easily less than unity and hence the sol would appear to be stabilised towards Ba ion if a little of KCl be already present in the sol.

In explaining the phenomenon of acclimatization of a sol we have observed that when only a few drops of barium chloride are added to a sol of arsenious sulphide, the sol may adsorb the Cl ions along with Ba ions and consequently when it is precipitated by say $Al(NO_3)_3$ the amount of $Al(NO_3)_3$ taken will be greater than the calculated amount because of the slight stabilisation of the sol produced by the adsorption of a few Cl ions from $BaCl_2$. This phenomenon will be more marked with mastic when coagulated by $BaCl_2$ and $Al(NO_3)_3$, or $MgCl_2$ and $Al(NO_3)_3$ because the coagulating power of the bivalent ions, $Ba^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ is not preponderantly greater than that of monovalent ions whilst the precipitating action of trivalent ions is very much greater than that of bivalent ions; consequently in presence of a few drops of $BaCl_2$ mastic will be stabilised by the adsorption of more Cl ions than Ba ions and hence the sol is likely to take up more of $Al(NO_3)_3$ in the presence of a few drops of $BaCl_2$ than in the absence of $BaCl_2$. Experimental work in these lines is in progress in this laboratory.

Finally we have to take into account the decrease of the degree of dissociation of the bivalent electrolytes in presence of an excess of the univalent electrolyte. For example in the coagulation of AS_2S_3 or Sb_2S_3 the amount of the monovalent salts required to coagulate a sol is about fifty times greater than the bivalent salt, consequently when these sols are precipitated by mixtures of monovalent and divalent salts there will always be an excess of the monovalent electrolyte and consequently in its presence the degree of dissociation of the bivalent electrolyte will be depressed due to the presence of an excess of the common ion say Cl^1 and consequently more of the bivalent electrolyte would be necessary for the coagulation of the colloids.

We have proved that in the coagulation of negative $Cr(OH)_3$, $Fe(OH)_3$, $Sn(OH)_4$, Sb_2S_3, etc., far greater quantities of K_2SO_4, $K_4Fe(CN)_4$, potassium citrate, etc., are necessary than of KCl. Similar results were obtained by Linder and Picton with As_2S_3 and by Weiser with prussian blue. One reason for this phenomenon is that the bivalent and polyvalent negative ions are more adsorbed by the negative sols than the monovalent ions, the other reason is that the salts with bi and polyvalent ions are less ionised than the salts with univalent ions. Consequently in order to obtain the necessary amount of adsorption for neutralisation and coagulation greater quantities of the electrolytes with polyvalent ions are necessary.

From the results of Weiser we find that when AS_2S_3 is coagulated by one electrolyte alone the amounts of electrolytes necessary for coagulating a definite volume of the sol are in the following proportions:

$LiCl : BaCl_2 = 50.5$; $LiCl : MgCl_2 = 46.6$; $HCl : MgCl_2 = 21.8$

Consequently the coagulation of As_2S_3 by a mixture of LiCl and $BaCl_2$ should show greater deviation from the calculated results than that obtained in the coagulation of the same sol by a mixture of LiCl and $MgCl_2$ because the coagulating power of $MgCl_2$ is not as widely divergent as that of $BaCl_2$ from LiCl. In other words, the behavious of $MgCl_2$ as a coagulating agent towards As_2S_3 is more akin to LiCl than that of $BaCl_2$ to LiCl; hence it is expected that with a mixture of LiCl and $MgCl_2$ in the coagulation of As_2S_3 more additive relationship should be noticeable than in the coagulation of the same sol by LiCl and $BaCl_2$. As a matter of fact, however, the results obtained by Weiser are otherwise. The coagulation of As_2S_3 by a mixture of LiCl and $MgCl_2$ shows a greater divergence from the additive relationship than with a mixture of LiCl and $BaCl_2$ in all the data of Weiser[1]. More or less similar results have been obtained by Freundlich and Scholz. These results seems to be anomalous. On the other hand, the results obtained by Weiser with a mixture of HCl and $MgCl_2$ seem quite normal. The coagulating ratio of HCl to $MgCl_2$ towards As_2S_3 is only 21.8; in other words HCl is a much better coagulating agent than LiCl. We have already emphasised that additive relationships are obtained with mixed electrolytes when the coagulating powers of the electrolytes are of the same order. Consequently in the coagulation of As_2S_3 by a mixture of HCl and $MgCl_2$ we ought to get more of additive relationship than with either LiCl and $BaCl_2$ or LiCl and $MgCl_2$. The results of Weiser actually confirm the above conclusion.

Weiser has observed: "It will be noted that LiCl has a more marked effect on the precipitation value of $MgCl_2$ than of $BaCl_2$. This is exactly what one

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[1] Compare Weiser: J. Phys. Chem. 28, 239 (1924) Tables 7 and 8.

would expect in view of the fact that the adsorption of Mg ions is not so great as that of Ba ion as evidenced by the higher precipitation value of $MgCl_2$."

If we accept the above statement of Weiser we should have also observed the marked effect of univalent salts like NH_4Cl in the coagulation of arsenious sulphides by HCl because the amount of adsorption of NH_4 ion and H ion should be more or less identical and should influence each other a great deal; as a matter of fact experimental results show that the precipitation values of NH_4Cl and HCl towards As_2S_3 are more or less additive. Similarly it is difficult to understand according to the point of view of Weiser why additive relationships are obtained in the coagulation of As_2S_3 by a mixture of $BaCl_2$ and $MgCl_2$ because the adsorption of Ba and of Mg would be affected by each other.

In a recent paper Frankfert and Wilkinson[1] have studied the adsorption of ions by copper ferrocyanide. They have observed that when copper ferrocyanide is shaken with KCl or KNO_3 or K_2SO_4 the filtrate is acid, whilst the filtrate after shaking with barium nitrate is practically neutral and with aluminum salts the filtrate is alkaline. Some of the results obtained by the above authors seem very peculiar and we are making experiments on the adsorption of substances by copper ferrocyanide and prussian blue.

In the foregoing papers we have proved that MnO_2, which is a negatively charged sol, can adsorb the basic part from salt solutions leaving the filtrate acid in all cases, whilst $BaSO_4$, $Fe(OH)_3$, $Cr(ON)_3$, etc., which are positively charged can adsorb the acidic portion of a salt solution leaving the filtrate alkaline. Similarly silica[2] can adsorb basic portion from salt solutions setting free the acid. Moreover Weiser[3] has shown that when NaCl is shaken with freshly precipitated $Cu(OH)_2$ alkali is set free. We have also shown that when a sol of mastic is coagulated by KCl, acid is set free. The results of Linder and Picton on the generation of acids by the coagulation of As_2S_3 sol by neutral salts are well known. Similarly, acid is set free when Sb_2S_3 sol is coagulated by KCl, $BaCl_2$, etc. It seems pretty clear therefore that negatively charged sols when coagulated by a salt can set free acid in the filtrate whilst positively charged sols give out alkali in the filtrate. Copper ferrocyanide as ordinarily prepared is negatively charged. But the amount of charge carried by particles of copper ferrocyanide is extremely small as we have repeatedly seen in cataphoretic experiments that the sol moves extremely slowly under the influence of electrical force. Hence the sol readily coagulates by the adsorption of a very small quantity of positive ions and at the same time the precipitated substance can also adsorb negative ions because of chemical affinity of the sol for negative ions and can again pass into a negatively charged sol. Moreover the substance is likely to form a positively charged sol by the preferential adsorption of positive ions from an electrolyte. With KCl the sol gets coagulated by the adsorption of K ions setting free HCl. If potassium ferrocyanide is added to the sol of copper ferrocyanide, at first the sol may be coagulated by the ad-

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[1] J. Phys. Chem. 28, 651 (1924).

[2] Glixelli: Compt. rend. 176, 1714 (1923).

[3] J. Phys. Chem. 27, 501, (1923).

sorption of positive ions; immediately the neutralised particles will readsorb ferrocyanide ions because of the chemical affinity of the neutralised particles for the ferrocyanide ions, setting free alkali. Frankfert and Wilkinson have added alkali to make the aluminum salts neutral. Apparently they have got in their aluminum solutions negatively charged $Al(OH)_3$ peptised by OH ions, consequently when copper ferrocyanide is added to such a mixture, the aluminum hydroxide gets coagulated as we have repeatedly observed leaving free the caustic alkali. That is why the above authors have always got the liberation of alkali with their aluminum salts and copper ferrocyanide. If a solution of pure $Al(NO_3)_3$ or $AlCl_3$ is used with copper ferrocyanide, free acid is liberated in the coagulation, in addition to the acid already existing in the solution due to the hydrolyis of aluminum salts. The negatively charged copper ferrocyanide adsorbs aluminum ions from Al salt solutions and sets free equivalent amount of acids, as there is very little preferential adsorption of Cl or NO_3 ions by copper ferrocyanide.

Prussian blue, mastic, etc., should behave like copper ferrocyanide because these substances are usually very feebly charged and are of an amphoteric nature.

In a previous paper[1] we have investigated the effect of neutral salts on the adsorption of copper and iron from solutions of copper sulphate and ferric chloride by hydrated manganese dioxide. Sodium chloride in normal or double normal concentrations has very little effect on the adsorption of copper, whilst ammonium chloride has a very small depressing effect. Sodium sulphate in normal solutions has a slight repressing effect. Ammonium sulphate in increasing concentrations decreases adsorption and the same effect is observed with KCl. The effect of an addition of dilute HNO_3 is to depress the adsorption of $Ag^{\cdot}$ ion from $AgNO_3$ by hydrated MnO_2.

Substances like cane sugar and alcohol which decrease the surface tension of water also decrease the adsorption of silver from $AgNO_3$ by hydrated MnO_2.

Linder and Picton[2] have shown that when As_2S_3 is precipitated by $BaCl_2$ or $SrCl_2$ the metallic radicles are adsorbed by the coagulated substance. If the coagulated sulphide is shaken with KCl or NaCl the adsorbed metal is displaced by $Na^{\cdot}$ or $K^{\cdot}$ and comes out in the solution. We have found that hydrated MnO_2 containing some adsorbed copper loses its copper when shaken with KCl or NaCl or the aqueous solution of any other electrolyte.

It appears therefore that the adsorption of hydrated MnO_2 will depend mainly on two factors (1) the adsorbability of the positive ion and (2) on the concentration of the ion which is going to be adsorbed. From our experiments on hydrated MnO_2 we find that from equivalent solutions of $NaNO_3$ and $AgNO_3$ more of silver is adsorbed than sodium, but adsorbed silver can be displaced by sodium by shaking the hydrated MnO_2 containing silver with a large excess of $NaNO_3$. In other words the tendency of silver ions to be adsorbed by MnO_2 in greater quantity than Na ion is counteracted by the large

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[1] Chatterji and Dhar: Kolloid-Z, 33, 18 (1923).

[2] J. Chem. Soc. 66, 63 (1895).

concentration of Na ion. Bearing the above facts in mind the following observation of Freundlich and Scholz would be very interesting: "At the first glance, our observations seem to be different in certain respects from this kind of biological action of electrolytes and from the ionic antagonism observed by Neuscholz[1] using lechithin sol. In both the latter cases it was frequently observed that the action of univalent cations could be nullified by the addition of divalent cations while the sulphur sol the action of divalent cation was decreased under the influence of univalent cations. This is probably only a superficial difference. The coagulation of the sulphur sol is realized only at such concentrations of univalent cations that small concentrations of divalent cations cannot annul their influence by displacing the adsorption. If we had studied small concentrations of univalent cations, we could have nullified their effect by divalent cations."

These conclusions of Freundlich are in agreement with the experimental observations already cited with hydrated MnO_2, As_2S_3 and Sb_2S_3 sols.

Lillie[2] has shown that cilia of the larva of a ringworm *Arenicola*, is liquefied by a solution containing sodium ion; the addition of a small amount of divalent cation stops this process. We can explain the above fact and other biological salt antagonisms in the following way:— The cells in the larva of a ringworm (or any other animal matter) are of an albuminous nature and like albumen are either weakly negative or weakly positive or may be neutral. We can assume that the cells are neutral or charged very slightly negatively, in presence of sodium chloride the cells would adsorb Cl ions due to chemical affinity and would become negatively charged and the larva would pass into liquid state. Now the addition of a little bivalent calcium ion would neutralize the negative charge due to the adsorption of Cl ions and would re-establish the original condition of the larva. There is a chemical analogy of this phenomenon of the change of mobility due to a adsorption of an ion, when sodium hydroxide is gradually added to a fairly concentrated solution of copper sulphate, copper hydroxide which is formed must be positively charged due to the adsorption of Cu ions, and the mixture is very mobile. If the addition of alkali is continued, a certain stage appears when the mobility of the system decreases considerably and a viscous bulky precipitate of cupric hydroxide is obtained. At this stage the whole of the copper is precipitated and the hydroxide is practically neutral. If more alkali is added the mixture becomes again mobile and the copper hydroxide becomes negatively charged due to the adsorption of OH ions and the precipitate becomes less bulky. Similar results are obtained in the precipitation of other hydroxides[3]. Moreover I have shown that ions occupy less volume than undissociated molecules[4].

Ringer[5] has shown that when the heart of a frog was perfused with a solution of sodium chloride, isotonic with the blood, the beats gradually diminished

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[1] Pflüger's Archiv. 181, 17 (1920).

[2] Am. J. Physiol 10, 433 (1904).

[3] Cf. Sen and Dhar: Kolloid-Z. 33, 193 (1923).

[4] Dhar: Z. Electrochem. 19, 748 (1913).

[5] J. Physiol 4, 29, 222 (1882).

in extent and ultimately ceased. If calcium chloride were added to the sodium chloride solution when the heart had ceased to beat, the excitability to stimuli returned and was soon followed by spontaneous beats.

In this case also we can assume that the chlorine ion from the sodium chloride solution is first taken up by the cells of the heart which become negatively charged. The addition of Ca ions, neutralises the charge and makes the heart more or less normal. It seems probable, therefore, that physiological salt antagonism is caused by the preferential adsorption of an univalent ion and its subsequent neutralisation by the bivalent oppositely charged ion or *vice versa*. It must be emphasised that animal cells are of a colloidal nature with large surfaces, behave more or less like amphoteric substances, and can readily take up either a feeble positive or a negative charge due to the adsorption of an ion.

Loeb[1] and coworkers, Osterhout[2] and others have shown that a marine *Gammarus*, *Fundulus*, etc., can only live in a mixture of NaCl, KCl and $CaCl_2$, and sometimes a mixture of NaCl, KCl, $CaCl_2$ and $MgCl_2$ is necessary.

In order to throw light on physiological salt antagonism, we are investigating the coagulation of various sols and adsorption with mixtures of two and three electrolytes.

Summary

1. Negatively charged stannic hydroxide has been obtained by the addition of $SnCl_4$ to a dilute solution of caustic soda and subsequent dialysis. The coagulation of the above sol by different electrolytes has been investigated. It has been found that the coagulation follows the Schulze-Hardy law with the exception of thorium nitrate.

2. The effect of the change in concentration of the sol on its coagulation by electrolytes has been investigated. It has been observed with this sol that the precipitation value of all electrolytes decreases with the decrease in the concentration of the sol. This result is in agreement with the general rule enunciated in a previous paper that the amount of electrolyte necessary for coagulation decreases with the decrease in the concentration of colloids, irrespective of the valency of the coagulating ion.

3. The influence of the change in concentration of mastic sol towards its coagulation by electrolytes has also been investigated. It is found that the behaviour of this sol towards dilution is abnormal and the precipitation value for KCl and $BaCl_2$ increases with the decrease in the concentration of the sol, whilst in the case of $Al_2(SO_4)_3$ the precipitation value decreases with decreasing concentration of the sol. It has been also observed that the coagulating power of $Ba^{\cdot\cdot}$ is only about seven times greater than that of KCl, whilst in the cases of other negatively charged sols, the coagulating power of Ba ion is approximately fifty times greater than that of K ion. Hence the sol is likely to adsorb appreciable quantity of chloride ion from either KCl or $BaCl_2$. This adsorp-

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[1] Pflüger's Archiv, 97, 394 (1903); Biochem. Z. 32, 308 (1911).

[2] Bot. Gazette, 42, 127 (1906).

tion of ions carrying the same charge as the colloid particles can explain the abnormal effect with KCl and $BaCl_2$ and the very low coagulating power of $BaCl_2$ towards mastic.

4. Preliminary experiments on the influence of dilution on the coagulation of prussian blue by monovalent $K^{\cdot}$ and bivalent $Ba^{\cdot\cdot}$ have been made. It has been found that the sol shows an abnormality towards dilution with KCl and is normal with $BaCl_2$. Weiser and Nicholas (*loc.cit.*) have, however, obtained normal behavior with KCl towards dilution of this sol.

5. Coagulation experiments have been made with Sb_2S_3, mastic, stannic hydroxide (negative), prussian blue, ferric-hydroxide (negative) and chromium hydroxide (negative). The behaviour of negatively charged stannic hydroxide, ferric hydroxide, and chromium hydroxide is normal; in other words, practically additive relationship of precipitation value has been obtained with the above hydroxide sols when precipitated by mixture of electrolytes having widely varying precipitating powers. On the other hand, Sb_2S_3, mastic, and prussian blue behave abnormally with mixture of electrolytes; in other words, the precipitation values of mixture of electrolytes of widely varying precipitating powers are always greater than the additive values.

6. The phenomenon of acclimatization can be explained from the point of view that colloid particles can adsorb ions carrying the same charge as the colloid. It follows, therefore, that As_2S_3, Sb_2S_3, mastic, etc., which are known to adsorb negative ions markedly should show this phenomenon of acclimitization more markedly than $Fe(OH)_3$ positive and negative, $Cr(OH)_3$ positive and negative, etc., which hardly adsorb ions carrying the same charge. Experiments of Freundlich and of Weiser show that As_2S_3 sol shows this phenomenon of acclimatization to a greater extent than positive $Fe(OH)_3$ sol. Our preliminary experiments also show that this phenomenon is more marked with mastic sol than with negatively charged $Fe(OH)_3$.

7. We are of the opinion that the three phenomena (a) abnormality of the sols to follow the general dilution rule, (b) abnormal behaviour towards mixture of electrolytes and (c) acclimatization are essentially connected and are mainly due to the adsorption of ions carrying the same charge as the sol. Thus As_2S_3, Sb_2S_3, S(Odèn), mastic, and Prussian blue behave abnormally towards dilution as well as with a mixture of electrolytes. On the other hand, $Fe(OH)_3$ positive and negative, $Cr(OH)_3$ positive and negative; $Sn(OH)_4$ negative, etc., are normal towards dilution as well as with a mixture of electrolytes. Moreover, the phenomenon of acclimatization has been found to be more pronounced with As_2S_3, mastic, etc., than with $Fe(OH)_3$ negative and positive.

8. It appears that the effect of ageing of sols is more pronounced with sols like Sb_2S_3, As_2S_3, etc., when coagulated by univalent salts like NaCl, KCl,etc.

9. When Sb_2S_3 sol is coagulated by a mixture of $BaCl_2$ and KCl, the adsorption of Ba ion is decreased to a great extent (55%) due to the presence of potassium ion, and the adsorption of potassium ion is also decreased (56%) due to the presence of barium ion. The sum of the adsorption of potassium and

barium ion expressed as equivalents is greater than the adsorption of barium ion when coagulated by $BaCl_2$ alone but less than that of K ion when coagulated by KCl alone. This has been explained from the view that ions of high precipitation values are adsorbed more than ions of low precipitation values.

10. "Ionic antagonism" need not be confined to cases where sols are coagulated by a mixture of electrolytes of widely varying precipitating powers. A certain amount of "ionic antagonism" should be noticeable when sols like As_2S_3, Sb_2S_3, etc., are coagulated by mixture of univalent electrolytes.

11. Certain cases of physiological salt antagonism has been explained from the point of view of adsorption of negative ions by animal cells.

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DIFFUSION OF CARBON THRU TUNGSTEN AND TUNGSTEN CARBIDE

MARY R. ANDREWS AND S. DUSHMAN

Introduction

In a previous paper[1] it was shown that when carbon diffuses into tungsten at a high temperature, a compound, W_2C, is formed, and that the cold conductance of the material decreases linearly with the carbon content until, when complete conversion to W_2C has been attained, a minimum conductance of seven percent that of the tungsten is reached. Further carbonization leads to the formation of a second compound, WC, and a corresponding increase in conductance, since WC has a conductance of 40% that of tungsten.

In connection with this earlier investigation, a number of observations were made on rates of carbonization and decarbonization under various conditions. A brief discussion of the mechanism of carbonization based on these preliminary observations was given in the paper referred to above. However, in view of the interest in the general subject of diffusion in metals, it seemed of importance to carry out more careful measurements on these rates, particularly since other published work on diffusion has usually been done at much lower temperatures than those used here. The present paper contains the results of this investigation.

Experimental Conditions

(a) *Carbonization.*

As was shown in the earlier paper, the rate of carbonization of a tungsten filament heated in a hydrocarbon vapor may be limited either by the rate at which the hydrocarbon molecules reach the surface of the filament, or by the rate at which the carbon (deposited on the surface by decomposition of the hydrocarbon) diffuses into the interior. In order to obtain data on rates of diffusion, care was taken in our carbonization experiments to have the filaments saturated at the surface with carbon. This was accomplished by first heating the filaments at about 1800°K in naphthalene vapor at a pressure of several bars. Under these conditions, the surface of the filament became covered with carbon before diffusion into the metal had progressed appreciably. After this preliminary coating, the filament was brought quickly to the desired temperature and the rate of formation of the carbide at constant temperatures was observed by interrupting the heating at intervals to measure the cold resistance. During any run, the pressure of hydrocarbon was maintained above that necessary to keep the surface of the filament coated with carbon.

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[1] "Production and Characteristics of the Carbides of Tungsten." Andrews: J. Phys. Chem. 27, 270 (1923).

(b) *Decarbonization.*

When a carbonized filament is run at a high temperature in vacuum, the W_2C gradually decomposes and the carbon evaporates, leaving, if the process be carried to completion, a filament of pure tungsten of the same conductance as before carbonization. This loss of carbon *in vacuum* is extremely slow. We are indebted to Dr. Irving Langmuir for the suggestion that carbon would evaporate from the surface of the filament with great difficulty, and thus the rate of diffusion of carbon to the surface would be reduced. Following this reasoning, we measured the rate of loss of carbon from filaments at known temperatures in very low pressures of oxygen. From preliminary work, it was known roughly at what rates carbon diffused to the surface, and the pressures of gas were adjusted to cause several times as many molecules of oxygen to strike the filament as there were atoms of carbon reaching the surface. This excess of oxygen was necessary to ensure prompt removal of carbon from the surface, but it also led to the formation of oxide of tungsten, which vaporized. Increase in conductance due to loss of carbon was, therefore, partially counterbalanced by decrease of conductance due to loss of tungsten. As loss of carbon was greatest, and attack on the filament least during the first part of any run, only the initial data obtained during such a run were considered sufficiently reliable for the subsequent calculations. It is of interest to note that the product of decarbonization, even in the presence of a great excess of oxygen, is almost pure carbon monoxide, not more than a very small percentage of carbon dioxide being formed.

(c) *Temperature Determination.*

A great deal of difficulty was encountered at the beginning in maintaining a filament at constant temperature during carbonization. Color-matching against a tungsten filament operating at the desired temperature in vacuum, proved far from accurate. For filaments whose surfaces are pure tungsten, the most practical method is control of the watts radiated. However, the emissivity of a filament covered with a layer of carbon is obviously much greater than that of pure tungsten. It was therefore necessary to make separate observations for such filaments on the relation between watts radiated and temperature. For this purpose, measurements were made, at the same color temperature, of the watts radiated by tungsten filaments and similar filaments coated with carbon. At a color temperature corresponding to 1800°K for pure tungsten, it was observed that the carbon-coated filaments radiated 2.4 times as much as the tungsten filament, while at 2000°K the ratio was found to be 2.2. It is known that a black surface must be at a somewhat higher temperature than a tungsten surface to radiate light of the same color. Since the carbon-coated filaments were blacker than those of clean tungsten, it follows that the former were photometered at a somewhat higher true temperature than the latter. The difference was slight; but, for this reason, and because the carbon coating may have increased slightly the diameter of the filament, the factor 2.2 has been used. Thus, to maintain them at any desired temperature, the coated filaments were run at 2.2 times the watts radiated by the same-size tungsten filaments at this temperature.

The cooling effect of the naphthalene vapor was regarded as negligible because of the low heat conductivity of this vapor at the pressures used (which never exceeded ten bars).

Mathematical Theory of Diffusion in a Wire

During carbonization, the compound W_2C forms a shell on the outside of the unaltered tungsten core, and as carbonization proceeds, the thickness of the shell increases at a rate governed by that of *diffusion of carbon thru the carbide*. During decarbonization, carbon disappears from the outer layers of the filament, and at any instant the latter consists of a carbide core surrounded by a tungsten shell. Thus the rate of decarbonization depends upon the rate of *diffusion of carbon thru tungsten*. Diffusion in both these processes is analogous to the diffusion of heat during the formation of ice on the surface of the water.[1]

Let us consider a tungsten filament of radius R which has been partially carbonized, leaving a residual core of metal, of radius r. (See Fig. 1).

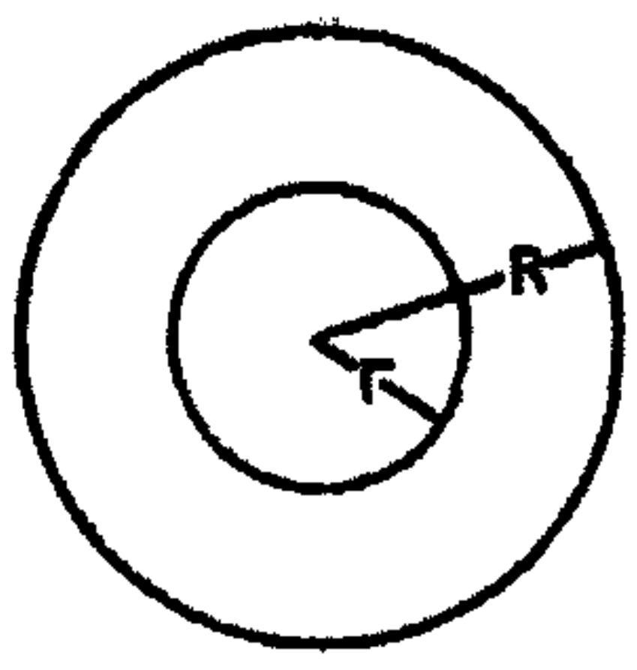

FIG. 1

Let C_1 denote the concentration of carbon (in grams/cm³) at the surface: That is, C_1 is the solubility of carbon in W_2C. We will assume that this concentration is maintained constant during carbonization.

Let C_2 denote the concentration of carbon dissolved in the tungsten and not present as W_2C. Thus C_2 is the solubility of carbon in metallic tungsten. Also, let C_o denote the amount of carbon required to convert unit volume of tungsten into W_2C. Assuming that the rate of formation of carbide is so rapid that the concentration gradient for carbon is linear thru the shell, the rate of penetration of carbon is given by the relation[2]

$$2\,C_o\,\pi\,r\,dr = \frac{2\pi\,D\,(C_1 - C_2)\,dt}{\log_e R/r} \qquad (1)$$

where D denotes the coefficient of diffusion of carbon thru W_2C.

The integral of equation (1) may be written in the form

$$\int_0^t K dt = \int_r^R r\,\log_e \frac{R}{r}\,dr$$

$$\text{or} \qquad Kt = -R^2 \int_x^1 x \log_e x\,dx \qquad (2)$$

$$\text{where } K = D\,\frac{(C_1 - C_2)}{C_o} \qquad (3)$$

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[1] Ingersoll and Zobel: "Mathematical Theory of Heat Conduction," Chap. 9.

[2] For an explanation of the derivation of this equation, the reader is referred to any treatise on heat conduction, as e.g., the book by Ingersoll and Zobel. Also see I. Langmuir: Convection and Radiation of Heat—Trans. Am. Electrochem. Soc. 23, 299 (1913.)

and $x = r/R$.

Integrating the right-hand side of equation (2) we get

$$\frac{4\,Kt}{R^2} = 1 - x^2 + 2x^2 \log_e x \qquad (4)$$

The simplest method of solving this equation is to plot the function $y = 1 - x^2 + 2x^2 \log_e x$ and thus obtain graphically values of $\frac{4\,Kt}{R^2}$ corresponding to given values of r^2/R^2. The value of $\frac{r^2}{R^2}$ is, of course, determined from conductance. Since the conductivity of W_2C is .07 of that of tungsten $\frac{r^2}{R^2} = \frac{S - .07}{.93}$ where S = the ratio of the conductivity of the partially carbonized filament to that of the original filament. Knowing the actual value of *t* corresponding to any value of r^2/R^2 it is possible to obtain the value of $K = \frac{D(C_1 - C)_2}{C_0}$. Since C_0 is known from the composition of W_2C we can calculate $D(C_1 - C_2)$ which we shall designate the *coefficient* of *penetration*.

The above calculations apply equally well to data obtained in decarbonization, with the single difference that concentration of carbon varies from C_2 to 0 instead of from C_1 to C_2. The coefficient of penetration in this case is, therefore, D_1C_2, where D_1 corresponds to the coefficient of diffusion thru tungsten.[1]

Rates of Carbonization and Decarbonization

It is evident that the experimental observations on rates of carbonization lead only to values of the *coefficient of penetration*. The methods used for the determination of C_1 and C_2 will be discussed in a subsequent section. Table I shows data obtained in a typical run on the rate of carbonization, while Table II gives similar data for a decarbonizing run.

TABLE I

Penetration in a 4 mil Wire at 2170°K

Total Time of Heating	Percent Conductance	r^2/R^2	$D(C_1 - C_2) \times 10^{10}$
0 min.	98.5		
1/2 min.	90.3	.894	18.6
1	84.5	.831	12.6
2	65.0	.622	25.4
3	54.1	.505	31.0
4 1/2	42.2	.378	34.8
6	30.7	.254	40.8
8	25.0	.193	38.0
13	19.1	.130	28.8
23	20.5		Average = 28.8

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[1] It is worth pointing out in this connection that the mathematical theory as presented above differs greatly from that which would apply to the case in which a solid solution is formed and not a chemical compound. The equations applying to the former case have been put in very convenient form for practical use by D. H. Andrews and J. Johnston: J. Am. Chem. Soc. 46, 640 (1924).

It will be observed that the minimum conductance was considerably above seven percent. This is undoubtedly due to the formation of a shell of the second carbide, WC, at the surface of the filament before the core was completely converted to W_2C. For this reason, the last two values of $D(C_1 - C_2)$ are lower than the preceding value. No satisfactory explanation has been found for the regular increase in the first six values. It may be due to the formation of longitudinal cracks in the filament which deepen as carbonization progresses. The existence of such cracks has been shown by microscopic examination. Or, it may be that the actual temperature of the conducting tungsten core rises (since the voltage rises) as carbonization progresses. Whatever the cause for this increase, it was thought best to take an average of all the values for $D(C_1-C_2)$ in any one run.

TABLE II

Decarbonization in Low Pressure of O_2
4 mil Filament at 2400°K

Total Time of Heating	Percent Conductance	r^2/R^2	$DC_2 \times 10^{10}$
0	23.3		
1/2 min.	44.7	.775	36*
1	50.3	.710	28
3	66.7	.533	27
8	86.0	.323	24
13	85.0		

*This value is regarded as the most accurate for the reasons given in a previous section.

Solubility of Carbon in Tungsten and in W_2C

To calculate the coefficient of diffusion of carbon in tungsten and in W_2C, it is necessary to know the values of the terms C_2 (the solubility of carbon in tungsten) and C_1 (solubility in W_2C).

In order to determine the value of C_2, the following experiment was carried out. A 12 mil filament was first carbonized slightly and then decarbonized in excess of oxygen at constant temperature. The resultant gases were passed over a glowing platinum filament to oxidize the CO to CO_2, which was then condensed in a liquid air trap. At intervals, the run was interrupted, and the collected CO_2 measured. As decarbonization neared completion, these intervals were made very short. At a certain point, the amount of CO_2 collected per minute began to decrease and continued to do so for some minutes, finally reaching a negligible constant value equal to the previously determined blank of the system. This blank was probably due to very small amounts of impurities in the oxygen used. It is evident that at the point at which the evolution of carbon began to decrease rapidly, all the W_2C in the filament was decomposed, and that the carbon evolved from that time on was that dissolved in the tungsten. Two such experiments were made, one at 2000°, and another at 2200°. The values obtained at 2000° are shown in Fig. 2. From this experiment, the concentration of carbon was calculated to be .009% of the weight of the tungsten. The value from the run made at 2200 was .05%. It is hardly likely that there is such a temperature coefficient for the solubility of carbon in tungsten, but it is possible that the second value is somewhat high because some of the carbon evolved after the break in the rate of evolution of CO may have been due to traces of W_2C still undecomposed. Using the weighted mean value, 0.010%, the value of C_2 becomes 0.002 gm/cm³.

Efforts to determine the value of the solubility of carbon in W_2C were unsuccessful, though several attempts were made to do so.

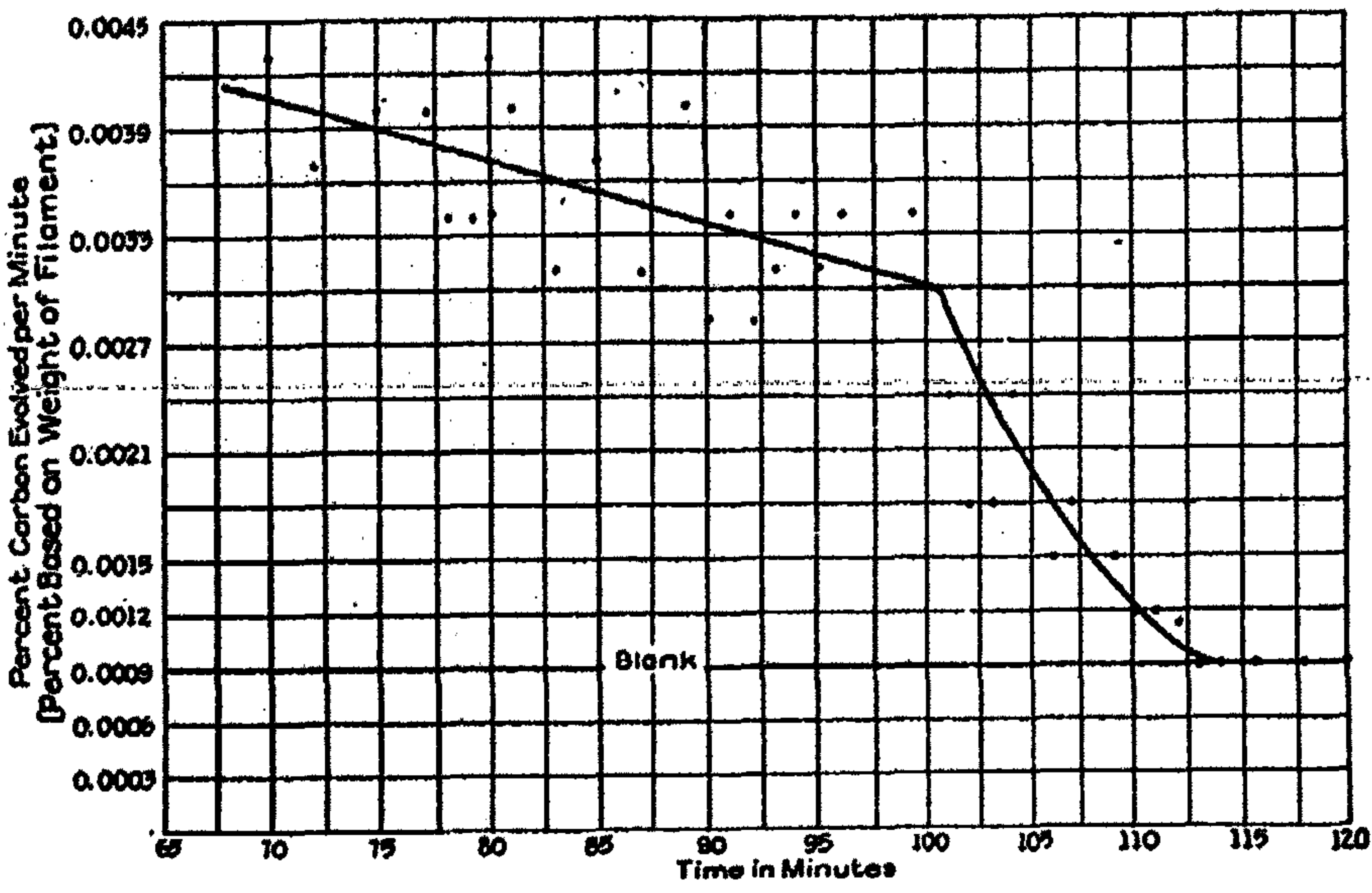

FIG. 2

Rate of Decarbonization of Tungsten in Oxygen at 2000° K.

Table III gives the values of D_1C_2 and D_1 for two wires at various temperatures. D_1 has been calculated on the basis of C_2 = .002 and on the assumption that this solubility does not change appreciably thru the temperature range used. Values of D_1C_2 are shown graphically in Fig. 3.

Table IV gives the values of $D(C_1\text{-}C_2)$ for a number of different wires. These are shown graphically in Fig. 4.

TABLE III

Coëfficients of Diffusion of Carbon thru Tungsten

Symbol on Fig. 3.	Wire	Temperature	$D_1C_2 \times 10^{10}$	$D_1 \times 10^7$
○	7 mil pure tungsten	2185°K	10	5
		2355 "	20	10
△	4 mil tungsten containing .5% ThO_2	2070 "	3.2	1.6
		2188 "	9.6	4.8
		2300 "	15.6	7.8
		2400 "	36.	18

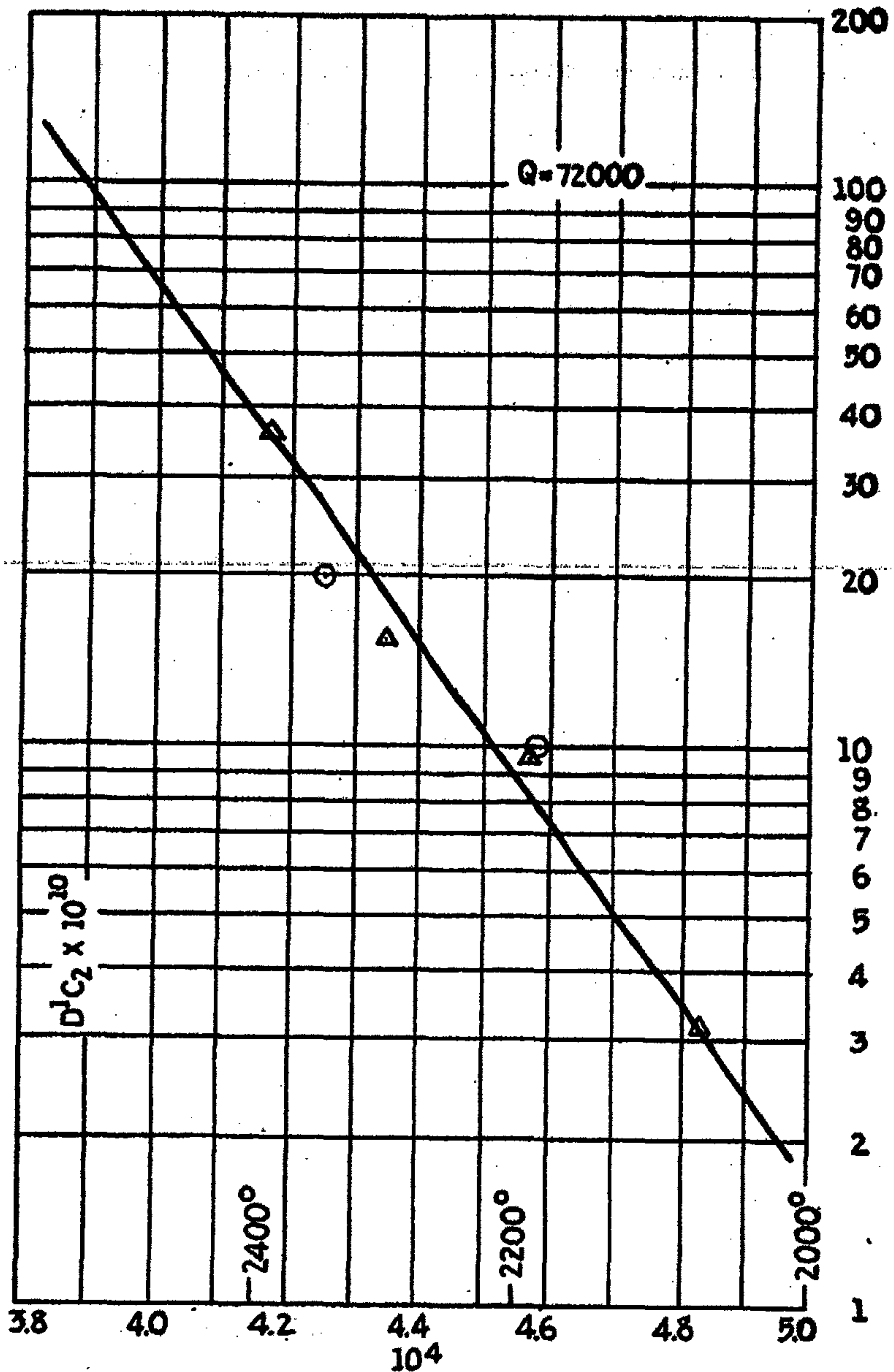

FIG. 3
Coefficients of Penetration of Carbon thru Tungsten

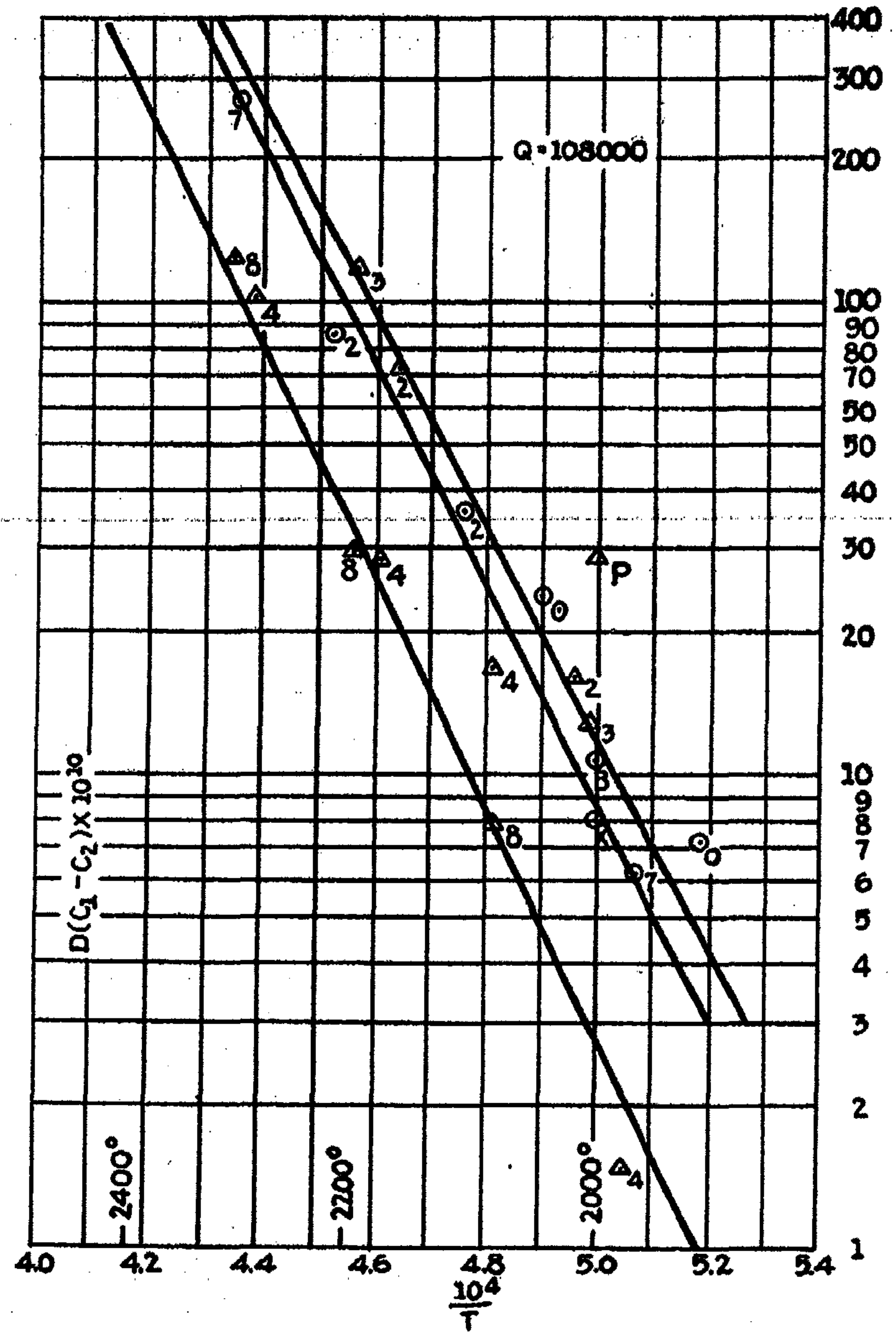

Fig. 4
Coefficients of Penetration of Carbon thru Tungsten Carbide

TABLE IV

Coefficients of Penetration of Carbon thru W_2C

Symbol on Fig. 4.	Wire	Temperature	$D(C_1 - C_2) \times 10^{10}$
O_7	7 mil pure tungsten fine grained	1975°K	6.2
		2295	270
O_2	2 mil pure tungsten fine grained	2100	36
		2210	86
Δ_8	8 1/2 mil[1]	2080	7.9
		2190	30.2
		2300	126
Δ_4	4.2 mil[1]	1980	1.5
		2075	16.8
		2170	28.8
		2280	103.
Δ_3	3. mil[1]	2005	12.8
		2195	118.
Δ_2	2. mil[1]	2015	16.
		2155	74.
O_0	2.8 mil[2]	1930	7.2
		2040	23.6
O_B	2.09 mil[3]	2000	10.7
O_x	2.0 " single crystal	2000	8.
Δ_p	2.9 mil[4]	2000	29.5

The coefficient of penetration thru tungsten carbide was measured for a number of wires in order to find out whether this process depends on either the quality or the grain-size of the wires. It will be observed from Fig. 4 that the values of the coefficient of penetration at any one temperature extend over a range of 300 to 400 percent, and that in general the smaller wires show the higher value. This cannot be ascribed to small grain-size in the small wires since the so-called single crystal wire and the "overlap" wire show values quite close to those found for normal wires of the same size. (The high value found for the Pintsch filament, a single-crystal thoriated wire, was probably due to error in temperature as this wire is quite variable in diameter.) Furthermore, it is evident since the diffusion takes place thru a shell of tungsten carbide or thru a shell of tungsten that has been derived from carbide, that the original

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[1] Tungsten containing a fraction of a percent of thoria: fine grained.

[2] Pure tungsten with very long grains (Overlap wire)

[3] Pure tungsten, fine grained. From this wire the 2.0 mil single crystal wire was made.

[4] Pintsch wire—Large crystal wire containing a few percent of thoria.

structure of the wire cannot have any direct bearing on this process. This is confirmed by photomicrographs of various carbonized wires, which show that the grain size of the carbide formed is independent of the structure of the original filament.

It is difficult to understand, therefore, the recent observation made by W. Geiss and J. A. M. v. Liempt[1], regarding the failure of a single crystal rod of tungsten to form carbide when embedded in charcoal powder and heated at 1900°C.

On the other hand, we have recently obtained in this laboratory very striking evidence that in such cases as the diffusion of thorium or yttrium thru tungsten, the rate is very much greater along grain boundaries than thru the lattice structure. These observations will be discussed in a subsequent paper.

The most probable explanation of the differences in coefficients of penetration observed in different sizes of wire, is that the assumptions underlying the mathematical theory (on which are based the calculations of the coefficients of penetration) are not quite in accord with the actual conditions.

Heats of Diffusion

It will be observed from Fig. 4 that in general, the values of the coefficients of penetration for any one wire lie on a straight line whose slope obviously is a measure of the heat of diffusion of carbon thru tungsten carbide. The slopes obtained for different wires are practically the same within the limits of experimental error.

Applying the modified van't Hoff equation

$$\frac{d\ln(D\ C)}{d\left(\frac{1}{T}\right)} = -\frac{Q}{R}$$

it is found that the heat of diffusion of carbon thru W_2C is about 108,000 cal/mol. Similarly from the slope of the line in Fig. 3, the heat of diffusion of carbon thru tungsten is found to be 72,000 cal/mol.

It is of interest to observe that this value of the heat of diffusion for carbon thru tungsten is somewhat less, but of the same order of magnitude as that observed by Langmuir[2] for the heat of diffusion of thorium thru tungsten, 94,000 calories.

On the basis of certain semi-theoretical considerations Langmuir and Dushman[3] have derived an equation of the form

$$D = K/N_o$$

$$\text{where:} \quad K = \frac{Q}{Nh} e^{-Q/RT}$$

and N_o = number of atoms of the diffusing substance per unit area. The other symbols have their usual significance.

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[1] Metalkunde, Vol. 16, p. 37 (1924).

[2] Phys. Rev. 22, 357 (1923).

[3] Phys. Rev. 20, July (1922)

This equation, then, gives the relation between the heat of diffusion and the absolute value of the diffusion constant at any temperature. By means of this equation, it is possible to calculate the absolute value of the diffusion constant at any temperature from the observed value of Q, the heat of diffusion. Table V gives values of D and D_1 calculated in this manner for different temperatures. For comparison, the values of D_1 as derived directly from the decarbonization data and values of C_2, and values of $D(C_1-C_2)$ are shown in columns 4 and 5 respectively.

TABLE V

Diffusion Constants calculated from the Heats of Diffusion

Temp.	D_1 from Q'	D_1 from experiment	D from Q	$D(C_1-C_2)$ from experiment
2000°	4.4×10^{-8}	9×10^{-8}	7.5×10^{-13}	$(3 \text{ to } 12) \times 10^{-10}$
2200°	2.3×10^{-7}	4.5×10^{-7}	$1. \times 10^{-11}$	$(3.6 \text{ to } 12) \times 10^{-8}$
2400°	$.88 \times 10^{-6}$	1.8×10^{-6}	7.3×10^{-11}	$(3.0 \text{ to } 8) \times 10^{-7}$

It will be observed that the two methods of determining D_1 yield results that agree quite satisfactorily, in fact within the limits of the possible errors in the value of C_2 used in deriving D_1 from experiment.

The values for D, however, are of an entirely different order of magnitude from any that are to be expected. Using these calculated values of D and the observed values of $D(C_1-C_2)$ the values of C_1-C_2 are found to be altogether too large. This may be because the conditions of diffusion thru a compound such as tungsten carbide are undoubtedly far more complex than those for diffusion thru the simple metallic lattice of tungsten. X-ray spectro-grams taken in this laboratory by Dr. W. P. Davey show that W_2C has a rhombohedral structure with the side of the unit triangle equal to 4.66°A and an axial ratio of 1.42. He calculates that the tungsten atoms are arranged in a similar manner to the calcium and carbon atoms in calcite, and that their nearest approach to each other is 1.42A.[1] This gives a complex structure already containing carbon, thru which carbon must diffuse, and the mechanism of this diffusion is probably different from that of carbon thru tungsten. Moreover, there may be an appreciable temperature coefficient to the solubility gradient (C_1-C_2). If this were the case, the value of Q, as calculated from the slope of the values of $D(C_1-C_2)$ would be too great. It is hardly conceivable, however, that this temperature coefficient of solubility could be sufficiently large to reduce Q to the value corresponding to values of D a thousand or ten thousand fold larger.

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[1] This work will be published later in more detail by Dr. Davey.

THE CONDUCTIVITY OF ELECTROLYTES

BY CECIL WHITFIELD DAVIES

It is well known that the theory of Arrhenius is unable to explain the way in which the conductivity of a "strong" electrolyte changes with changing concentration. An alternative theory advanced by several writers supposes strong electrolytes in dilute aqueous solution to be completely dissociated, and attributes the diminution in equivalent conductivity with increase in concentration entirely to the electrical forces which exist between the ions. This theory has attracted attention especially since its recent mathematical development by Debye[1].

The objects of the present paper are to show that the postulation of complete dissociation is in complete harmony with the experimental data for very dilute aqueous solutions of uni-univalent electrolytes; and to advance an empirical relationship which expresses the conductivity of such a solution in terms of the concentration, the mobilities of the ions present and a universal constant. In the later sections of the paper the relationship is extended to multivalent electrolytes.

Ionic Conductances at Low Concentrations

If a salt is completely dissociated in solution we should expect its conductivity at sufficiently low concentrations to be the sum of two independent parts: the conductance of the cation (at the concentration considered) plus the conductance characteristic of the anion at this concentration. MacInnes[2] has endeavoured to show that this is actually the case for several binary salts, the ionic conductances being found by multiplying the conductivity at any concentration by the corresponding transport number. Unfortunately, the agreement shown by his figures is not very satisfactory. The discrepancies, however, may well be due to the fact that MacInnes' figures refer to comparatively high concentrations—0.01, 0.1 and 1 N. Consequently a viscosity correction had to be applied to the conductivity data, and this alone produces some uncertainty. Further, even if the salts considered are actually completely dissociated, it does not follow that the mobility of each ionic species, at comparatively high concentrations, will be quite unaffected by the nature of the other ions present.

The figures presented here consist of an extension of MacInnes' calculations to the most dilute solutions investigated. An additional advantage secured by considering such solutions lies in the fact that the variations in conductivity are adequately represented by Kohlrausch's law: $\Lambda_\infty - \Lambda_0 = K\sqrt{c}$, where c is the equivalent concentration. It may be noted that this empirical

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[1] Physik. Z. 24, 305 (1923).

[2] J. Am. Chem. Soc., 43, 1217 (1921).

rule of Kohlrausch is supported by Debye's theory which demands such a relation between conductivity and concentration in dilute solutions.

In Table I are given the data for several chlorides at 18°. The experimental conductivity figures are taken from Noyes and Falk's summary of the data[2], and the corresponding values at infinite dilution were obtained from these by plotting against the square root of the concentration and extrapolating.

The transport number values used were also obtained graphically. It was found that if the experimental values up to a concentration of about 0.1 N, together with the value at infinite dilution (obtained from the mobilities of the ions concerned), were plotted against the square root of the concentration, an almost straight line was usually obtained and from this the probable values at low concentration could be read off with considerable accuracy.

TABLE I

Equiv.		KCl			NaCl	
Concn.	Λ_{KCl}	n_a	$\Lambda_{Cl'}$	Λ_{NaCl}	n_a	$\Lambda_{Cl'}$
0	129.92	.5038	65.45	108.76	.6017	65.45
.0001	129.08	.5038	65.03	108.03	.6018	65.02
.0002	128.73	.5039	64.86	107.75	.6018	64.85
.0005	128.04	.5039	64.52	107.11	.6020	64.48
.001	127.27	.5040	64.14	106.42	.6022	64.08
.002	126.20	.5040	63.59	105.48	.6024	63.53
Equiv.		LiCl			HCl	
Concn.	Λ_{LiCl}	n_a	$\Lambda_{Cl'}$	Λ_{HCl}	n_a	$\Lambda_{Cl'}$
0	98.69	.6632	65.45	380.0	.1722	65.45
.0001	97.96	.6635	65.00	378.7*	.1717	65.01
.0002	97.67	.6637	64.83	378.1*	.1715	64.83
.0005	97.01	.6641	64.43	377.0	.1710	64.46
.001	96.34	.6647	64.04	375.9	.1706	64.10
.002	95.44	.6652	63.50	375.3	.1700	63.78

*Interpolated values. The conductivity values quoted for HCl at the two lowest concentrations show the marked falling away from the curve which is usual among acids.

Columns 4, 7, 10, and 13 of Table I show the conductance of the chloride ion as obtained by means of the formula $\Lambda_{MCl} \times n_a = \Lambda_{Cl'}$ where n_a is the anion transport number. It will be seen that, taking account of the probable errors in the conductivity and especially in the transport number values, the conductance of the chloride ion in these solutions can be regarded as determined entirely by the concentration, and as independent of the nature of the salt from which derived.

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[2] J. Am. Chem. Soc., 34, 461 (1912): With the exception of KCl, where the values quoted by Noyes and Falk have been combined with the more recent figures of Weiland: J. Am. Chem. Soc., 40, 131 (1918).

Variation of Ionic Conductance with Concentration

The values in Table I for the conductance of the chloride ion cannot be advanced as direct support for the theory of complete dissociation since these might be interpreted equally well by the classical theory, with the not unreasonable assumption that in such dilute solutions the degree of ionisation is substantially the same for all binary chlorides. But the figures do show the facts to be compatible with the theory of complete dissociation. If this theory is provisionally accepted, more definite evidence in its favour is found in the consequences of the method of treatment described above.

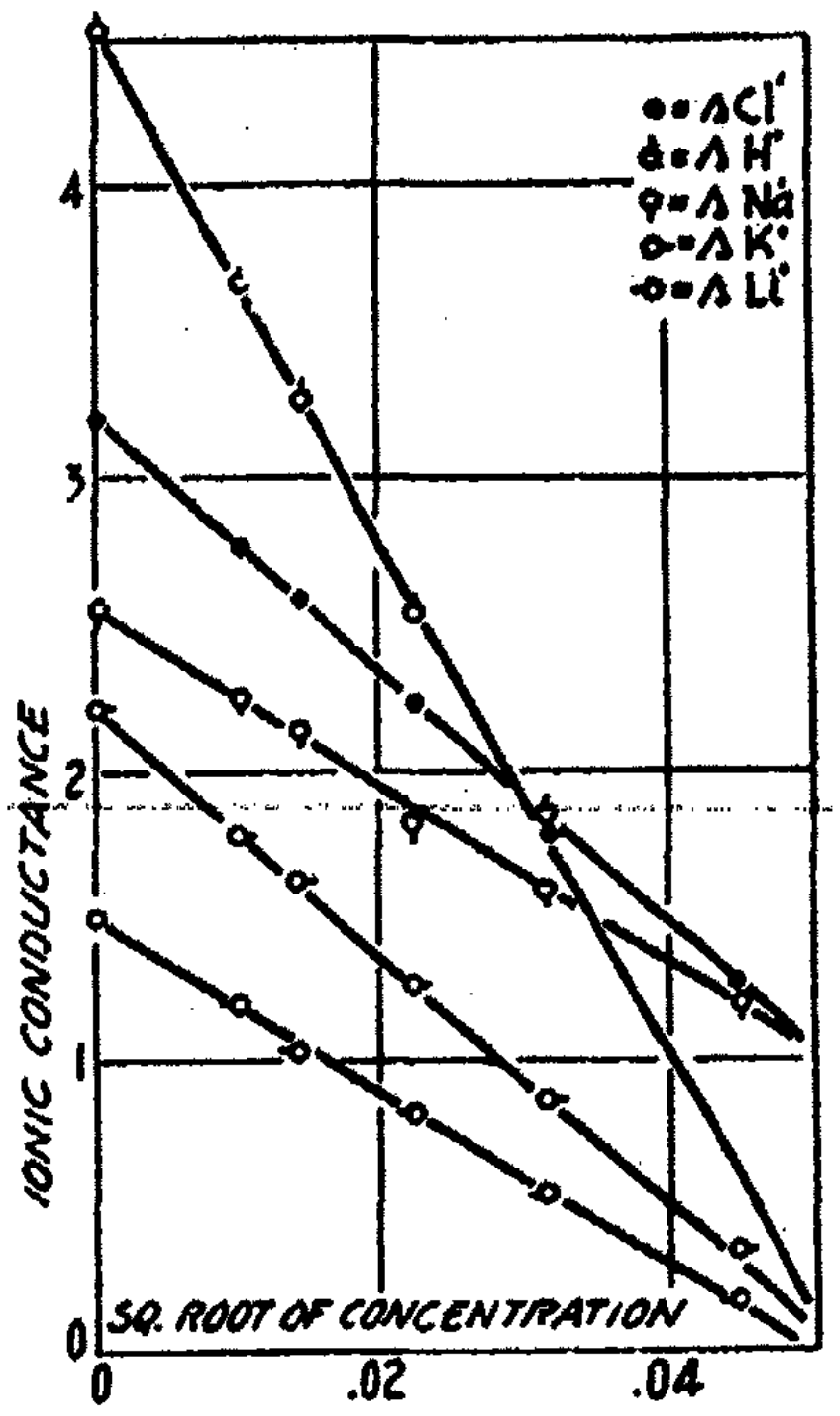

FIG. 1

Figure 1 shows the conductances of several ions, those of chloridion being obtained from Table I and those of the others by subtraction.

The change in conductance is proportional to the square root of the concentration for concentrations below about 0.002 N, and *the slope of the line is found to be directly proportional to the square root of the mobility of the ion.* That is to say, the equation

$$\Lambda_\infty - \Lambda_c = K.\sqrt{c}.\sqrt{\Lambda_\infty} \qquad (1)$$

holds for any univalent ion where Λ_∞ is its mobility or conductance at infinite dilution, Λ_c its conductance at concentration c and K a universal constant. The equation is illustrated in Table II; column I shows $\frac{\Delta\Lambda}{\Delta\sqrt{c}}$ as read from Figure 1, and column IV gives $\frac{\Delta\Lambda}{\Delta\sqrt{c}\times\sqrt{\Lambda_\infty}}=K$.

TABLE II

Ion.	$\frac{\Delta\Lambda}{\Delta\sqrt{c}}$	Λ_∞	$\sqrt{\Lambda_\infty}$	K
Cl'	43.2	65.45	8.09	5.34
K'	42.6	64.47	8.03	5.31
Na'	31.6	43.31	6.58	4.80
Li'	29.8	33.24	5.76	5.17
H'	88.4	314.55	17.73	4.99

The constancy of the value of K is satisfactory having regard to the probable degree of accuracy of the data. For instance, if the conductivity value for NaCl at 0.0005 N were 106.9 instead of 107.1 the value K = 5.2 would be obtained. An alteration of 0.3% in the experimental transport numbers would have the same effect.

Application to Conductivities of Salts

It will be seen that the testing of equation 1 by direct reference to ionic conductances is a tedious and uncertain operation. Fortunately, it is possible to test the relationship without the use of transport numbers. If $\overline{\Lambda}_c$ is the conductivity of a uni-univalent salt at concentration c and $\Lambda^{\cdot}_c$, Λ'_c the conductances of cation and anion respectively, then

$$\Lambda^{\cdot}_{\infty} - \Lambda^{\cdot}_c = K\sqrt{c}\sqrt{\Lambda^{\cdot}_{\infty}}$$

$$\Lambda'_{\infty} - \Lambda'_c = K\sqrt{c}\sqrt{\Lambda'_{\infty}}$$

$$\text{and } \overline{\Lambda}_{\infty} - \overline{\Lambda}_c = \Lambda^{\cdot}_{\infty} + \Lambda'_{\infty} - \Lambda^{\cdot}_c - \Lambda'_c = K\sqrt{c}\,(\sqrt{\Lambda^{\cdot}_{\infty}} + \sqrt{\Lambda'_{\infty}}) \qquad (2)$$

$$\text{or, } \frac{\overline{\Lambda}_{\infty} - \overline{\Lambda}_c}{\sqrt{c}.\,(\sqrt{\Lambda^{\cdot}_{\infty}} + \sqrt{\Lambda'_{\infty}})} = K \qquad (3)$$

Table III shows the values of K obtained by means of equation 3 for a variety of uni- univalent electrolytes at 18°, the conductivity data being taken as before from Noyes and Falk's compilation (loc. cit). It will be seen that K varies no more in any vertical column than it does in reading horizontally. That it is to say, the variations in K on passing from one salt to another are no greater than are the variations due to slight irregularities in the conductivity data.

To obtain a mean value for K the values at 0.0001 N are omitted as less accurate than the others and the values at 0.002 N are also excluded since Kohlrausch's $c^{1/2}$ rule appears to fail at about this concentration. The average for the remainder is K = 5.24.

Application to Transport Numbers

For any uni- univalent electrolyte at concentration c. equations 1 and 2 give for the conductance of anion and salt,

$$\Lambda'_c = \Lambda'_{\infty} - 5.24\sqrt{c}\sqrt{\Lambda'_{\infty}}$$

$$\overline{\Lambda}_c = \overline{\Lambda}_{\infty} - 5.24\sqrt{c}\,(\sqrt{\Lambda^{\cdot}_{\infty}} + \sqrt{\Lambda'_{\infty}})$$

The anion transport number is given by

$$n_a = \frac{\Lambda'_c}{\overline{\Lambda}_c} = \frac{\Lambda'_{\infty} - 5.24\sqrt{c}\sqrt{\Lambda'_{\infty}}}{\overline{\Lambda}_{\infty} - 5.24\sqrt{c}(\sqrt{\Lambda^{\cdot}_{\infty}} + \sqrt{\Lambda'_{\infty}})} \qquad (4)$$

Transport number data therefore provide an independent series of measurements for testing the relationship expressed in equation 1. The application of the equation is illustrated for four electrolytes in Fig. 2, where circles are used to denote experimental values, taken from Noyes and Falk's summary[1], and

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[1] J. Am. Chem. Soc., 33, 1454 (1911).

TABLE III

Equiv. Concentration.					.0001		.0002		.0005		.001		.002	
Salt.	Λ_∞	$\sqrt{\Lambda^{\cdot}_\infty}$	$\sqrt{\Lambda'_\infty}$	$\Sigma\sqrt{\Lambda_\infty}$	$\overline{\Lambda}$	K	$\overline{\Lambda}$	K	$\overline{\Lambda}$	K	$\overline{\Lambda}$	K	$\overline{\Lambda}$	K
KCl	129.92	8.03	8.09	16.12	129.08	5.2	128.72	5.26	128 03	5.25	127.27	5.20	126.22	5.13
NaCl	108.76	6.58	8.09	14.67	108.03	5.0	107.75	4.87	107.11	5.03	106.42	5.04	105.48	5.00
LiCl	98.69	5.76	8.09	13.85	97.96	5.3	97.67	5.21	97 01	5.42	96.34	5.36	95.44	5.25
KNO_3	126.23	8.03	7.86	15.89	125.40	5.2	125.08	5.12	124.34	5.32	123.55	5.33	122.50	5.25
$NaNO_3$	105.20	6.58	7.86	14.44	104.45	5.2	104.09	5.43	103.53	5.17	102.75	5.36	101.80	5.26
$LiNO_3$	95.02	5.76	7.86	13.62	94.30	5.3	93.99	5.35	93.36	5.45	92.71	5.36	91.81	5.27
KIO_3	98.38	8.03	5.83	13.86	97.64	5.3	97.34	5.30	96.72	5.36	96.04	5.34	95.04	5.39
$NaIO_3$	77.38	6.58	5.83	12.41	76.69	5.6	76.44	5.36	75.83	5.59	75.19	5.58	74.30	5.55
$LiIO_3$	67.32	5.76	5.83	11.59	66.66	5.7	66.43	5.43	65.87	5.60	65.27	5.59	64.43	5.58
HCl	379.8	17.73	8.09	25.82	378.5	5.0	378.0	4.93	377.0	4.85	375.9	4.78	375.3	3.90
$AgNO_3$	115.70	7.34	7.86	15.20	115.01	4.5	114.56	5.30	113.88	5.36	113.14	5.33	112.07	5.34
KF	111.10	8.03	6.83	14.86	110.37	4.9	110.13	4.62	109.48	4.87	108.80	4.89	107.82	4.94
$KClO_3$	119.50	8.03	7.42	15.45	118.63	5.6	118.35	5.26	117.68	5.27	116.92	5.28	115.84	5.30

TABLE IV

Equiv. Concentration.					.0001		.0002		.0005		.001		.002	
				$v^{\cdot}v'\times$										
Salt.	$\overline{\Lambda}_\infty$	$\sqrt{v^{\cdot}\Lambda^{\cdot}_\infty}$	$\sqrt{v'\Lambda'_\infty}$	$\Sigma\sqrt{v\Lambda_\infty}$	$\overline{\Lambda}$	K	$\overline{\Lambda}$	K	$\overline{\Lambda}$	K	Λ	K	Λ	K
$CaCl_2$	116.63	10.14	8.09	36.46	115.17	4.0	114.55	4.03	113.34	4.03	111.96	4.06	110.07	4.02
$MgCl_2$	110.89	9.53	8.09	35.24	109.43	4.1	108.87	4.05	107.68	4.07	106.35	4.07	104.52	4.05
$Ba(NO_3)_2$	117.03	10.51	7.86	36.74	115.32	4.7	114.65	4.58	113.30	4.54	111.72	4.57	109.50	4.58
$Pb(NO_3)_2$	122.80	11.04	7.86	37.80	120.73	5.5	119.94	5.35	118.08	5.58	116.13	5.58	113.54	5.48
K_2SO_4	132.50	8.03	11.75	39.46	130.7	4.6	130.0	4.48	128.5	4.53	126.9	4.49	124.6	4.48
$MgSO_4$	114.48	9.53	11.75	85.12	109.90	5.4	108.07	5.33	104.21	5.40	99.89	5.42	94.14	5.34
$ZnSO_4$	114.92	9.63	11.75	85.32	109.7	6.1	107.7	6.12	103.5	5.99	98.6	6.05	92.2	6.09
$CuSO_4$	115.32	9.68	11.75	85.52	109.95	6.3	107.95	6.09	103.56	6.15	98.56	6.20	91.94	6.11
$K_4Fe(CN)_6$	159.5	8.03	19.5	110.12	....	..	....	....	....	....	....	....	137.0	4.57
$Ca_2Fe(CN)_6$	147.0	10.2	19.5	237.6	....	..	....	....	....	....	....	....	75.5	6.73
$La(NO_3)_3$	122.8	13.5	7.86	64.08	....	..	....	....	....	....	....	....	110.8	4.19
$La_2(SO_4)_3$	129.5	13.5	11.75	151.5	....	..	....	....	....	....	....	....	60.1	10.3

crosses to denote values calculated by equation IV. The values at infinite dilution are derived from the $\bar{\Lambda}_{\infty}$ values, the mobility of Cl being taken as 65.45.

The actual value of the test can be estimated by inspection of Fig. 2. It is unfortunate that transport numbers have not yet been found experimentally at the low concentrations for which equation 4 applies; but it is, at any rate, interesting that comparatively large changes in transport number such as occur with LiCl and HCl are accounted for without special assumptions. The rapid change in transport number in the case of HCl is due to the widely differing mobilities which are roughly in the ratio 1 to 5. In the case of LiCl the change in transport number is equally rapid, although the difference in mobilities is not nearly so great; this is due to the fact that the mobilities are smaller, and the smaller the mobility the greater will be the value of the ratio: $\frac{K\sqrt{\Lambda}}{\Lambda}$

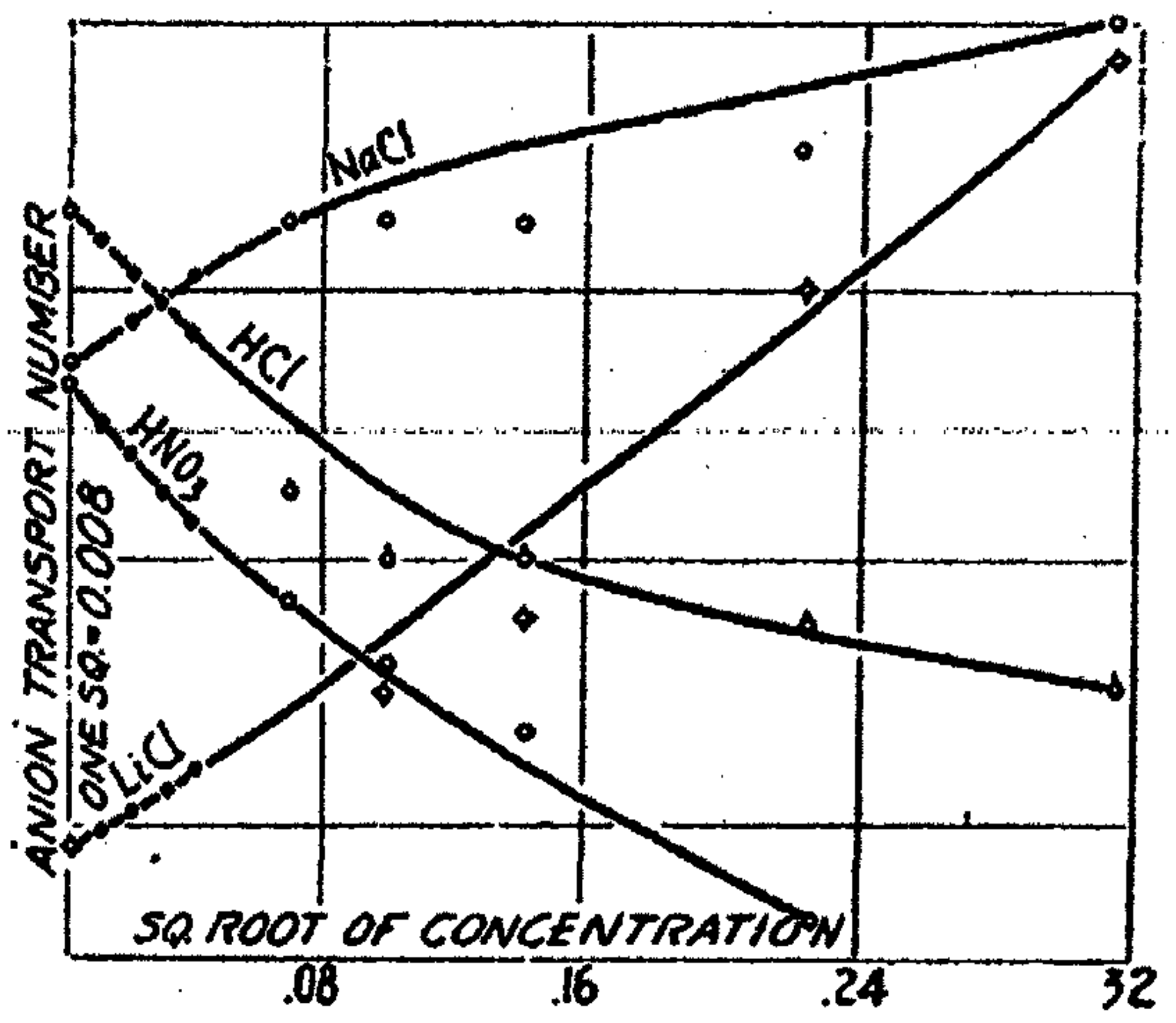

FIG. 2

Extension to Multivalent Ions

Ionic conductances cannot be found directly in the case of salts of multivalent ions, for transport number data are scanty and from what data exist it is evident that the transport number—concentration curves are more complex than are those of uni- univalent salts so that interpolated values cannot be trusted.

Equation 2 however can be extended so as to apply to these salts by introducing valency factors, when it takes the form

$$\bar{\Lambda}_{\infty} - \bar{\Lambda}_{c} = 5.24\sqrt{c}.v^{\cdot}v'(\sqrt{v^{\cdot}\Lambda^{\cdot}_{\infty}} + \sqrt{v'\Lambda'_{\infty}}), \qquad (5)$$

where $v^{\cdot}$, v' are the valencies of cation and anion and the other symbols have the same meanings as before. Equation 5 is applied to various multivalent electrolytes in Table IV. The divergencies of K from the mean value 5.24 are far greater here than in Table III; but the data also appear much less satisfactory, since the conductivities at infinite dilution are not additive and consequently the mobilities of the ions are in doubt[1]. Whether the variations in K are to be attributed to a failure of the equation or to inaccuracies in the values of Λ_{α} is therefore an open question.

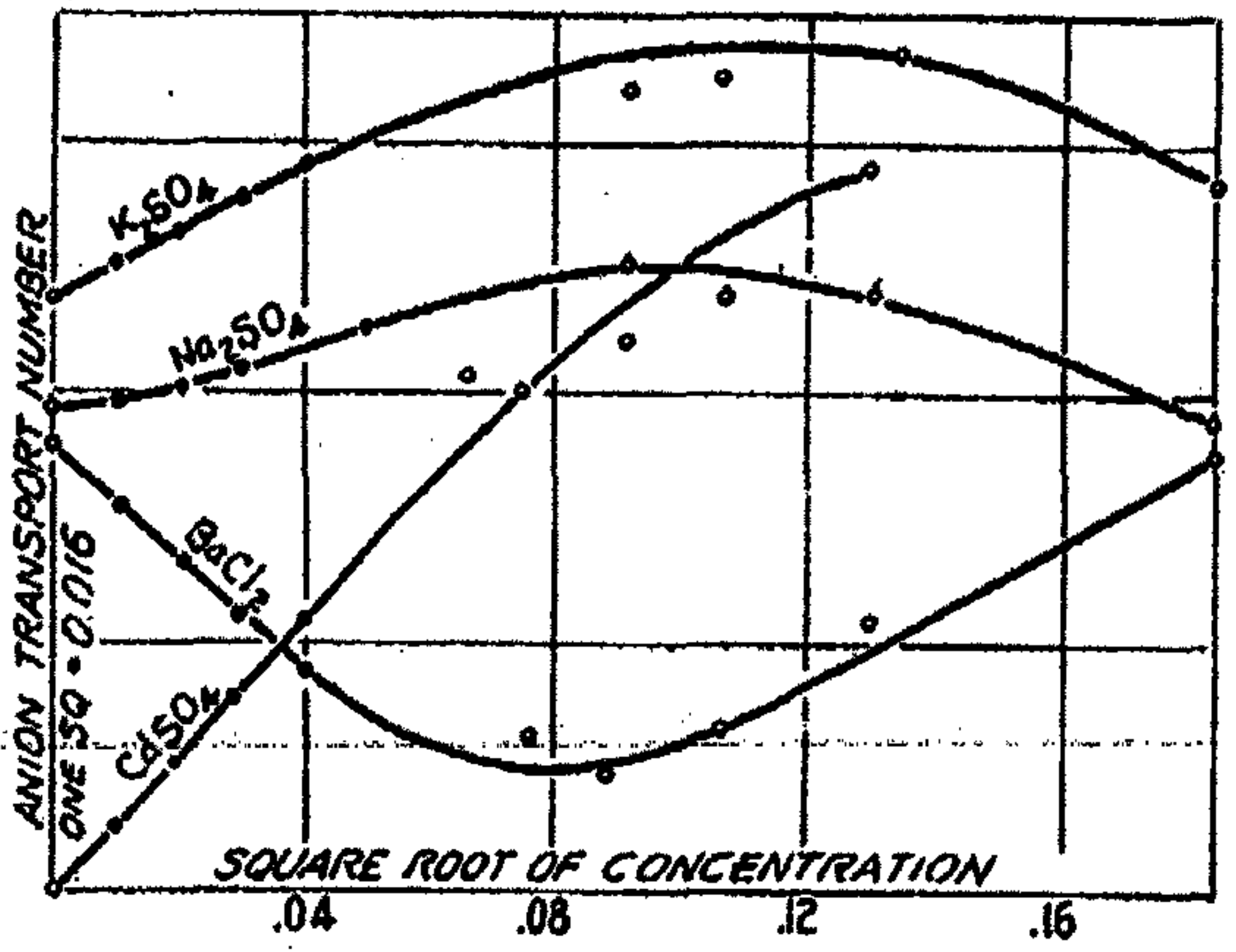

Fig. 3

In Fig. 3 the transport numbers of four more multivalent electrolytes are compared with numbers calculated by formulae similar to that applied to uni-univalent salts in equation 4. The experimental numbers are those quoted by Noyes and Falk (loc. cit.) from papers by Jahn and associates[2].

The Effect of Temperature

The actual value of the constant K in equations 1, 2 and 5 for any solution containing a completely ionised electrolyte will depend on factors such as the dielectric constant of the solvent, its viscosity and the temperature.

The effect of temperature was investigated, using the data of Noyes and Coolidge[3] for sodium and potassium chlorides in water at temperatures up to 306°. The equivalent conductivities at infinite dilution of the salts at the various temperatures were obtained as before by extrapolating from the conductivity $-c^{\frac{1}{2}}$ curve. The mobilities of the ions were then derived on the assumption that the transport number of KCl throughout is 0.500; any errors thereby introduced into the values of $\sqrt{\Lambda'_{\alpha}}$ will be very small.

Table V shows the mean value of K up to 0.002 N for each temperature, as found by equation 3; column 4 gives values for $\frac{K}{T^3} = k'$, where T is the absolute temperature.

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[1] It seems likely that Kohlrausch's $c^{\frac{1}{2}}$ rule holds strictly only for the limit $c = 0$, its practical applicability being more limited in the case of multivalent ions.

[2] Z. physik. Chem., 58, 647 (1907).

[3] Z. physik. Chem. 46, 365 (1903).

TABLE V

t	T	K	$k'\times10^7$
18°	291	5.24	2.12
140°	413	15.6	2.22
218°	491	23.9	2.03
281°	554	34.7	2.03
306°	579	35.3	1.80

It will be seen that for these salts in water K is practically proportional to the cube of the absolute temperature, and that their conductivities may be represented by the formula $\bar{\Lambda}_\alpha - \bar{\Lambda} = 2.12\times10^{-7}\,T^3\sqrt{c}\,(\sqrt{\Lambda^{\cdot}_\alpha}+\sqrt{\Lambda'_\alpha})$.

Non-Aqueous Solvents

It would be interesting to apply equations 2 and 5 to the conductivities of electrolytes in non-aqueous solvents. Unfortunately the data at present available are for the most part so inconsistent and unsystematic that the results of such a treatment would be conflicting and probable misleading. In the case of liquid ammonia there exist series both of conductivity data and of transport numbers, but here the assumption of complete dissociation would appear to be unjustifiable.

Comparison with Debye's Theory

The expression theoretically derived by Debye takes for uni-univalent electrolytes at 18° the form:

$$\frac{\bar{\Lambda}_\alpha - \bar{\Lambda}}{\bar{\Lambda}_\alpha} = \sqrt{2c}\left[0.139\left(\frac{\Lambda'_\alpha}{\Lambda^{\cdot}_\alpha}+\frac{\Lambda^{\cdot}_\alpha}{\Lambda'_\alpha}\right)+0.233\times10^8 b\right]$$

where *b* is a "mean ionic radius" and the other symbols have the same meanings as before. The first term in the square bracket can be evaluated for any salt but the second term can be only obtained by difference. Debye's equation cannot therefore be tested by the experimental data, although these may be used for evaluating "b" which is found to be in the neighbourhood of 1×10^{-8} for all binary salts, though for salts containing bivalent ions the values are about six times as great.

It is evident that Debye's expression is irreconcileable with the empirical equation described in this paper. But it should be noted that Debye's expression is only approximate, since the laws governing the motion of an ion through a solvent are not certainly known and Debye in deriving his equations was forced to assume the validity of Stokes' law.

The same difficulty is encountered in looking for a theoretical significance for equation 2; for as long as the laws governing the motion of an ion through a solvent are unknown, the quantity $\sqrt{v\Lambda_\alpha}$ cannot be interpreted in terms of fundamental properties of the ion, such, for example, as its effective radius. It is hoped, however, that the empirical relationships described in this paper may prove an aid in the advancement of the theory of the subject, and a useful starting point in the investigation of more concentrated solutions.

In conclusion the writer gratefully acknowledges many helpful criticisms offered by Mr. L. J. Hudleston during the preparation of this paper.

The Edward Davies Chemical Laboratories,
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October 23, 1924.

NEW BOOKS

The Structure of Crystals. *By R. W. G. Wyckoff. 24 × 16 cm. pp. 462. New York: Chemical Catalog Company, 1924. Price: $6.00.* In the preface the author says that "the present monograph aims to outline the methods of crystal structure deduction as they now exist and to treat the available diffraction data from the more exacting standpoint they make possible. The very fact that this enlarged subject of crystal analysis draws its method of attack from several of the old sciences introduces a serious error into its adequate presentation; among these older sciences it is now more or less of an outcast. Most chemists seem to find in the purely physical means of experimentation and in the introduction of theoretical crystallography a proof that it does not belong to chemistry; for many physicists it is difficult to believe that the physical processes alone are insufficient; and crystallography (as distinct from mineralogy), to which crystal analysis is in many ways most clearly related, is practically non-existent in this country."

The subject is presented in two parts, methods of crystal analysis and results of crystal analysis. In Part I the chapters are entitled: the symmetry characteristics of crystals; some properties of X-rays; the interaction of X-rays and crystals; the production and interpretation of Laue photographs; X-ray spectrometry and spectrography; powder spectrometry and spectroscopy; a generally applicable method for determining the structures of crystals; a brief historical outline of the development of existing X-ray diffraction methods. In Part II the chapters are entitled: an introduction to the discussion of existing crystal structure results; the crystal structures of elements and of metallic alloys; the crystal structures of carbides, oxides, sulphides, etc.; the crystal structures of halides, cyanides, etc.; the crystal structures of nitrates, carbonates, sulphates, organic compounds, etc.; incomplete crystalline and non-crystalline diffraction phenomena; some applications of diffraction information.

"It sometimes happens that crystals will develop which are built up of two or more individuals having a definite but not parallel arrangement. These are twins. Thus components of a twin may be turned through an angle of 180° about some line of the crystal (the twinning axis) or they may be reflections of one another in a plane (the twinning plane). The surface along which the two individuals are in contact is the composition plane. In some twins the components are entirely separate from one another except at the plane of meeting (the contact twins); in others the separate parts closely intergrow (the penetration twins). Though some compound crystals as these can frequently be distinguished, for instance by the presence of reentrant angles, many twinned forms imitate almost exactly a single crystal of a higher symmetry," p. 56.

"The characteristic (line) spectra of the elements have been carefully studied and measured. The radiations producing them presumably arise from changes in the energy content of atoms and thus are primarily atomic, as opposed to molecular, phenomena. In accordance with this conclusion it has invariably been found that the X-ray spectrum from a compound is almost exactly the simple sum of the spectra of its component elements.

"Four distinct series of line spectra for an element have been discovered. They are usually designated as the N-series, the M-series, the L-series, and the K-series. For a particular atom the N-series lines have the longest, the M-series lines shorter, the L-series lines still shorter, and the K-series lines the shortest wave lengths. Each of these series consists of relatively few lines. The same lines occur from different elements, with progressively altered wave lengths. In passing from element to element in the direction of increasing atomic number the wave lengths of a line in a series decrease in a regular fashion. By plotting the square root of the frequency, ν, of corresponding lines against atomic numbers (N), a group of nearly straight lines will be obtained. The many relations that have been found to exist between lines in the same series and different series find extensive use in the development of theories of atomic structure.

"It has been said that the K-series spectra will be emitted when and only when the impressed voltage is at least a fraction of one per cent greater than that which corresponds, by the quantum relation, to the frequency of the shortest K-line. The wave length with an energy equivalent through the quantum relation to this critical voltage may be called the quantum wave length. If the voltage is above this value for an element which displays all four series then the characteristic spectrum of the element will consist of not only the K-lines but those of the L-, M- and N- series as well. Whereas the K-lines are called into being together, the L-series has three and the M-series possibly five critical voltages. With increasing potential across a tube the N-series lines would first make their appearance, probably in several sections, to be followed by the five (?) parts of the M-series, the three parts of the L-series, and finally by the K-lines. It would thus be possible by an appropriate adjustment of voltage to produce only a portion of the L-, M- or N-series of an element but the K-series must be had either in its entirety or not at all.

"All four series are not found for most atoms. N-series lines have been observed from only a few of the heaviest elements. The M-lines have been observed from the elements from dysprosium (atomic number = 60) to uranium (atomic number = 92). The L-series has been measured for zinc and all of the heavier elements. Spectra in the K-series are recorded from sodium to platinum," p. 71.

"It has customarily been supposed that no phase relationships exist between the secondary rays produced in a crystal and that consequently these rays would result in only a distributed fogging. This is unquestionably true of most of them and the possibility of their being produced within the crystal under investigation must always be taken into account. They must also be considered in the choice of materials to serve as absorbing agents and in the design of spectrometers and other measuring instruments. In recent experiments with white X-rays, however, an especially strong reflection has been found of wave lengths characteristic of atoms in the reflecting crystal. As yet the properties of this "characteristic reflection" are incompletely understood; but its very existence and the opportunity it offers of producing distinctive diffraction effects from only a part of the atoms of a crystal make it of immediate interest and probably of great future value to crystal analysis," p. 80.

"The assumption that scattering power follows approximately the atomic number of the scattering atoms is in agreement both with earlier knowledge and with crystal structure data. Existing information suggests that the amount of X-rays of ordinary wave lengths scattered by an atom will depend upon both the numbers and the positions of the electrons surrounding its nucleus. Since the number of these electrons parallels the atomic numbers of the elements it is to be expected that the scattering power of an atom for such X-rays will be greater for heavy than for light atoms. The amount of radiation scattered by an atom will depend upon the interference which occurs between rays sent out by its electrons and this in turn will be a function of its electronic configuration. If the distance between these electrons were small compared with the wave lengths of the scattered X-rays, their intra-atomic interference would be negligible and there would be a linear proportionality between scattering power and atomic number. Some early measurements have indicated a simple proportionality between atomic number and the amplitude of reflected X-rays: thus in calcium fluoride two fluoride ions ($N = 10$) are closely equivalent in reflection power to one calcium ion ($N = 18$); or in potassium chloride no difference can be distinguished between the scattering of a potassium ion ($N = 18$) and a chloride ion ($N = 18$). But in the isomorphous sodium fluoride, though sodium ions and fluorine ions have the same number of electrons ($N = 10$) a difference can be detected in their scattering powers. Furthermore many crystal structure data show that the heavier elements scatter appreciably more, electron for electron, than do atoms of low atomic weight. As a consequence it is not legitimate in crystal analysis to make more than a qualitative application of this proportionality between amplitude and atomic number. Whenever feasible, it is best to limit intensity comparisons to planes composed of only one kind of atom," p. 101.

"The grave injuries to the health of the experimenter which result from exposure to X-rays require that care be taken in shielding of X-ray tubes during the preparation of diffraction photographs. This protection must be more effective than that employed in the ordinary medical use of X-rays. Because of the long exposures required in obtaining crystalline diffraction, minute leaks which would be negligible over a period of some seconds may become of considerable importance after several hours. For these reasons all X-ray tubes used in crystal analysis should be enclosed in boxes covered with a thickness of lead sufficient to prevent the deterioration after several months of photographic plates placed outside the boxes," p. 113.

"It has been shown that series of planes can be passed through the atoms of a crystal parallel to any imaginable face (hkl) and that the X-ray diffraction effects from a crystal can be conveniently interpreted as reflections from such series of parallel atomic planes. . . An indefinitely large number of these series of planes can be imagined in the tin crystal sections used for making Laue photographs. They will be inclined at a large variety of different angles to the X-rays for any one crystal setting. Many of them will meet the requirements of equation (16) for the reflection of some wave length present in the white X-radiation used. It is to be expected from this standpoint that a Laue experiment will yield a number of spots each capable of being considered a "reflection" from some possible crystal face (hkl). Since the inclination of the possible atomic planes is governed solely by symmetry, the distribution of spots upon the photographic plate will depend only upon the symmetry of the crystal and its orientation with respect to the X-ray beam. Thus all cubic crystals with X-rays traveling along four-fold axes will give Laue spots at precisely the same positions. This would be equally true for any two similarly oriented crystals with identical axial ratios and angles," p. 116.

"The large number of different wave lengths producing reflections materially limits the useful data to be obtained from a single Laue photograph. If one were prepared in the usual manner but with monochromatic X-rays, few crystal planes would be in the proper position to reflect and the resulting pattern would consist of a very limited number of spots. If, however the crystal specimen were kept in continual rotation one plane after another would be brought to reflect this monochromatic beam. As a consequence a Laue photograph rich in spots would be obtained in which each reflection was due to waves of the same length. A beam of practically monochromatic X-rays can be produced with a molybdenum target tube by absorbing all X-rays but the most intense doublet in the characteristic K-series of molybdenum with a zirconium filter. The indices of the planes producing the spots observed in one of these photographs can be found by using the gnomonic rotation net to follow the paths of the crystal planes during rotation. It is, however, a much more lengthy procedure than the index determination in a simple Laue photograph," p. 145.

"Spectrometric and spectrographic data, in recording reflections from individual crystal faces, furnish information that is invaluable in crystal analysis. The spectrometer observations are potentially the more valuable because they offer the possibility of direct measurements of intensity relationships. It has been shown, however, that not only will it be a difficult matter to measure these intensities with certainty and accuracy but that they would not now be of great use in locating the atoms in crystals were they available. Measurements of position and approximate estimates of intensity are made much more rapidly and certainly by the photographic procedures than by ionization chamber methods. As a consequence spectrographic procedures are the more widely useful at the present stage of the development of crystal analysis," p. 176.

"A diffraction pattern is obtained when a thin film of crystalline powder is substituted for the single crystal of an X-ray spectrograph. If the individual crystals of this powder are haphazardly oriented so that they make all possible angles with the incoming X-ray beam, all orders of reflection from all possible atomic planes, above a certain minimum spacing, have the chance to register themselves at one time. The spectrum lines which result from these reflections of monochromatic X-rays constitute a *powder photograph*. The principle underlying the production of these photographs was brought forward as an early explanation of some Laue patterns from solid paraffin. They became important, however, only when characteristic X-radiation was later used.

"If the powder is finely ground (to less than about 250 mesh) and its crystals have a completely unordered arrangement, then a series of sharp diffraction images is obtained without rotation of the specimen. Such a powder pattern can be greatly simplified by filtering the X-rays to render them essentially monochromatic. Any one line is composed of reflections from only a few particles of the powder; consequently more energy is required to produce one of these photographs than to record other X-ray diffraction phenomena. The outstanding advantage of powder diffraction methods obviously lies in their ability to treat the many crystalline materials which do not grow large single crystals," p. 178.

"This secondary radiation is very pronounced for crystals containing elements a little lighter than the target element; for instance there will be a large amount of scattered rays from crystals containing elements immediately lighter than zirconium, if molybdenum radiation is used. The radiation shows itself mainly as a general fogging of the film; for lighter elements near the target material this blackening may be so intense as completely to obliterate the true diffraction pattern. The only reason for not always placing the filter next to the film arises from the difficulty of making large enough pieces which will be uniform over their entire length. In many cases, especially where faint lines are sought or where there is a large amount of secondary radiation and satisfactory filters are not available, it is profitable to use two films instead of one. . . . Good photographs of crystals of high symmetry can be produced with the powder either contained in a fine thin-walled glass tube or spread out into a film upon paper or with collodion as a binder. In dealing with strongly absorbing materials it has often been the practice to dilute the unknown powder with flour or some other light material. Where these extraneous substances are non-crystalline, their general scattering is enough to obscure faint diffraction lines; those like flour which are crystalline themselves produce many faint reflections that may interfere with the ones due to the unknown powder. For these reasons the only thoroughly satisfactory sample would be a compressed rod of powder; for strongly absorbing materials these rods must be so fine, however, that their preparation is difficult. Another procedure which may be useful consists in coating a silk fiber with powder held together by a small quantity of binder," p. 181.

"Ammonium chloride is the only crystal yet encountered which has a symmetry of atomic arrangement different from, and not simply higher than, the observed cyrstallographic symmetry; and a subsequent study of the crystal structures of the ammonium alums suggests that this may be only an apparent exception. It has been found that in the alums there is no chemically permissible way of placing the hydrogen atom of the ammonium groups so that they will have positions which conform to the symmetry of the crystal as a whole. As a consequence it is seen that in its symmetry properties, as well as chemically, the ammonium group in the alums behaves as a single entity which has essentially spherical symmetry. If the ammonium group can act as a sphere in the alums, it may also do so in all ammonium salts; in that case the symmetry of the atomic arrangement in ammonium chloride is holohedral instead of hemimorphic hemihedral. Future work will doubtless throw additional light upon this apparent violation of the fundamental assumption underlying all crystal structure investigation—that the positions of the atoms in a crystal conform to its symmetry. The violation is largely a formal one because an ammonium hydrogen atom presumably would be no longer possessed of electrons and consequently could give no appreciable indications of its position by its influence on either light or X-rays," p. 211.

"If it were true that the geometrically simplest arrangements or those which seemed simplest in the light of the existing chemical and other preconceptions are the correct atomic arrangements in crystals, then a great emphasis on the necessity of treating experimentally all possible atomic arrangements would perhaps be of only formal interest. The reliable data show, however, that such is not in fact the case. Thus simple crystal structures which seem chemically and crystallographically plausible can readily be imagined for pyrrhotite of the composition FeS or for carborundum (CSi); nevertheless the actual atomic arrangements in both appear to be much more complicated. The worthlessness of apparent chemical analogies and relationships as a means of predicting crystal structures finds many illustrations. For instance silver and cuprous oxides have the same structure but the cuprous halides have one atomic arrangement (the zinc sulfide grouping), silver chloride and bromide have another one (the sodium chloride grouping) which is in turn different from the stable modification of silver iodide (the zinc oxide arrangement); similarly all of the cesium halides have an ammonium chloride-like structure except the fluoride which resembles the other alkali halides in being structurally isomorphous with sodium chloride. This present failure of prediction as applied to the results of crystal analysis is the greatest encouragement to pursue its development; for if its results could be foretold experimental studies with X-rays would have little, while in reality they must eventually have much, to contribute towards the problems of the laws governing atomic combination," p. 229.

"Powder photographic, but no other, data have been obtained from lithium, sodium and potassium. Metallic potassium yields only a general blackening at ordinary temperature but crystalline diffraction is definite at -150° C, although the individual crystals were too large to give a good powder photograph. This failure of potassium at room temperature to furnish a crystalline diffraction pattern has been interpreted to mean that it is amorphous. Well defined crystals of potassium have, however, been grown from the molten metal and potassium has a definite and sharp latent heat of fusion and melting point. It giving only amorphous scattering is then probably to be attributed rather to the large amplitudes of thermal agitation of its atoms than to any lack of order in their arrangement. Cooling of such a material should result in the successive appearance and gradual strengthening of a crystalline pattern at the expense of the general blackening. This experiment has not yet been tried upon potassium. Sodium, however with a higher melting point shows such a poor crystalline pattern upon a much blackened background," p. 232.

"X-ray diffraction patterns have been produced from many specimens of carbon. Except for those from the diamond only the diffraction lines characteristic of graphite were found in these experiments. In many kinds of "amorphous" carbon, however the individual crystals are so extremely minute that their reflections are much widened. Both crystalline silicon and the so-called "amorphous" product have invariably been found to give the diamond type of pattern.

"Enough data are at hand to establish with great certainty the atomic arrangement in the diamond. Both crystallographic and optical examinations leave no doubt of its cubic character. Reflections from an octahedral face combined with the density show that $m/n^3 = 8$. The data from the early Laue photographs, which are confirmed by powder measurements, give no reasons for taking a unit containing more than eight atoms," p. 243.

"The symmetry and crystal structure of carborundum present an interesting and puzzling problem for which there is not as yet a satisfactory answer. In the past it has been supposed that CSi crystallizes in the rhombohedral division of the hexagonal systems, the rhombohedral angle being almost 90°. On the basis of studies of face development it has recently been concluded, however that three distinct modifications exist, all with practically identical axial ratios and all crystallizing in the hexagonal system. Laue photographs which are strong evidence for their separate existence have been prepared from crystals belonging to these three supposed types," p. 264.

The powder photographs of most liquids and glassy solids consist not of an amorphous scattering but of a series of one or more broad but distinct diffraction bands, p. 383. Powder photographs have been prepared from several compounds which form liquid crystals. In all cases the turbid as well as the clear liquids yield only liquid patterns, p. 386.

"One of the most interesting contributions of crystal structure knowledge arises from its bearing upon the nature of valence relations in the solid state. From such sources as the Gay-Lussac Law of volumes and the kinetic theory of gases, as well as numerous results of recent physical research, there is unmistakable evidence for the existence of chemical molecules in gases. The extension of the gas laws to dilute solutions also has indicated that the solute is distributed in some cases throughout the solvent as small and constant associations of atoms. Furthermore it seems impossible to imagine other than a molecular constitution for typical organic compounds whether they are in the physical state of gas, liquid or solid. There has, however, been no authentic information to show that such constant associations of atoms as are commonly understood by the term chemical molecule exist in other liquids and solids. The practically universal assumption by chemists that under all physical circumstances the normal condition is one in which a few atoms are associated together as molecules has thus been an experimentally unwarranted extrapolation from the existing knowledge. For this reason evidence for the non-existence of chemical molecules in most inorganic solids need not be in contradiction of previous experiments.

"From crystal structure data it seems quite certain that no molecules are to be distinguished in such crystals as sodium chloride. If a sodium and a chlorine atom were bound together as a molecule in rock salt, then since the forces holding them together would be greater than those acting between either atom and any other within the solid mass, their distance apart would be different from other interatomic distances within the crystal. A study of the structure of sodium chloride crystals, however, shows that each chlorine atom is surrounded by six equally distance sodium atoms and each sodium atom by six equally distant chlorine atoms. The repetition of this equality in atomic separations makes the entire crystal the next physical entity larger than the atoms of which it is composed. A reference to the structures of the other inorganic crystals which have been investigated shows that in most of them the usually assumed chemical molecules can not be distinguished. Nevertheless wherever such associations as the sulfate, carbonate, or nitrate groups are present they can be identified within the crystal structure. A few inorganic compounds have non-polar and other physical properties which suggest that definite molecules are present in their crystals. Tin tetraiodide is such a substance and molecules of SnI_4 can be distinguished in its crystal structure. Likewise the molecule can be found within crystals of hexamethylene tetramine ($C_6H_{12}N_4$), the only truly organic compound the structure of which has yet been adequately and completely elucidated," p. 392.

"The existing crystal structure data show conclusively that there is no direct connection between the manner of arrangement of the atoms in a crystal and its magnetic properties. Among the strongly ferromagnetic metals, iron at room temperature is body centered in atomic arrangement, nickel is face centered, and cobalt is both face centered cubic and hexagonal closest-packed. The comparatively weakly paramagnetic chromium has the same atomic arrangement and nearly the same interatomic distance as iron; and diamagnetic copper is face centered like nickel and cobalt. When the magnetic properties of a Heussler alloy were changed by a suitable heat treatment, no alteration could be detected in its powder pattern. The apparent identity in crystal structure of alpha- and beta-iron (the latter not being ferro-magnetic) is in accord with these observations. The data on the Heussler alloy and the study of this inversion in iron indicate that a sharp change in the permeability of a substance need not be accompanied by a change in crystal structure. The same thing is shown for substances of variable composition by the fact that no difference in diffraction pattern can be observed for two pyrrhotites, one of which in containing a slight amount more of "dissolved" sulfur than the other had assumed ferro-magnetic properties. This absence of a connection between atomic arrangement and magnetic properties is very strikingly emphasized by the failure of diffraction measurements to give an indication of the existence of the intensely ferro-magnetic "permalloy" amongst the iron-nickel series of alloys," p. 403.

Wilder D. Bancroft

The Mechanical Properties of Fluids. *By Sir George Goodwin et al. 22×15 cm, pp. xv+362. New York: D. Van Nostrand Company, 1924. Price: $6.00.* This is a collective work with an introduction by Sir George Goodwin and ten chapters entitled: liquids and gases by Allan Ferguson; mathematical theory of fluid motion, by Horace Lamb; viscosity and lubrication by A. G. M. Michell; stream-line and turbulent flow; hydrodynamical resistance, by A. H. Gibson; phenomena due to the elasticity of a fluid, by A. H. Gibson; the determination of stresses, by G. I. Taylor; wind structure, by A. E. M. Geddes; submarine signalling and the transmission of sound through water, by C. V. Drysdale; the reaction of the air to artillery projectiles, by F. R. W. Hunt.

Ferguson accepts the formula of Ramsay and Shields as giving the true molecular weight of liquids, p. 21, without making any reference to the apparently discordant results of Walden and others. If we substitute the energy per unit area for the surface tension, we get a quantity which is called the total molecular surface energy. Bennett and Mitchell have shown that this is constant over a fairly wide range of temperature, and have used this constancy as a test of non-association.

Ferguson believes in the contact angle, p. 23, though he admits that it is zero for water and glass. He states that it is not proper to call the weight of a falling drop $2\pi r\gamma$. Theoretically it should be $\pi r\gamma$ if it were a static phenomenon, and experimentally it is $3.8r\gamma$, p. 27.

Instead of solving van der Waals' equation for the condition that the three roots shall be coincident, Ferguson says, p. 41, that "it is preferable to write down the condition that at the critical point the isothermal has a point of inflexion with a horizontal tangent. If we therefore differentiate van der Waals' equation with respect to *v*, put $\partial p/\partial v$ and $\partial^2 p/\partial v^2$ equal to zero, the resulting equations, combined with the original equation of state, serve to determine p_c, v_c, and T_c. This method is preferable, since it is perfectly general and may be applied to characteristic equations which are not cubics in *v*, and to which, therefore, the equal-root method, beloved of writers on physical chemistry, is not applicable."

One can of course try to improve on the van der Waals formula as has been attempted by Clausius, Dieterici, Keyes, and many others; but the subject may also be studied from a different point of view, p. 43. "Instead of attempting to devise an equation which shall represent the properties of a substance over a wide range—a process which usually results in a cumbrous formula—we may try to arrive at an equation which shall be simple and manageable in form, so that the various physical constants of the fluid may be worked out readily from the corresponding thermodynamic relations, while at the same time the equation shall represent a very close approximation to the truth over a limited range, the range chosen being one of practical importance. Whether such a formula can, or cannot, be extrapolated beyond the limits of the range is a matter of secondary interest—what is important is that the formula should be as exact as may be within these limits."

As a case in point Ferguson cites, p. 44, Callendar's equation,

$$V=\frac{T}{p}-\frac{c}{T^n}+b.$$

This equation has been applied very successfully to elucidate the properties of steam over a range of pressure from zero to thirty-four atmospheres; the value of *n* appropriate to steam is 10/3.

Michell says that "the law of viscous resistance is most clearly conceived in the case of *laminar motion*, which may be defined as a state of motion of a body of fluid in which the direction of the motion of the particles is the same at all points and the velocity is the same throughout each of a series of planes parallel to one another and to the direction of motion. A volume of fluid in laminar motion can thus be regarded roughly as a series of very thin layers of solid material, sliding one upon another in a common direction," p. 97.

"The value of the coefficient of viscosity, μ, varies greatly from one fluid to another, and in any one fluid it changes with the temperature, and to a smaller extent with the pressure of the fluid. Its value is in general much higher for liquids than for gases. Liquids in which the value of μ is low are said to be 'limpid,' 'thin,' or 'light,' while those in which it is comparatively great are said to be 'viscous,' 'thick,' or 'heavy.' There is, however, no necessary or general correspondence between the density of a liquid and its viscosity. Thus mercury, the heaviest of known liquids at atmospheric temperatures, is one of the least viscous," p. 98.

"With regard to the motion of fluids parallel to solid walls with which they are in contact, there is strong evidence that, in the case of liquids at least, the relative tangential velocity σ at the wall is zero. Some of the evidence will be referred to later in connection with the flow of liquid through tubes under great pressure, and in the discussion of the theory of lubrication. Even when the mutual molecular attraction of a liquid and solid appears to be comparatively small, so that the liquid does not tend to spread over, or "wet" the surface of the solid, as is the case with mercury and glass, there is no observable sliding or slipping of the fluid over the solid at their common surface. If the tangential tractional force between liquid and solid, and consequently the rate of shear in the liquid near the surface are finite, the relative tangential velocity, being zero at the surface, must be still small at all points of the liquid near the surface.

"In gases, the same rule as to the relative velocity being zero at a solid surface is found to apply under ordinary circumstances, at least as a very close approximation. When, however, a gas is at such low pressure that its molecules are at distances apart comparable with the dimensions of the volume of gas which is being dealt with, phenomena are observed which can be regarded as arising from an appreciable velocity of slipping of the gas over the solid surface. According to Maxwell, the motion of the gas is very nearly the same as if a stratum, of depth equal to twice the mean free path of the gas molecules, had been removed from the solid and filled with the gas, there being no slipping between the gas and the new solid surface," p. 102.

Michell states, p. 108, that "the most convenient form of "absolute viscometer for liquids is that described by W. Stone. In this instrument the pressure is applied by a column of mercury of which the height is automatically maintained constant, and other devices are provided which further simplify the manipulation of the instrument and the calculation of the results from the observations."

"Although viscous liquids and plastic solids have been used from the earliest times to diminish friction between solid bodies moving in contact with one another, and although the practice of thus "lubricating" the bearings of machines has doubtless been universal since machines were first constructed, no rational explanation of the action of the lubricant was known until Osborne Reynolds, in 1886, gave a clear interpretation of the phenomena in terms of the theory of viscosity. Reynolds' explanation was only complete in a quantitative sense in the case of journal bearings furnished with special, and at that date unusual, means for supplying ample quantities of lubricant. He showed that in such cases the solid surfaces are completely separated from one another by fluid films of appreciable thickness, and that such films are maintained and enabled to support the pressure imposed on them quite automatically by the relative motion of the parts. The theory has since been extended to bearings of other kinds than journal bearings, and by its application new types of bearings have been devised for various purposes which have proved far more efficient than the forms which they were designed to replace.

"While this 'viscosity theory' of bearing lubrication is not quantitatively complete in all cases, and while there are probably other modes of lubrication in which viscosity does not play an essential part, it is at present true that all the most efficient known types of bearings which operate with sliding, as distinguished from rolling, contact utilize the principle of lubrication which was discovered by Reynolds," p. 122.

"The fact otherwise inexplicable, that the conditions and laws of viscous lubrication were not discovered until the end of the nineteenth century, is doubtless due to the circumstance that it was only at about that epoch that mechanical workmanship became generally of such a quality that the necessary conditions were often complied with. With rougher workmanship the necessary continuous films cannot be formed, but the two members of the bearing come into actual or virtual contact, at least at some points, and thus bring about mixed conditions of solid and viscous friction incapable of being referred to any simple or consistent laws.

"Even with workmanship which may be regarded as perfect the ultimate stage of failure initiated by any cause is contact of the solid surfaces, either directly or through the small particles of solid impurities which are always to some extent present in the lubricant. There is thus suggested as a criterion of the safety of any bearing from such failure, the thickness of the lubricating film at its thinnest part under the working conditions which reduce this thickness to a minimum," p. 131.

"When a straight bar of uniform cross-section is twisted by the application of equal and opposite couples applied at its two ends, it twists in such a way that any two sections which are separated by the same distance are rotated relative to one another through the same angle," p. 229. Taylor points out, p. 231, that it is possible to deduce a function ψ which "is simply related to the shear; in fact the shearing strain at any point is proportional to the rate of change in ψ at the point in question in the direction in which it is a maximum."

It is only possible to deduce ψ directly in a very few cases; but it was shown by Prandtl that a soap film stretched over a hole in a flat plate can be made to be "a graphical representation of the function ψ for the given cross-section. Actual values of ψ can be obtained from it by multiplying the ordinates by $4\gamma/p$", p. 232.

"The contour lines of the soap film in planes parallel to the plate correspond to the 'lines of shearing stress' in the twisted bar; that is, they run parallel to the direction of the maximum shear stress at every point of the section. It is evident that the torque and stresses in a twisted bar of any section whatever may be obtained by measuring soap films in these respects. . . . It is evident that, since the value of $4\gamma/p$ for two films is the same, we may, by comparing inclinations at any desired points, find the ratio of the stresses at the corresponding points of the cross-section of the bar under investigation to the stresses in a circular shaft of radius h under the same twist. Equally, we can find the ratio of the torques on the two bars by comparing the displaced volumes of the soap films. This is, in fact, the form which the investigations usually take," p. 233.

"It is well known that the stress at a sharp internal corner of a twisted bar is infinite or, rather, would be infinite if the elastic equations did not cease to hold when the stress becomes very high. If the internal corner is rounded off the stress is reduced; but so far no method has been devised by which the amount of reduction in strain due to a given amount of rounding can be estimated. This problem has been solved by the use of soap films," p. 239.

Under submarine signalling Drysdale says, p. 291, that "again the value of R for steel is about 395×10^4, so that on passing from water to steel $r = 28$ approximately, and the efficiency of transmission is about 13 percent, while from steel to air it is only 0.004 percent. Hence for sound to pass from water through the side of a ship to the air inside, the efficiency would be only 13 percent of 0.004 percent, or 0.00052 percent, were it not for the fact that the plates of a ship are sufficiently thin to act as diaphragm, and thus allow a greater transmission than if they were very thick. In any case, however, the loss of energy is extremely great, and this has led to the practice of mounting inboard listening devices, either directly on the sides of the ship or in tanks of water in contact with the hull, as will be described later."

"The practical construction of underwater receivers and hydrophones will be dealt with later, but it will be well at this point to give some idea of their essential features. The simplest form of such a receiver, which is analogous to the simple trumpet for air reception, is called the Broca tube, which consists of a length of metal tube with a diaphragm over its lower end. When this is dipped into the water, the sound from the water is communicated through the diaphragm to the air inside the tube, and the observer listens at the free end. This is moderately effective, but not very sensitive or convenient, as it makes no provision for amplifying the sound, and it is not easy to listen through long bent tubes, so that the observer must generally listen only a few feet above the water. Modern hydrophones are therefore nearly all of an electrical character containing microphones or magnetophones from which electrical connections are taken to ordinary telephone receivers at the listening point.

"Microphones are generally used as they are more sensitive, and there are two types of microphone which correspond approximately to pressure or displacement receivers respectively. The former is termed the "solid back" type, in which a number of carbon granules are enclosed between a metal or carbon plate forming or attached to a diaphragm and a solid fixed block of carbon at the back. If pressure is applied to the diaphragm it compresses the granules and increases their conductivity, so that a greater current passes from a battery through the microphone and the receivers and reproduces the sound through the pressure variations. In the 'button' type of microphone, on the other hand, the carbon granules are enclosed in a light metallic box or capsule covered by a small diaphragm, and the whole arrangement is mounted on a larger diaphragm, so that its vibrations move the capsule as a whole and shake up the granules, with only such changes of pressure as result from the inertia of the capsule. In this case it is the motion or displacement of the diaphragm which produces the variations of resistance in the microphone.

"The commonest type of simple hydrophone consists simply of a heavy circular metal case of disc form with a hollow space covered by a metal diaphragm to the centre of which a button microphone is attached. It is fairly sensitive but has no directional properties," p. 293.

"A number of forms of submarine siren, in which plates or cylinders provided with holes through which jets of water pass when the plates or cylinders are rotated, have been devised both in this country and in Germany, and are extremely powerful. By suitably bevelling the holes, the water pressure can, of course, be made to rotate the plates, but this is objectionable from the signalling point of view, as it involves a gradual running up to speed and a consequent variation in the frequency of the note. On this account the plate or cylinder is usually rotated independently at a constant speed by an electric motor, and signalling is effected by switching on and off the high-pressure water supply. These sirens have not, however, come greatly into use, as the electromagnetic transmitters are so much more convenient, and they will therefore not be described in detail," p. 307.

"A remarkably interesting and effective form of directional inboard listening device, however, is that known as the Walser gear, devised by Lieutenant Walser of the French navy, in which the sound is brought to a focus, as in a camera obscura, and the direction determined by the position of this focus. For this purpose a "blister," consisting of a steel dome of spherical curvature and about 3 ft. 6 in. diameter is fitted to the hull, and this steel dome is provided with a large number of apertures into which thin steel diaphragms are inserted. These diaphragms being on the spherical dome collect the sound and direct it to a focus at a distance of 5 or 6 ft. A trumpet, to which a stethoscope tube is attached, is mounted on an arm turning on a vertical axis, so as to be able to follow the focus and point in the direction of the sound from whatever direction it comes. Two of these blisters are generally mounted somewhere forward on the two sides of the hull, and an observer seated between them applies the tubes from the two trumpets to his ears, so that he can follow the position of the source on either side, the direction being given on a scale when maximum intensity is obtained," p. 311.

"A method of sound ranging which promises to be of much greater value for navigation, but which has not yet been fully developed as it was of little value in war time, is the wireless acoustic proposed by Professor Joly. In the original experiment of Collodon and Sturm in 1826, the velocity of sound in water was determined by striking an underwater bell and igniting a charge of gunpowder simultaneously. By knowing the distance from the source and observing the interval of time between the flash and the sound of the bell the velocity was determined, as light travels practically instantaneously over any ordinary distance. Conversely, if the time interval and the velocity are known, the distance of the source can be at once determined, as in the familiar method of ascertaining the distance of a lightning flash by noting the time between the flash and the thunder clap. The advantage of employing an underwater method is that sound is transmitted more effectively through water, and that there are not water currents comparable with winds to affect the velocity appreciably

"Unfortunately a flash of light is of no value in a fog, but wireless waves are little affected by it, and travel with the same speed as light, so that if a wireless flash and an underwater explosion are generated simultaneously at a lighthouse or other known position, and the ship is provided with a wireless equipment and a directional hydrophone, the distance of the station can be at once determined on the ship by noting the interval between the two impulses. As the velocity of sound in sea water is nearly a mile a second, the distance can be determined within a quarter of a mile by a simple stop-watch, and the direction of the source found by either the directional hydrophone or directional wireless, without any communication with the station. If the lighthouse or lightship simply sends out wireless impulses simultaneously with the strokes of the submarine bell at convenient intervals, all ships in the vicinity can locate their positions from time to time without delay or mutual interference, and if they are within the range of two such stations they can do so without any directional apparatus.

"The recent developments in directional wireless have rendered the application of sound ranging to navigation of less importance, but even now wireless direction finding is not always reliable, especially at sunrise and sunset; and there is also liability to error on steel ships owing to their distorting effect on the wireless waves. As hydrophones become increasingly employed on ships for listening to submarine bells, etc., the ability to obtain accurate ranges by wireless acoustic signals will doubtless prove of great value.

"Although not strictly speaking an acoustic device, some mention should be made of the leader gear or pilot cables as an aid to navigation of harbours and channels in foggy weather. For this purpose it is necessary to be able to follow some well-defined track with a latitude of only a few yards, so that sound ranging is inadequate. But if a submarine cable carrying alternating current of sonic frequency, say 500 cycles, is laid along the desired track, and the ship is provided with search coils with amplifier and telephones, the alternating magnetic field produced by the cable induces alternating electromotive forces in the coils, and thus gives a sound in the telephones when the ship is sufficiently near the cable. By using two inclined coils on the two sides of an iron or steel ship it is found that the sound is loudest when the telephones are connected to the coil which is nearer to the cable, so that the ship can be steered along it, and keep a fairly definite distance to one side of it, so that vessels passing in opposite directions will not collide. This device, which was first put forward by Mr. C. A. Stephenson of Edinburgh in 1893, was revived during the war by Captain J. Manson, and is now coming into use both in this country and in the United States. An 18-mile cable has been laid by the Admiralty from Portsmouth Harbour down Spithead and out to sea," p. 317.

"Before concluding this article, reference ought to be made to the wonderful achievements of M. Constantinesco, as showing the possibilities of what may be called acoustic engineering. For the purposes of underwater signalling, the power transmitted, although large in comparison with what we have heretofore contemplated in connection with sound, rarely exceeds a hundred watts; and it has been left for M. Constantinesco boldly to envisage the possibility of transmitting large amounts of power by alternating pressures in water of sufficiently high frequency to be described as sound waves. For many years it has been customary to illustrate the phenomena of alternating electric currents by hydraulic analogies, and the present writer has even written a book in which such analogies have been used as a means of giving a complete theory of the subject; but the obvious possibility of using such alternating pressures in water for practical purposes was entirely missed until M. Constantinesco conceived it, and immediately the idea occurred it was evident that the whole of the theory was ready to hand from the electrical analogies. In a surprisingly short time, therefore, M. Constantinesco has been able to devise generators, motors, and transformers capable of dealing with large amounts of power transmitted by hydraulic pipes in the form of accoustic waves of a frequency of about 50 cycles. The generator is, of course, simply a high-pressure reciprocating valveless pump, and the motor can be of similar construction, but by having three pistons with cranks at 120°, three-phase acoustic power can be generated and employed in the motors. The first commercial application of M. Constantinesco's devices has been to reciprocating rock drills and riveters, for which this method is especially suitable, as the reciprocating motion is obtained simply from a cylinder and piston without and valves whatever, and the power is transmitted by a special form of flexible hydraulic hose pipe comparable with an electric cable. It is not too much to say that M. Constantinesco's ideas have opened up an entirely new field of engineering, and their development may have far-reaching effects," p. 321.

Wilder D. Bancroft

Atoms and Rays. *An introduction to modern views on atomic structure and radiation. By Sir Oliver Lodge. 23 × 16 cm; pp. ix + 208. London and New York: Ernest Benn; George H. Doran, 1924. Price: 21 shillings; $3.00.* Of late years, the beaches which divide the wooded fastnesses where laymen go about their human business, from the open seas of science where sail the exploring fleets, have more and more often formed meeting-grounds; officers, men, and cabin boys of one scientific squadron after another have taken short leave ashore to exchange goods and news with such natives of the lay hinterland as would come down to meet them on the strand. Sometimes, too, the fires of the rendezvous have attracted the notice of the men of other fleets, who find that they hear better gossip by talking with their fellow-sailors in the lingua franca of the coasts than in dry interchanges by the signalling codes of the high seas.

Sir Oliver Lodge is one of the most welcome of such shoreward visitants; and he is no ordinary rollicking A. B., full of tales more picturesque than truthful. He is one of the lords admiral; and, like Diego Valdez, he knows the men and tongues of many shores, that which he speaks is to be listened to above the crackling of thorns in the camp fire, and he needs no other interpreter to compel understanding among his hearers.

Of all the books lately written to expound the New Physics to non-experts, "Atoms and Rays" is one of the very few which are really worth buying. The reader with a taste for something more than "Our Scientific Correspondent" provides, can sit down to think and to enjoy; the professor of some other branch of science (who is often worse educated than any thoughtful layman) can widen his horizon, and can learn at the same time a lesson in the art of first-class teaching; and the same lesson also cannot fail to impress itself upon even the specialist in mathematical physics who stands in no need of the actual instruction here presented. And all will gain by the emphasis of a view which Sir Oliver evidently approves, namely that the proper aftermath of rigid experimentation and reasoning, is, and should be, a deeply aesthetic appreciation.

In the publication of any book which deals rather with results than with the weapons with which they were won, there is always one risk: the risk that the undergraduate student of the subject, whose aim it should be to master methods and logic that he may himself employ, will miss the whole point of his training if he is led to think that he knows a thing because he has read it in a book. Instruction in methods of enquiry is, fortunately, the primary object of any sound University course; it is the mainspring of all scientific investigation as opposed to amateurish superficiality. Sir Oliver Lodge is, of course, better aware of this than most people; and it may be doubted whether any other author could more judiciously have blended the salutary powder of logic with the satisfying jam of results, than in the twenty-six spoonfuls with which he serves us here.

To have welded into a *consecutive* story the very various developments in electricity, radioactivity, spectroscopy, radioenergetics, and relativity, which have grown up so rapidly around the chemist's atom and ion would have been historically misleading, since so many of these remained largely independent for so much of their course and are only now flowing together; yet, because the core of the book deals with line-spectra in relation to the whole, there is introduced a continuity which carries the reader on. The author favours, at the same time, the plan of a fugue; he is not afraid of repeating himself when, (if one may hazard a guess) he includes the text of one or two public addresses in his chapters. As he points out, such repetition serves valuably to hammer home the truth; and the attentive reader cannot but be grateful for it, especially when it gives opportunity for fresh parables or similes as illuminating as those (for instance) on pages 56, 57 and 95. Continually these analogies challenge our interest, and rob recondite theories of their terror without unduly disguising the technical difficulties of their genesis. Throughout the book one is stimulated by the simplicity, flow, and power of the language and the thought which it clothes.

The author dwells again and again on the Ether as an entity nearly as real as atoms and electrons; it is for him the ultimate unifying principle, and he upholds ("in my view") what is of course, a most fascinating hypothesis, that matter and energy have their common basis in ether-whorls. The present reviewer lays no claim to knowledge on these questions; but *is* it a matter of universal consent among the competent authorities (of whom Sir Oliver is one of the chief) that, e. g., "to say that the force between the atoms was electrical is the same thing "as saying that they are held together by the Ether?" We must all welcome attempts to bring home that which has previously been the wandering scapegoat of the physicists' sins of omission; and if other eminent physicists can assure us that Ether is as actual to them as it is to Sir Oliver Lodge, we shall gladly scotch a faint suspicion that its existence is not quite as axiomatic as this book would cause some readers to believe.

It is interesting to glean the views of one of such experience, concerning the present day. Speaking of "the remarkably brilliant present generation of physicists," he draws a striking parallel between the progress in his subject up to now, and the well-defined stages in the evolution of astronomy; and chemists, especially those chemists who are not *au fait* in modern work, should well mark the final prophecy;—

"We are living in the dawn of a kind of atomic astronomy "which looks as if it were going to do for chemistry what Newton did "for the Solar System."

Irvine Masson

L'Energétique des Réactions chimiques. *By G. Urbain. Collection Langevin-Perrin-Urbain. 23×14 cm; pp. viii+267. Paris: G. Doin, 1925. Price: 25 francs.* Professor Urbain's book deals with Thermodynamics and its application to chemical problems. Its title will probably be more attractive than a description of the book as a treatise no Thermodynamics, but the text would be perfectly correctly described by such a designation. Opinions differ as to the value of a knowledge of Thermodynamics to chemists, but the author adopts the view that: "no one can call himself a chemist if he is ignorant of the principles of thermodynamics [not "Energetics," be it noted] and of the manner of correctly applying them to chemical phenomena in general and to chemical equilibria in particular." There must, however, be many to whom the title of chemist might correctly be given who have little knowledge of thermodynamics. It was Bunsen who said: "Ein Chemiker, der kein Physiker ist, ist gar nichts," or something to that effect, but Bunsen's physics probably did not include thermodynamics. The work of Emil Fischer, Perkin, Remsen, Thorpe, and other most successful organic chemists owed and owes very little to thermodynamic considerations, and not every chemist has the training and outlook of a Nernst, a Bancroft, or a Donnan. When Urbain says further that "Thermodynamics is the type of the sciences of principles, as atomism is the type of the sciences of explanations" he gets nearer the truth. Even those organic chemists who have troubled themselves with principles have usually turned to some form or other of thermodynamics, and Lapworth, Nef, and van't Hoff have found this knowledge no hindrance in their attempts to penetrate a little further into the reality of phenomena than the rather crude but remarkably effective and practical hieroglyphic of "Strukturchemie." Professor Urbain emphasizes that thermodynamics, resting as it does on immediately measured and perceived magnitudes, is the most practical of sciences: "it substitutes nothing for the reality of the facts which result from the direct witness of our senses." This feature makes the science a little tiresome to some, since the imagination has not so wide a field over which to roam when its images can be checked at any moment by an appeal to experimental figures.

In the first part of the book an exposition of the general principles of thermodynamics is given on the usual lines. Greater stress is perhaps laid on generalities than is usual in other books, and in particular the chapter on "General Laws of Displacement of Equilibrium" (pp. 48-60) will require careful study. Most students would perhaps benefit by a more algebraic treatment of the subject. The following chapter on the ideal gas is very clear, but at the end it is not pointed out that the derivation of the usual adiabatic law is not possible on the two assumptions usually made in defining an ideal gas, but requires a further assumption which is passed over in the text.

The part of the book dealing with the Modern Theory of Affinity begins with a long account of chemical constraints and catalysis which has really very little to do with the subject. It may be true that "no chemist has realised a reaction of a reversible path"; but it is equally true that no chemist has "added a molecule of bromine to a double bond," and Professor Urbain's insistence on the fictitious character of reversible processes is perhaps calculated to mislead the reader. The changes of entropy and free energy in a chemical reaction do not depend on the chemical change being reversible; it is only the *calculation* of these changes which is made to depend on a reversible path. The results are equally true whether the change is reversible or not. The author seems to realise this, since he says that "these considerations do not belong to the domain of pure thermodynamics, but they belong to the border-land." It is made clear that most of the work of the organic chemist is, energetically speaking, skating over thin ice. Very few of his compounds are in truly stable states, but "although the only spontaneous change possible is that which consists in passing from a less stable to a more stable state, one can, in a very large number of cases, pass by way of states of successive stability."

In the discussion of equilibrium it is pointed out that chemically inert phases may be left out of account: they are of no greater importance that the beaker containing the system. Recent discussions on the phase rule seem to have overlooked this simple fact. The Law of Mobile Equilibrium is stated in the form that "whenever the state of mobile chemical equilibrium of a system is modified by an exterior action, the system reacts chemically in a sense which opposes this action." This obviously includes the law of mass action, although this is not stated.

The sections on affinity follow the usual lines. The free energy drop is taken as a measure of affinity without further justification, and its value is found for chemical reactions in the usual way. Professor Urbain does not overlook the external work term in the expression for the affinity which nearly every other author forgets or tries to show is superfluous. After all, it is merely a matter of algebra. The discussion on p. 130, in which it is proposed that the criterion of the possibility of a reaction presupposes that the reaction is complete, is surely not correct. The actual change may be as small as is wished, and there is no reason why any such limitation should be introduced. The applications in the rest of the book are extremely clearly set out and well chosen.

The Phase Rule is deduced in terms of the chemical potentials, but in a very neat and simple manner, and its applications are carefully explained.

The book ends with a short but detailed treatment of the "Third Principle proposed by Nernst."

J. R. Partington

Die Fermente und ihre Wirkungen. *Parts I-III. By Carl Oppenheimer with one chapter on Physikalische Chemie und Kinetik, by Richard Kuhn. Fifth edition. Leipzig: George Thieme, 1924. Price: $1.90 each.* Ever since its first appearance in 1900, Oppenheimer's "Die Fermente" has been indispensable as a book of reference, and this, greatly increased, new edition will be welcomed by the ever growing band of biochemists. The first three parts, now under consideration, (the whole work will run to about ten parts of 160 pages each) comprise the general part of the work, the remaining seven will constitute the Special Part, dealing with the detailed description of the individual enzymes.

The General Part is divided into two sections, treating respectively of the Chemistry and the Biology of the enzymes, and it is the former of these which will appeal most strongly to physical chemists. Of special interest will be the chapter on the Physical Chemistry and Kinetics of Enzymes, which has been written by Dr. Richard Kuhn of Munich, Prof. Herzog, who undertook this section in former editions having been unable to continue his cooperation.

In this section will be found a very complete account of the present state of knowledge on the subject. Perhaps the greatest interest now attaches to the questions of the influence of hydrogen ion concentration on the rate of enzyme action, the existence and nature of a compound or complex between the enzyme and substrate, with its attendant problem of the nature of specificity of action, and supreme question of all, the chemical nature of the enzymes themselves.

The first of these problems, since the publication of the classic paper by Sörensen in 1909, has received a large measure of attention and the effect of hydrogen ion concentration is now taken into account in all enquiries in which enzymes are involved. As regards the question of the nature of the combination between enzyme and substrate the rival theories of chemical union and adsorption are discussed in detail; but the convictions of the author evidently lie with the former of these alternatives. The fact seems to be that the relation between concentration of enzyme and substrate and rate of action are too complicated to admit of a decisive interpretation, even when the initial velocities in any given system are considered. The products of the reaction which an enzyme accelerates have in many cases an undoubted influence on the activity of the enzyme. Moreover it appears from the recent investigations of Willstätter on invertase, with which the author of this section of the work was also associated, that the enzyme may be accompanied by inactive substances, the amount and possibly even the nature of which vary in different preparations and that these also have the property of combining with and thus partially inactivating the enzyme. These impurities may be regarded as competing with the substrate for possession of the enzyme and their effect varies with the relative concentrations of the enzyme preparation and the substrate.

Of great interest in relation to the association of enzyme and substrate is the determination by kinetic measurements of the affinity constants of an enzyme for its substrate and the decomposition products thereof (Michaelis) and the application of these ideas to the establishment of a quantitative theory of specificity (Willstätter and Kuhn). A striking example of the use of such a theory is afforded by the hydrolysis of cane sugar and raffinose by invertase.

As regards the chemical nature of the enzymes, in spite of many important advances, especially quite recently at the hands of Willstätter and of Euler, nothing very definite can yet be said: "What we usually obtain as so-called soluble enzymes are preparations which contain all sorts of materials and especially proteins, as well as precursors and inactive derivatives of enzymes, colloidal mixtures on which small amounts of the actual enzyme are adsorbed." What we do know is summed up by Oppenheimer in the words: "The enzymes are substances of colloid nature and high molecular weight, they are amphoteric electrolytes and possess a great tendency to complex formation." This amounts to a confession of ignorance and until further progress is made in the isolation and characterisation of the prime agents many obscurities and uncertainties will remain in the study of enzyme action.

Arthur Harden

The Specific Heats of Gases. *By J. R. Partington and W. G. Shilling. 23×15 cm; pp. 252. London and New York: Ernest Benn; D. Van Nostrand Company, 1924. Price: 30 shillings; $8.00.* Whether from the theoretical or the technical standpoint the subject of this volume is one of first-rate importance. One may instance, on the one hand, the relationship between heat capacity and the conceptions of the kinetic gas theory, and on the other hand the significance of specific heat in connexion with internal combustion engines and refrigerators. It is all the more remarkable that apparently no attempt has hitherto been made to prepare a comprehensive and critical survey of the work done in this field. The gap has now been filled by Professor Partington and Mr. Shilling who have not only contributed experimentally to our knowledge of specific heat, but have in the present volume made a remarkably thorough historical study of the methods employed and the results obtained by the numerous investigators who have given their attention to this subject.

Following an introductory chapter devoted to general theoretical considerations, to units, and to the various equations of state, the authors describe in detail and review critically all work which has been carried out aiming at the determination of C_p, C_v, and γ. The sources of error are fully considered, and the whole of the available data having been tabulated and sifted, a series of values for different gases is presented which the authors consider to be the most trustworthy.

The book is not intended for the beginner, but rather as a volume for reference which the expert may consult. Among the topics which come under consideration in addition to those already mentioned are the special case of steam, the thermal capacity of a dissociating gas, the bearing of specific heat on the efficient working of a producer plant, and the heat losses in furnace practice, so far as the products of combustion are concerned.

Attention is drawn to Behn and Geiger's improvement of Kundt's dust figure method, and to the further modification employed by the authors in their study of the heat capacity of nitrous oxide. The introduction of this improvement is probably not generally realised.

Another point, affecting the well-known Clément and Désormes method and not generally appreciated, is the necessity of finding in each case the optimum size of the expansion orifice. With too small an aperture the expansion is unduly prolonged and is therefore no longer adiabatic. With too large an aperture the gas surges backwards and forwards, because "the momentum of the first rush would leave a pressure in the expansion vessel below that of the atmosphere." The orifice required for oxygen is smaller than that required for nitrogen, indicating that the amount of overshooting varies with the density of the gas.

The authors have carried out their task in a thoroughly competent manner, and the volume will be a valuable addition to the bookshelves of both the physical chemist and the engineer.

J. C. Philip

THE DEDUCTION OF THE TYPE OF A TWO-COMPONENT SYSTEM BY MEANS OF THE ADDITION OF A THIRD COMPONENT

BY F. A. FREETH

Introduction

The following paper is confined to condensed systems. Its object is to show how a great deal of published material, which at present is of rather an uncertain character, may be greatly enhanced in value by means of a comparatively slight amount of further experimental work. In addition it is also shown that phenomena of great interest and complexity must necessarily occur at temperatures very near to those at which several authors have recently published experimental results. A very large number of condensed two-component systems have been examined by the method of thermal alalysis.

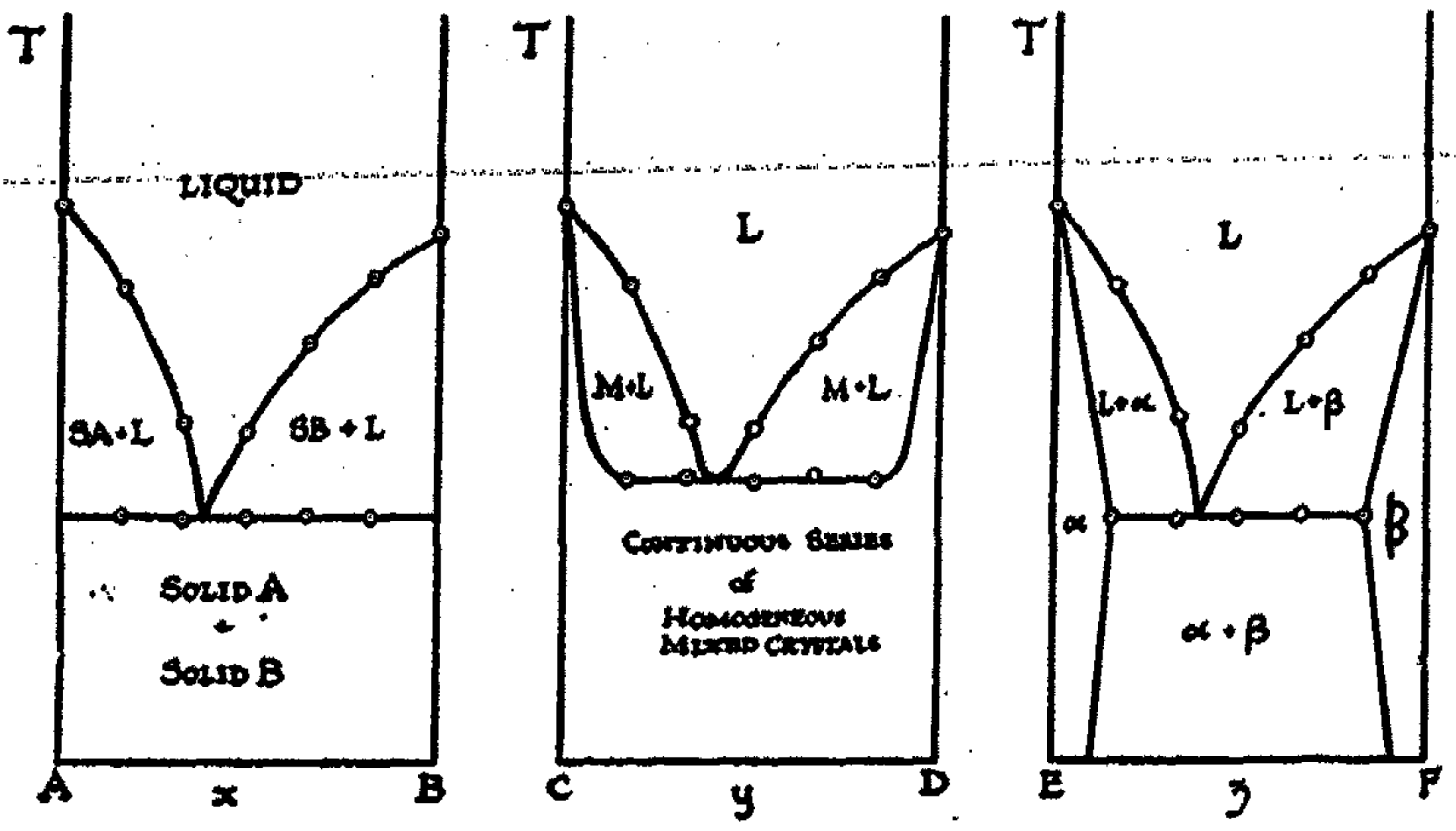

FIG. 1

This method, though ingenious and admirable in many ways, is manifestly unsuitable in the following cases:—

(a) Where the latent heat of solidification of the solid phase is small.

(b) In mixtures which are very rich in one of the components.

Before entering into a systematic examination of the subject, we will consider a concrete case for a moment. It is difficult to imagine that thermal analysis as usually carried out would distinguish between the three systems shown in Fig. 1, especially when it is remembered that the positions of the imaginary experimental points are identical in each case.

In the above three systems pressure is assumed constant, temperature is plotted vertically and composition horizontally. The various phases and mixtures of phases which occur are shown on the diagrams. It is manifest that the condition of the system at temperatures at which solid phases only can exist varies considerably between the three cases. In Fig. 1 case *x*, solid A and solid B are immiscible, in case *y* the components are miscible in all proportions and in case *z* to a limited extent.

We will now undertake a systematic examination of the more important of the various cases which occur and show how they can readily be distinguished.

It was shown in 1893 by van Rijn van Alkemade[1] that the general types of equilibrium which can occur could be deduced by a graphical treatment of Gibbs ζ function. This method was applied with great success at a later date by Roozeboom[2] in the deductions of the general types of mixed crystals.

It will be remembered that the ζ values for all liquid states, quite independently of whether they are realizable or not, approach the axes tangentially, and that when pressure and temperature are maintained constant ζ at equilibrium is at a minimum.

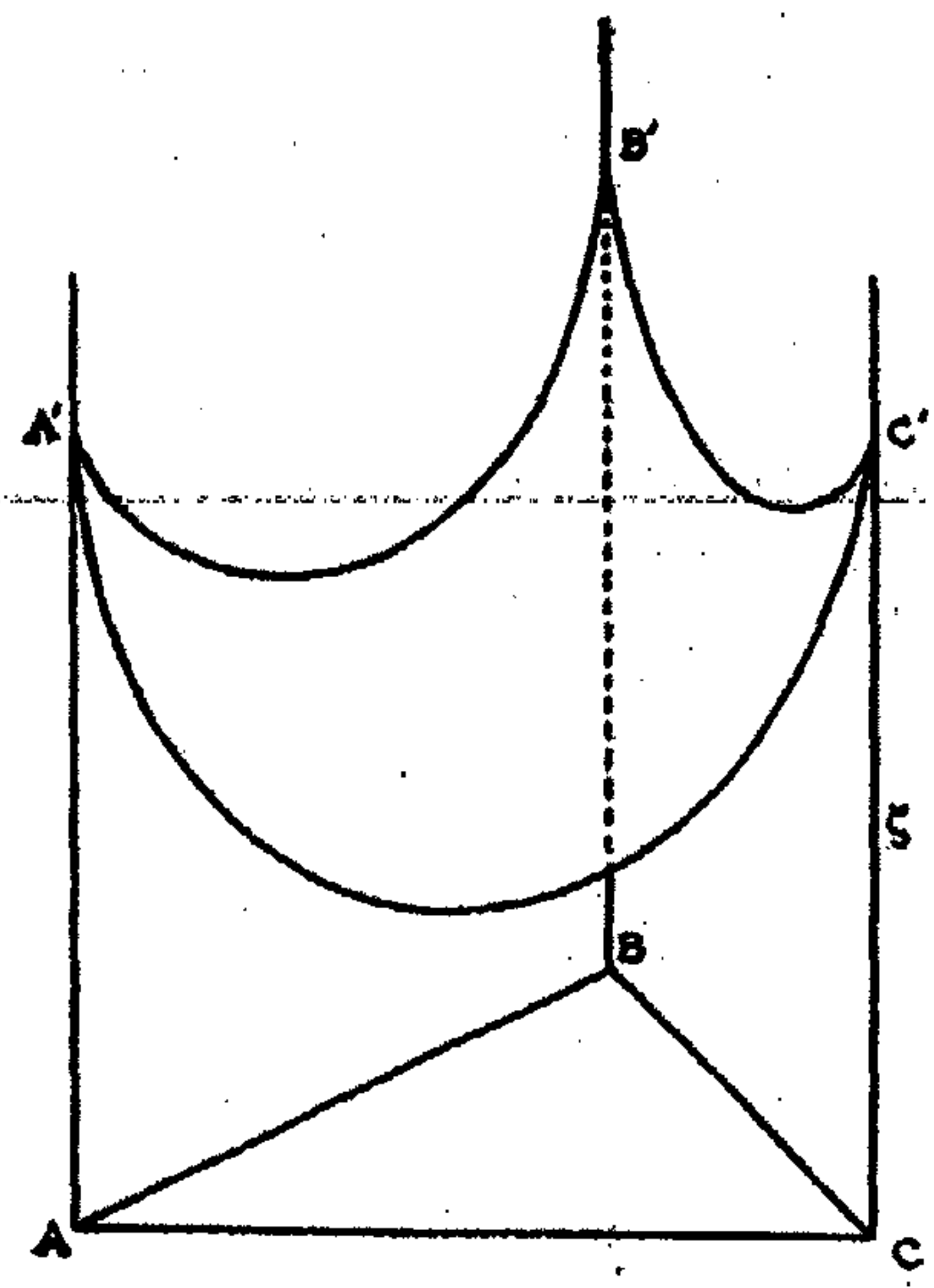

Fig. 2

The general form of the ζ surface for the liquid phase in a three-component system at constant temperature is shown in Fig. 2, in which A', B' and C' are the ζ values of liquid A, B and C at the assumed constant temperature and pressure. If A and B happen to be stable solids at the temperature under consideration whilst C is still a liquid stable equilibrium in the three component system will be given by the projection of the two tangential cones of contact and the triangular plane representing respectively mixtures of solid A+solution, solid B+solution and solid A+solid B+solution.

The above statement is shown graphically in Fig. 3.

In Fig. 3, A', B', C' are the ζ values of liquid A, B, and C respectively. Since A and B are solid at the temperature under consideration, the ζ values of the solid phases are lower than those of the liquids. These are given by the points S_A and S_B.

The range of solutions which can be in equilibrium with S_A are given by the line x y which is the locus of all tangents from S_A to the ζ surface. Similarly w z is the range of solutions which can be in equilibrium with S_B. Complexes of solid and solutions are given by the conical surface generated by the tangents of contact passing through the three component system from one of the two component systems to the other.

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[1] Z. physik. Chem. 11, 289 (1893).

[2] Z. physik. Chem. 30, 385 (1899).

It will at once be noticed that all solutions saturated with respect to A lying on the line m y, all saturated with respect to B on the line m z and the corresponding mixtures of solid and solution are metastable with respect to complexes of $S_A + S_B +$ Solution, (such complexes lie on the plane of contact with the ζ surface which runs through S_A S_B.) because the portions of the surface of the cones under consideration, lie above the plane S_A S_B m. The projection of the above tangents, etc., upon the plane of concentration gives us the typical three-component isotherm of the simplest type.

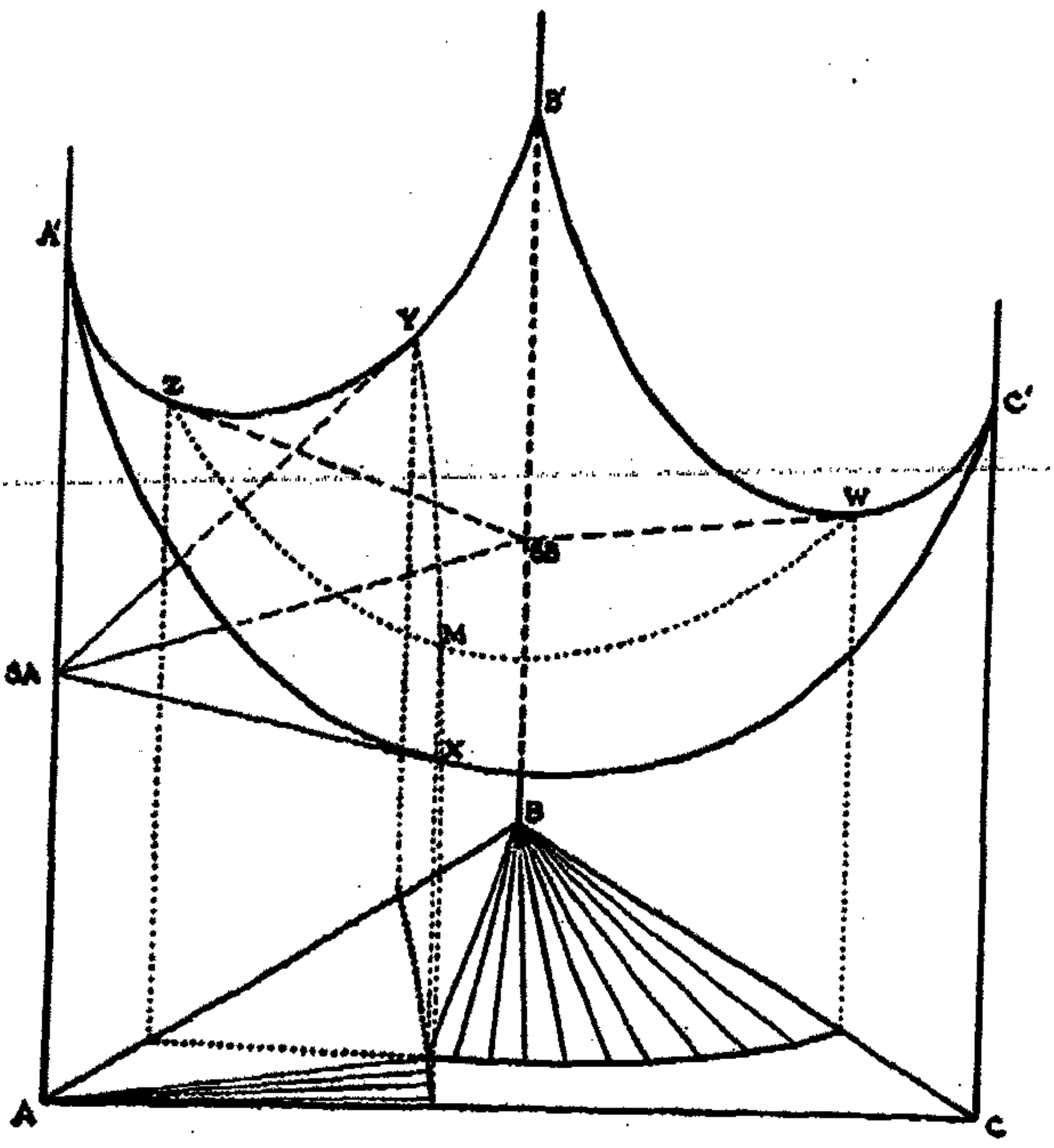

Fig. 3

From the above, it will be seen that we can look upon a solubility diagram at constant temperature as a projection of cones of contact, etc., on the composition surface, and that such a diagram will be profoundly altered by the state of combination of the solids.

It has been pointed out by Schreinemakers[1] that any two solid substances will always yield a characteristic solubility diagram which is the same in type for every possible liquid used as solvent, provided that the liquid in question does not form compounds with either of them. This in fact is the principle underlying the method under consideration, which is to determine an isotherm in a three-component system where the new third component is a suitable liquid and to use this isotherm as a sure indication of the nature of the two-component system. The limitations of the method and the necessary precautions will be discussed later.

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[1] Z. physik. Chem. 65, 553 (1909).

The Cases which can arise

1. *The distinction between the three cases shown in Fig. 1.*

An isothermal in the three-component system A, B, and a suitable liquid will with its corresponding surface correspond exactly to Fig. 3.

The state of affairs which will arise in the system C, – D, – liquid, E at a temperature somewhat below the minimum at which liquid and solid can coexist is shown in Fig. 4.

As before temperature is plotted vertically. C′, D′ and E′ are the ζ values of the liquid components. C and D are solid. So S_C, and S_D with

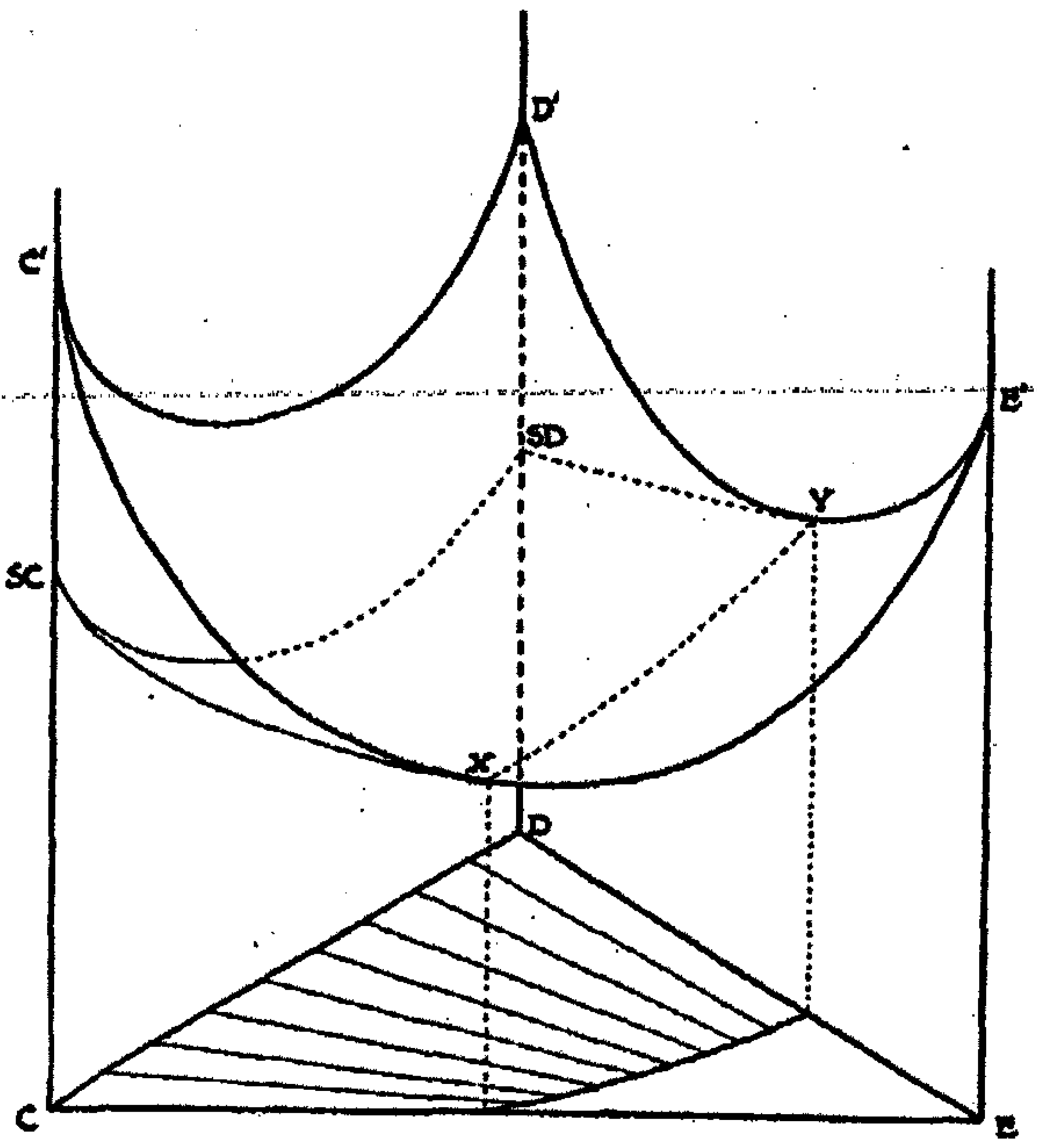

Fig. 4

lower values than the liquids are the ζ values for the solid phases of these two components.

Since, however, C and D form a continuous series of mixed crystals in the solid state, the ζ value of all solids will be a continuous curve namely S_C and S_D.

The stable solutions saturated with respect to solid phases will be given by the series of tangents from the line S_C S_D to the ζ surface, which are best visualised by imagining the path traced out by a rolling contact traversing underneath the line S_C S_D and touching the ζ surface in such a manner that every straight line which can be drawn on the surface from any point on the line S_C to S_D is lower in respect to ζ than any other line which can be drawn from this point to the ζ surface.

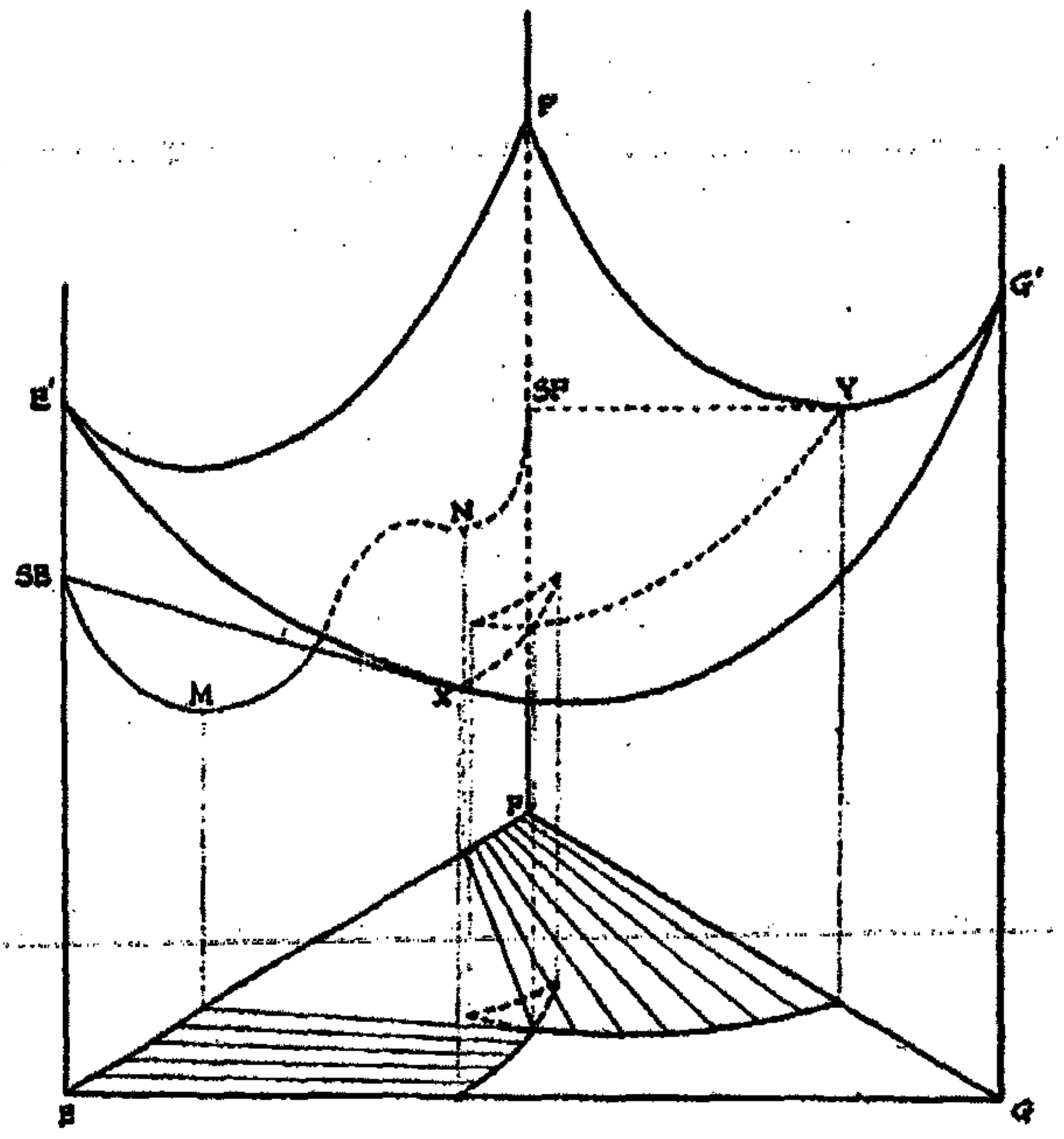

FIG. 5

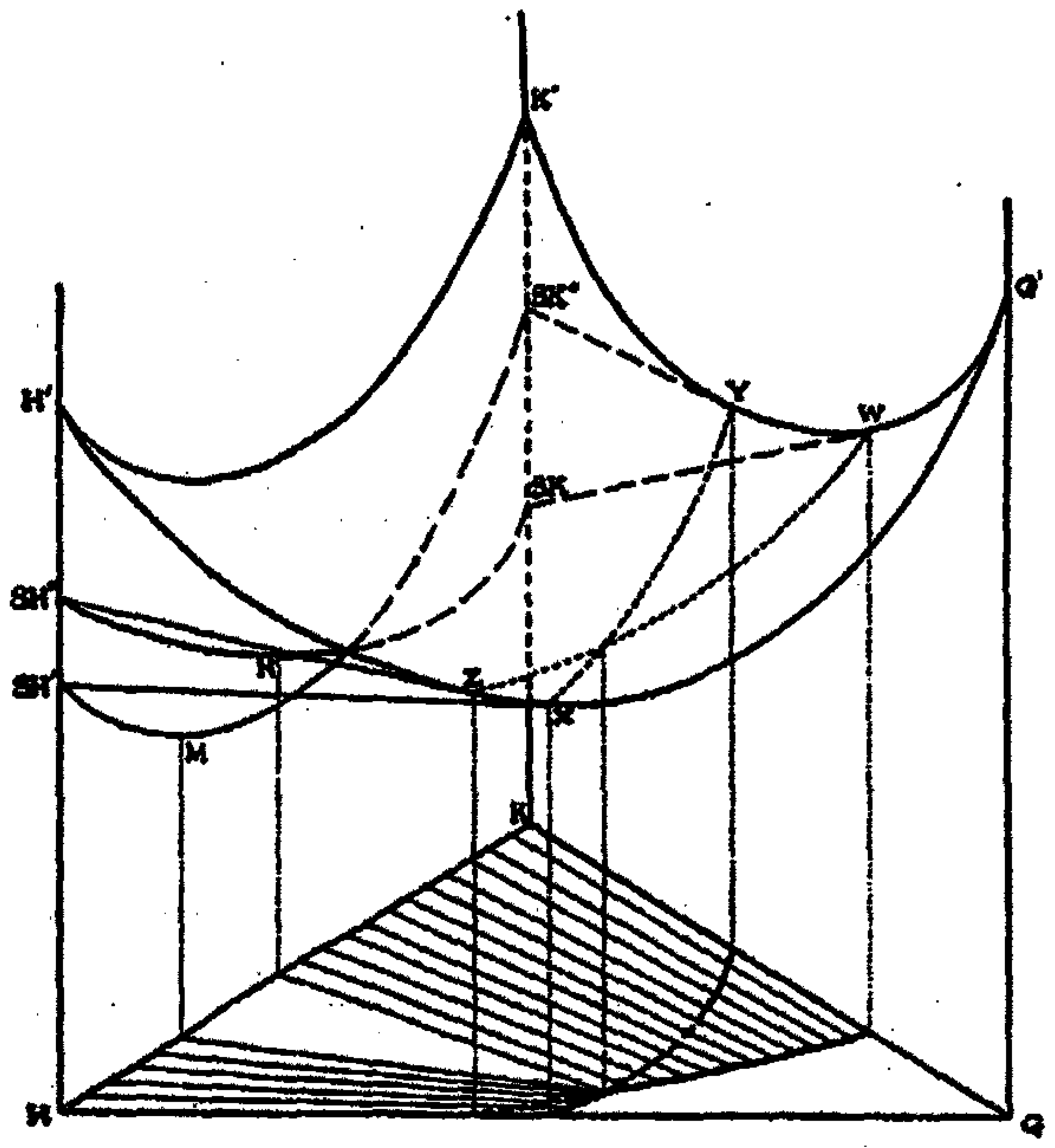

FIG. 6

The addition of a third liquid component (g) to the system E, F (Fig. 1), will give rise to an isothermal at a temperature below that of the eutectic, as shown in Fig. 5.

For the sake of completeness, the two possible cases are given (the second in Fig. 6), though it will be impossible to distinguish between them by the isothermals which will be produced.

Summarizing, we may say that the three totally different isothermals in Fig. 7 are derived from very similar liquidus curves in the original two-component systems.

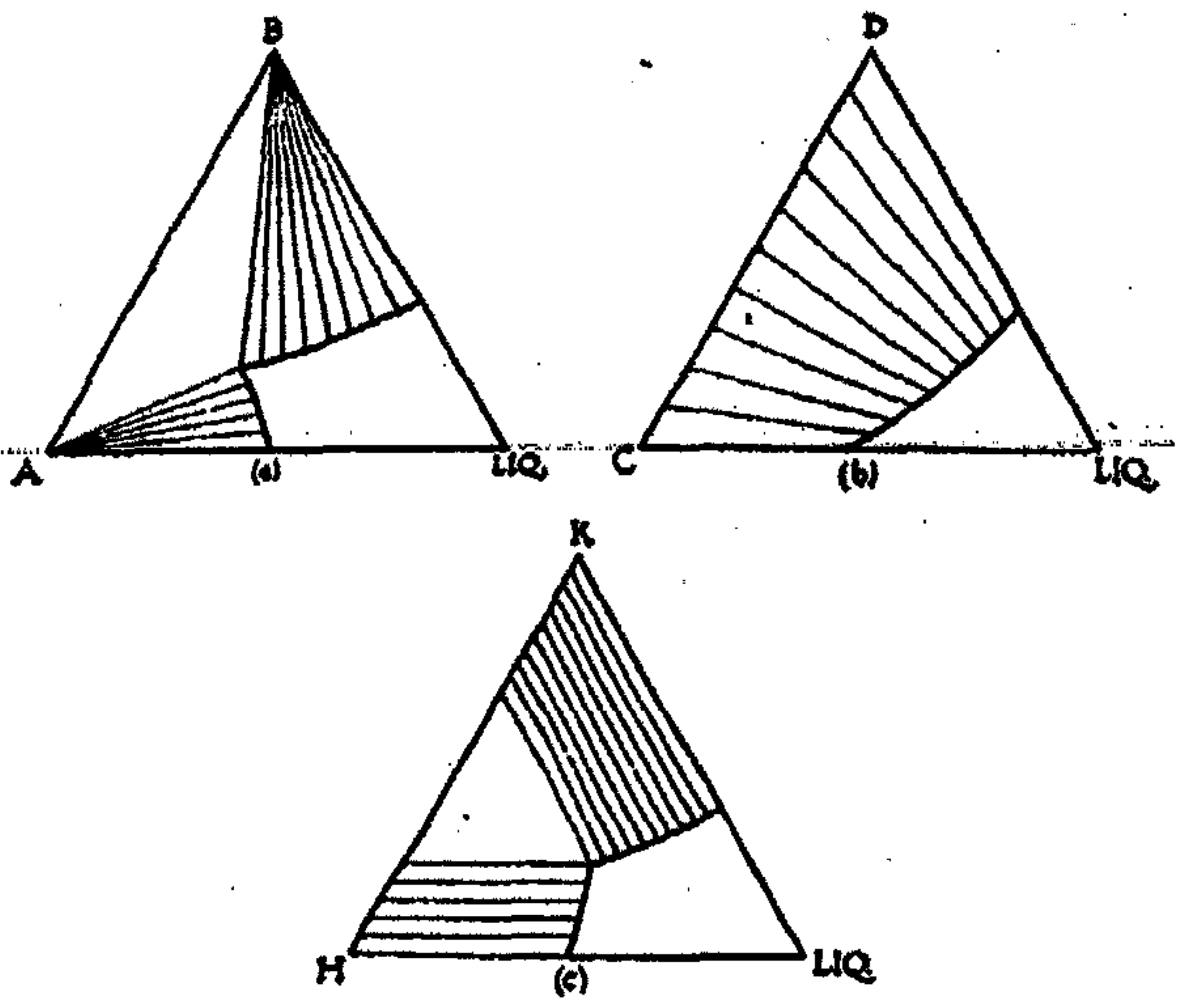

FIG. 7

2. *Other cases.*

The only other cases which may easily be confused are given in Fig. 8.

System A B (Fig. 8) will give when treated with a suitable liquid at a constant temperature lower than A′, an isotherm similar in type to Fig. 7, B, whereas the system C D, (Fig. 8) will give an isotherm similar in type to Fig. 7 (c). It is manifest that the small heterogeneous triangular area in Fig. 7 (c), might easily be missed.

Practical Examples of the Application of the Theorem

1. *The System Sodium Nitrate—Potassium Nitrate.*

The system potassium nitrate—sodium nitrate forms the subject of two recent papers by Madgin and Briscoe[1]. The results which they obtained are shown in Fig. 9 (a). It is immediately obvious from this figure that a continuous series of mixed crystals is formed between these two salts, and that at the minimum (point B) the liquid and the solid phase have the same composition.

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[1] J. Chem. Soc. 123, 1608, 2914 (1923).

Hissink[1] is of the opinion that the equilibrium is in type similar to that shown in Fig. 1, (z) viz., that there are two series of mixed crystals with a eutectic. Also Carveth[2] came to the same conclusion.

As has been previously pointed out, the determination of the nature of the solid phase in systems of this character is by no means an easy matter. It will now be shown that, if Madgin and Briscoe's present contention is right, there is in all probability an at present unknown transition temperature of sodium nitrate. The reasons for this statement are as follows:—

It was shown by Retgers[3], that at ordinary temperatures, potassium nitrate and sodium nitrate only form mixed crystals with each other to the extent of about 0.5%. That is to say, a very important change has taken place in the system potassium nitrate—sodium nitrate between the temperature at which the first liquefaction occurs (B) and ordinary temperatures. An isotherm, using water as a solvent, at a temperature slightly below B, (Fig. 9 a) would be in the form shown in Fig. 7 (b). That is to say we should have a continuous series of solutions in equilibrium with a continuous series of solid phases.

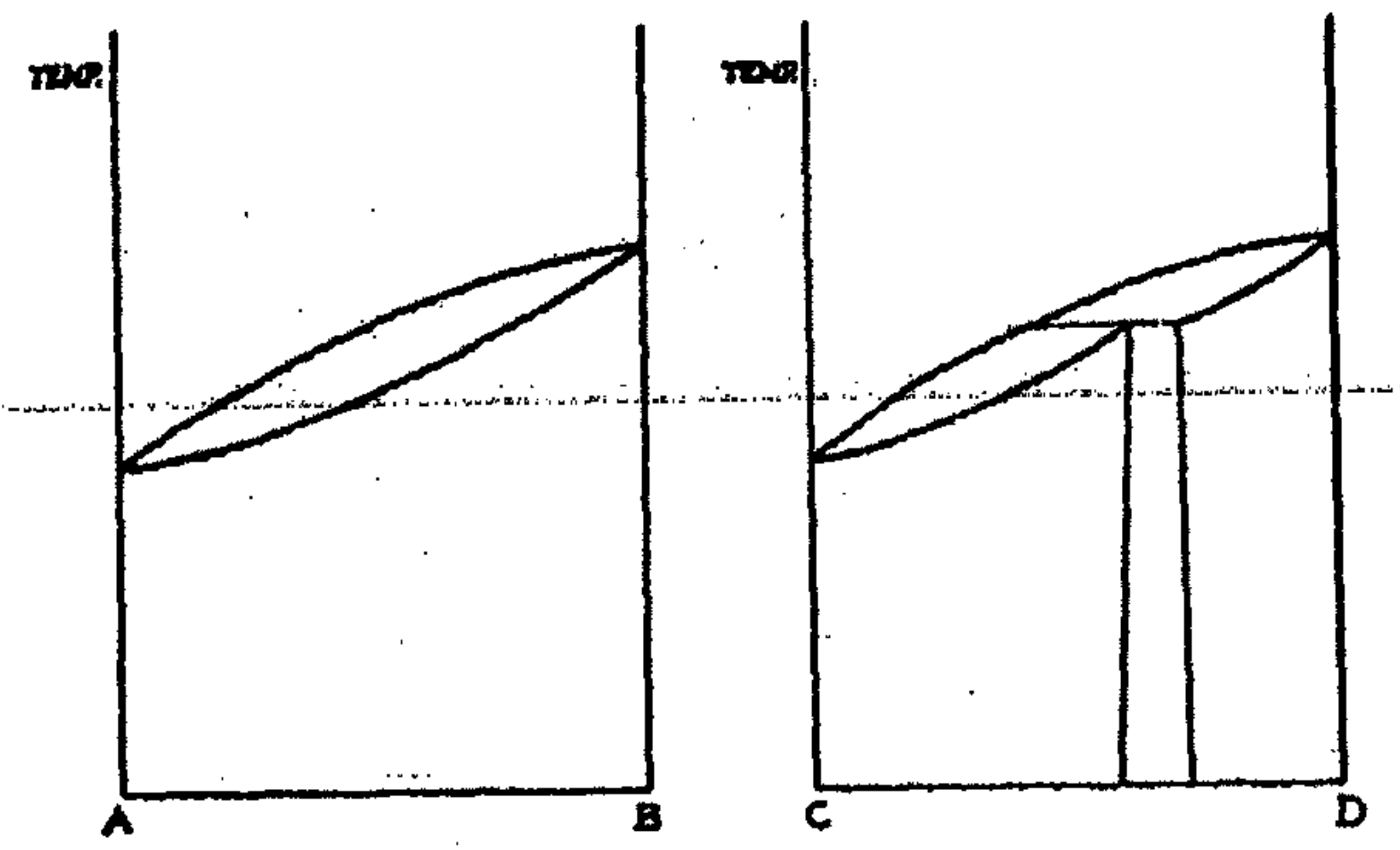

Fig. 8

Potassium nitrate has a transition temperature at 130°C. Madgin and Briscoe state that this transition temperature is lowered by the presence of sodium nitrate. That it should be raised or lowered is obvious from the fact that at a higher temperature these two substances form a continuous series of mixed crystals.

The most likely way in which we can arrive at a condition which is in agreement with Retgers' isothermal is by assuming that there is an unknown transition temperature of sodium nitrate, as shown in Fig. 9 (b). In Fig. 9 (b), G is the transition temperature of potassium nitrate; F is the unknown transition temperature of sodium nitrate; G H and G K are equilibrium pairs of solids on the potassium nitrate side; F H and F M are equilibrium pairs of solids on the sodium nitrate side; M H K is (at constant pressure) an invarient com plex of three solids; below this line a point such as Y represents

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[1] Z. physik. Chem. 32, 537 (1900).

[2] J. Phys. Chem. 2, 209 (1893).

[3] Z. physik. Chem. 4, 620 (1889).

mixtures of two limiting mixed crystals O and P. An isothermal with water as a third component at temperature Y would give results similar to those obtained by Retgers.

If, on the other hand, sodium nitrate has not a transition temperature as previously supposed, then Madgin and Briscoe's results require a more unusual interpretation, which make those of Hissink more acceptable.

The scheme shown in Fig. 9 (c) would explain both Madgin and Briscoe's results and those of Retgers, and also make it unnecessary to suppose sodium nitrate has a transition temperature.

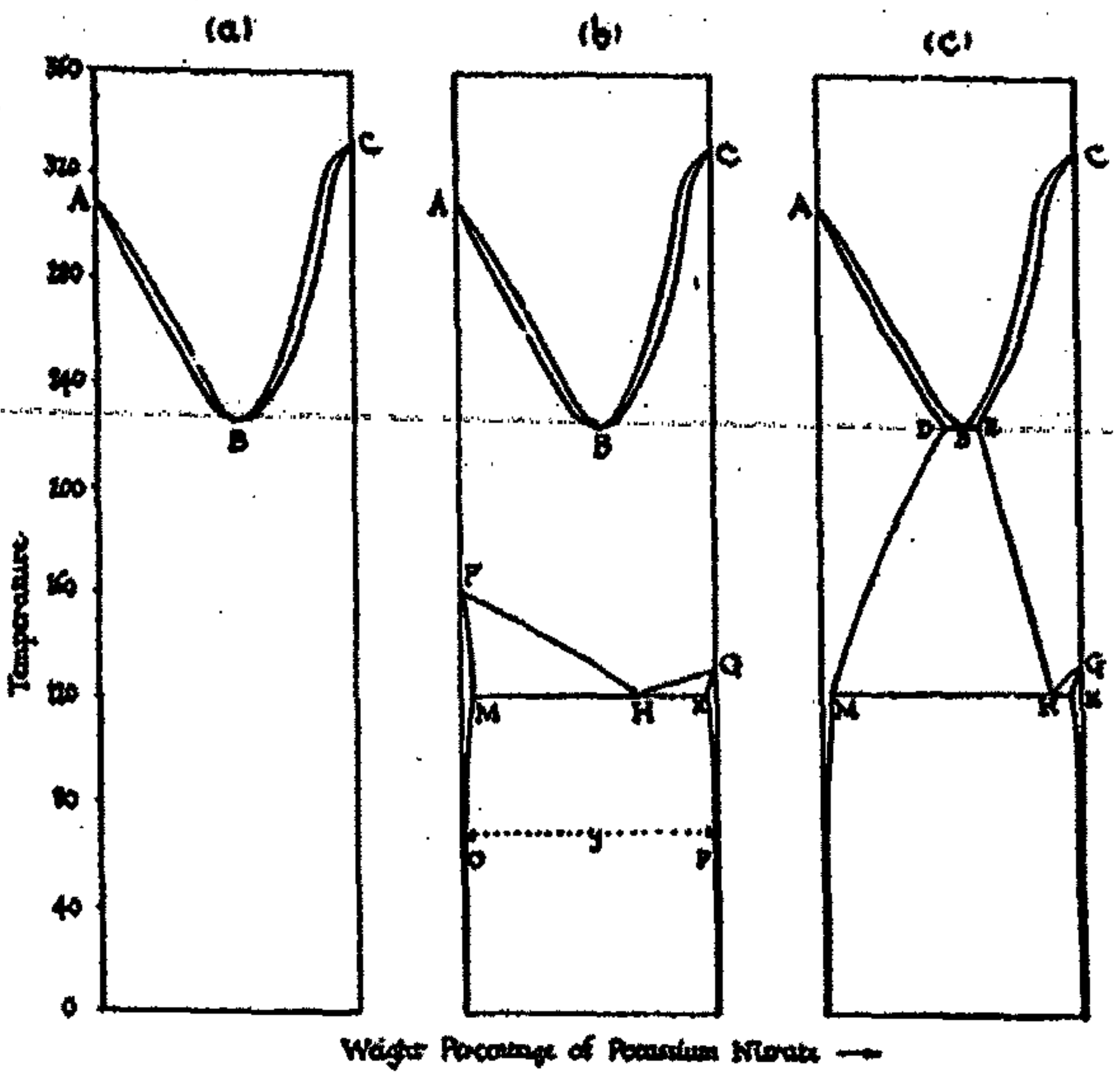

Fig. 9

It will be seen therefore that an isothermal of the system water—potassium nitrate—sodium nitrate at a temperature of about 140°C. would throw a very valuable light upon the true constitution of the solid phases of this system.

Although there might be a little difficulty on account of the pressure of the water vapour and an autoclave would be required, yet the types of isotherm which would decide the point under consideration are so fundamentally different, that it would be impossible to mistake them.

2. *System d-Camphor Oxime—l-Camphor Oxime.*

The phenomena which occur in this system are described by Roozeboom[1] As this journal is not readily accessible, the following short account of the phenomena which were observed will make the subsequent explanation clearer.

Fig. 10 (a) shows Roozeboom's original diagram. The line A B is the melting point curve, along which solids of identical composition to the liquids

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[1] Proc. Royal Acad. Amsterdam, 2, 74.

are deposited. The line C D E represents the temperatures at which the two forms of each of the components can exist. The point G represents the temperature at which a racemic compound begins to form. G F and G H represent the lowering of this temperature by either of the components.

The first criticism to be made upon this diagram is that as it stands (a) H G F represents mixture of two limiting mixed crystals, and that Roozeboom's statements would be better explained by Fig. 10 (b), in which G K represent the composition of the racemic compound; any point in the area F G K representing mixtures of the compound and a limiting mixed crystal on the line F G; any point in the area G H K representing mixtures of the compound and limiting mixed crystals on the line G H.

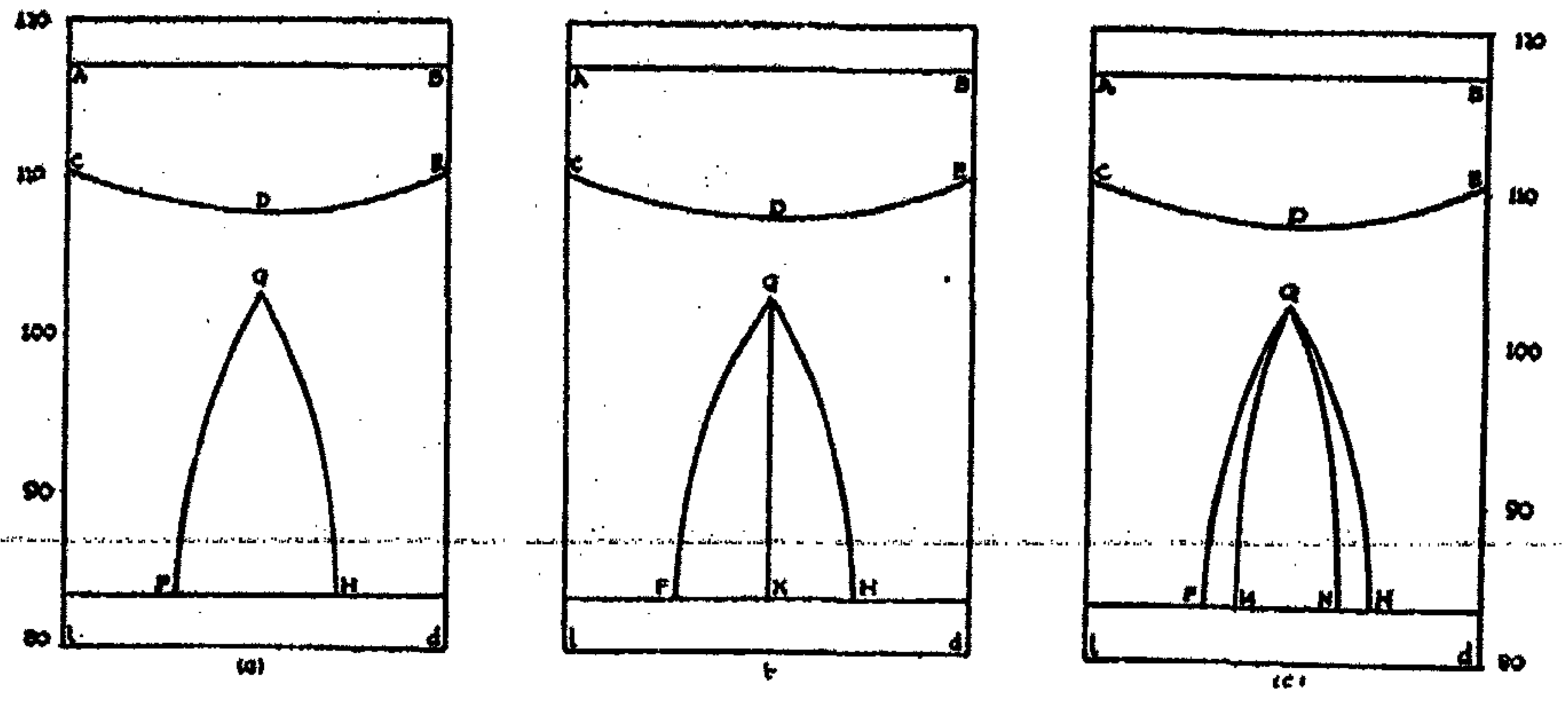

Fig. 10

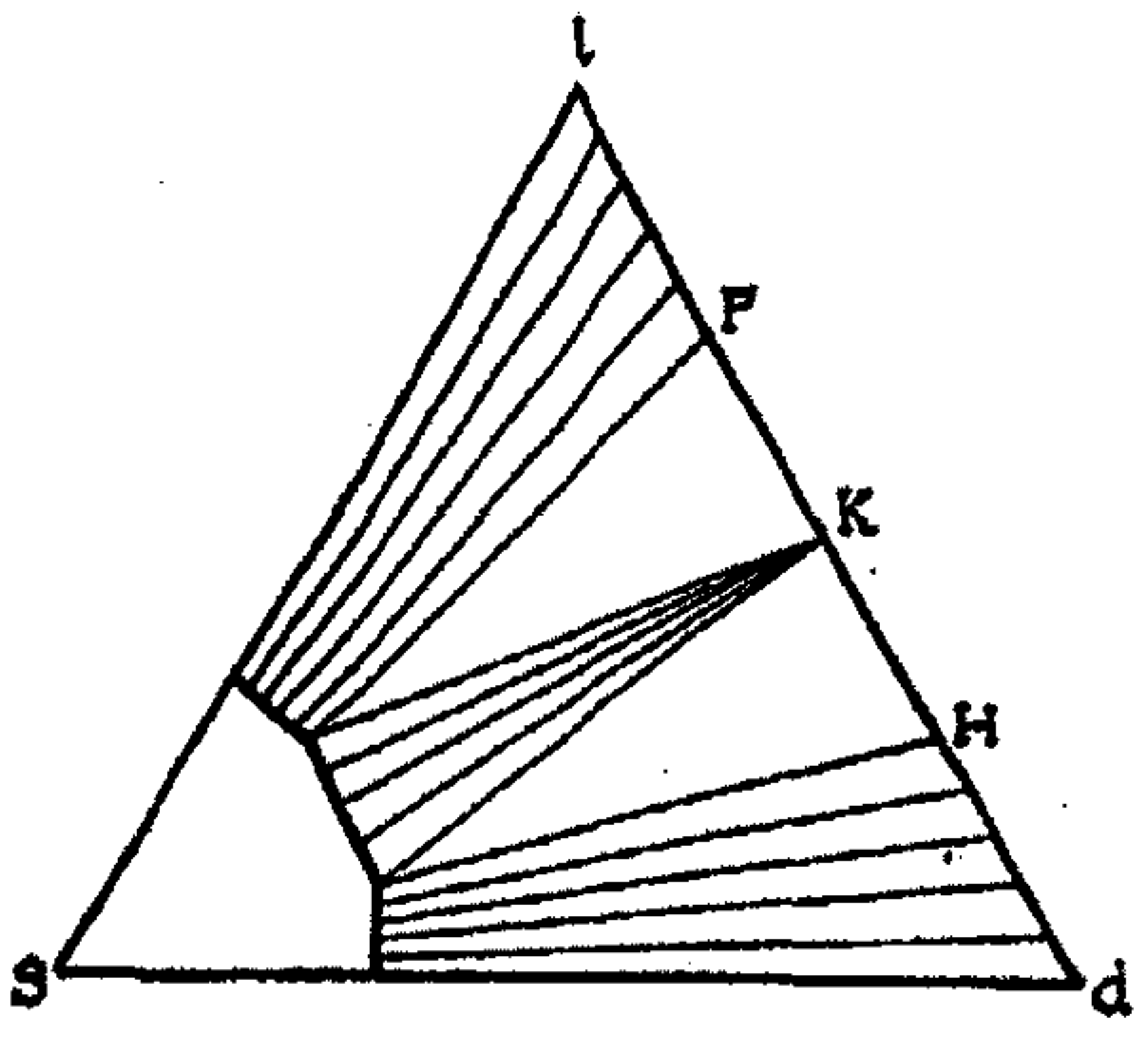

Fig. 11

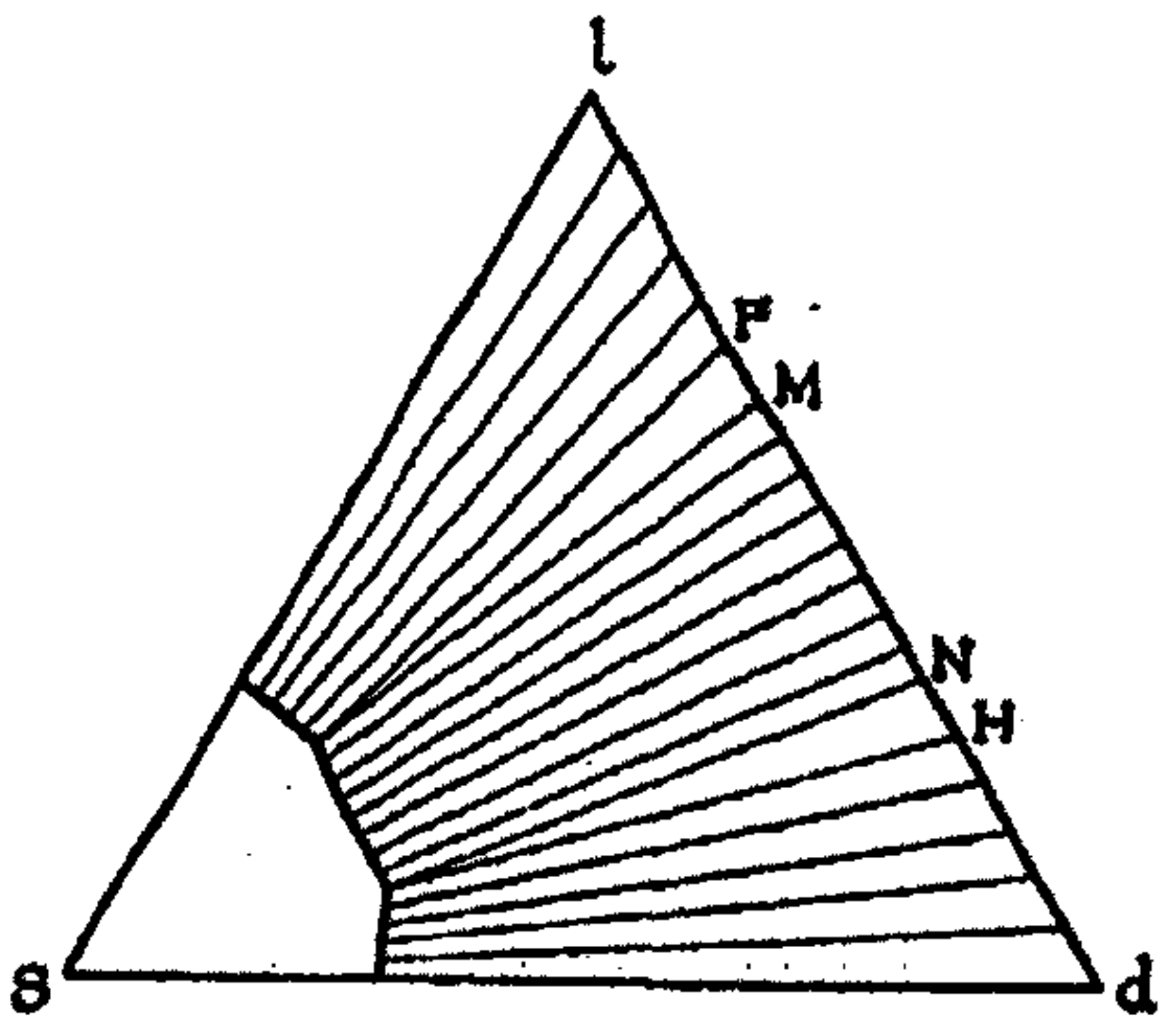

Fig. 12

Fig. 10 (b), however, makes the most unlikely supposition that two substances which have been entirely miscible in the solid state, suddenly begin to form a compound, itself immiscible with its components, yet which coexists with a series of mixed crystals of varying composition, without its own composition being altered.

It is highly probable that the scheme shown in Fig. 10 (c) is the true one. In this diagram, the compound itself forms mixed crystals with the component. G M and G F represent limiting series of mixed crystals which can co-exist at given temperatures, as do also G M and G H.

The theorem under discussion would yield a ready proof to these statements on the following lines:—At an isothermal of say 85°, Fig. 10 (a) would give a diagram similar to Fig. 7 (c); Fig. 10 (b) would give the diagram shown in Fig. 11, whilst Fig. 10 (c) would give the diagram shown in Fig. 12.

It will be seen that the above three isothermals are very different in type and could be easily distinguished.

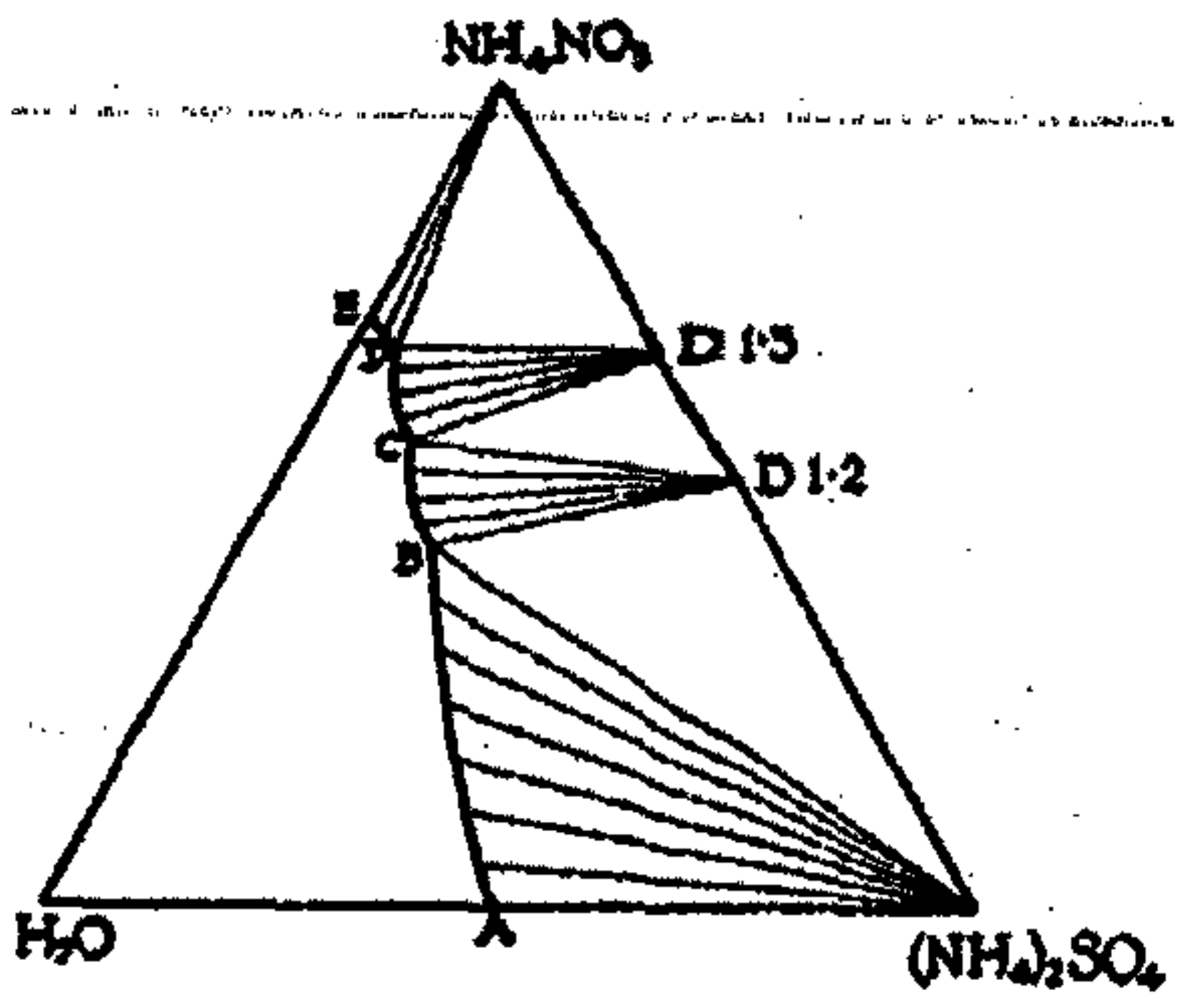

FIG. 13

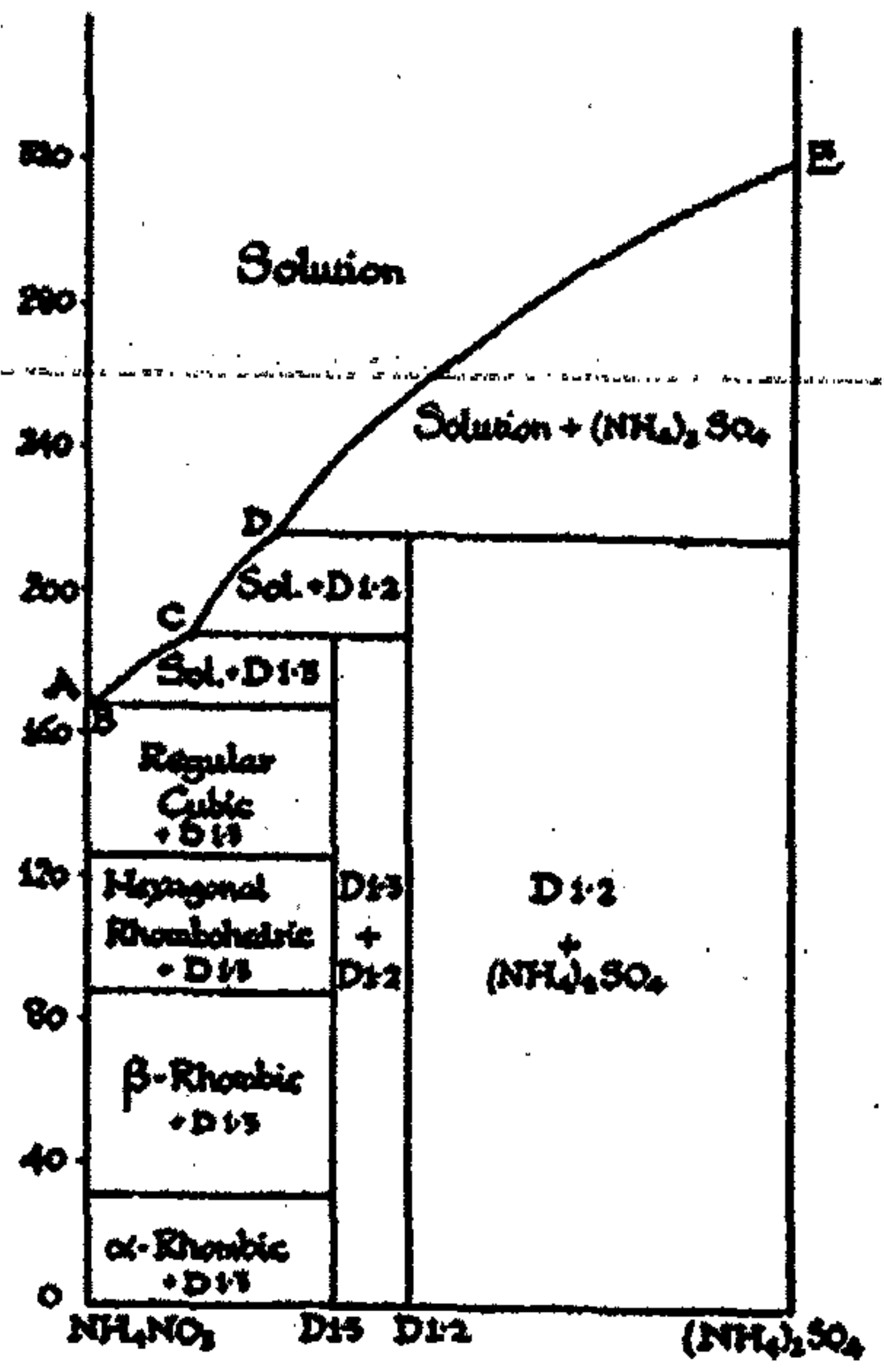

FIG. 14

3. *The System Ammonium Nitrate—Ammonium Sulphate.*

This system is described by Perman and Howells.[1] These authors came to the legitimate conclusion that since the melting point of ammonium nitrate is raised by ammonium sulphate, these substances form mixed crystals. If this is the case, the considerations that follow will show that the relationships between the two salts in the solid state must be of an almost unheard of complexity.

Schreinemakers and Hoenen[2] have shown that at 30°C. the above system in the presence of water forms two perfectly distinct double salts (see Fig. 13) of the composition $3AmNO_3, Am_2SO_4$, $2AmNO_3, Am_2SO_4$, which they called

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[1] J. Chem. Soc. **123**, 2130 (1923).

[2] Chem. Weekbl., **1909**, 51.

D 1.3 and D 1.2. It will be noticed that the double salt D 1.3 has a very small solubility in ammonium nitrate. Also Perman and Howells on page 2129 of the paper referred to above say:—

"A special difficulty encountered in this system was the slight solubility of the sulphates in fused ammonium nitrate."

Unpublished large scale results by the writer, at a temperature of 70°C. have yielded the above two double salts.

It is therefore highly probable that the diagram shown in Fig. 14 represents the true state of affairs.

The pressure is assumed to be so high that ammonium sulphate melts without volatilisation.

This is an entirely normal ordinary form of diagram.

All that need be assumed to explain Perman's results is that ammonium sulphate has such a small solubility in ammonium nitrate that it is almost impossible to measure it.

Schreinemakers' results and those of the writer correspond entirely with the above diagram.

If Perman and Howells are right in their assumption, the lower part of the above diagram is still correct, and we have to assume that two double salts have an upper range of stability above which they break down, forming a series of mixed crystals. An isothermal at a temperature of say 170°C. using water as a third component would give an answer to this problem.

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EXPERIMENTS ON THE SIGN OF THE ELECTRICAL LAYER FURTHEST AWAY FROM THE SURFACE OF A SOLUTION IN CONTACT WITH AIR OR A METAL

BY R. D. KLEEMAN AND C. R. PITTS

The surface of a liquid containing ions should include, according to theory[1], one or more double layers of electricity. The electrical effects produced by bubbling gases through liquids, the liquid assuming an electrical charge while the corresponding opposite charge is carried away by the gas, are probably intimately connected with these layers. Their existence is definitely shown by the fact that a bubble of gas in a liquid moves if placed in an electric field. The direction of motion of the bubble is as if only the charged electrical layer nearest to the surface of the bubble existed. The sign of this particular layer can in this manner be determined. Experiments along these lines have been carried out by McTaggart.[2] He kept a bubble of gas under observation in the center of a horizontal glass tube filled with a liquid by rotating it rapidly about its axis, and applied at the same time an e.m.f. to the column of liquid; he thus determined the mobility of the bubble under unit field, as well as the sign of its innermost charge.

The object of the experiments to be described in this paper is to determine the sign of the electrical layer *furthest* away from the liquid surface of a number of solutions. This sign need not necessarily be opposite to that of the electrical layer nearest to the liquid surface, as we shall see later. A method of doing this is suggested by the well known fact that metal filings, falling in a liquid under their own weight, give rise to a fall of potential along their path, whose direction may be determined by two electrodes in the liquid connected to a galvanometer.[3] This fall of potential is caused by the frictional resistance of the liquid to the motion of the particles peeling off, to some extent, the outermost layer of electricity surrounding each particle at the beginning of its motion. The corresponding charge of electricity of opposite sign is gradually shed by the particle further ahead. At the same time a reconstruction of the disturbed electrical layer is going on. A continuous repetition of this process takes place along the path of the particle. Hence it would be continually shedding electricity of both signs along its path but of which there would be an excess of one sign at the beginning of the path and an excess of the other kind at the end. A fall of potential would accordingly be generated along the path of the particle.

I. Surface of Liquid in Contact with Air

This method may also be applied to bubbles of air or other gas rising in a liquid. In that case the experiments would indicate the sign of the electrical

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[1] R. D. Kleeman: Phys. Rev., (2) 20, 174-185 (1922).

[2] McTaggart: Phil. Mag., 27, 297 (1914); 28, 367 (1914).

[3] J. Billitzer: Z. Elektrochem. 8, 638; Ann. Physik, 2, 902 (1903).

layer furthest away from the liquid surface. Experiments along these lines were carried out by means of an apparatus shown diagrammatically in Fig. 1. A glass tube *A* about 6 cm in diameter and 30 cm long was clamped with its axis vertical in a stand. The lower end of the tube was closed by a stopper through which passed a glass tube about 3 mm in diameter which had the blower of an atomizer attached to the lower end *a*. Over the upper end *b* of the small tube a piece of rubber tubing was partly drawn and then doubled back and tied to the glass tube. The rubber covering the opening of the tube was pierced at a number of places by a thin sewing needle. Hence when the tube *A* contained a liquid and the blower was operated, small bubbles of air were formed on the surface of the rubber and rose to the surface of the liquid, whose size depended on the pressure of the air in the blower. These bubbles could be made so small that they looked like smoke and then rose with a velocity of about 1 cm per second.

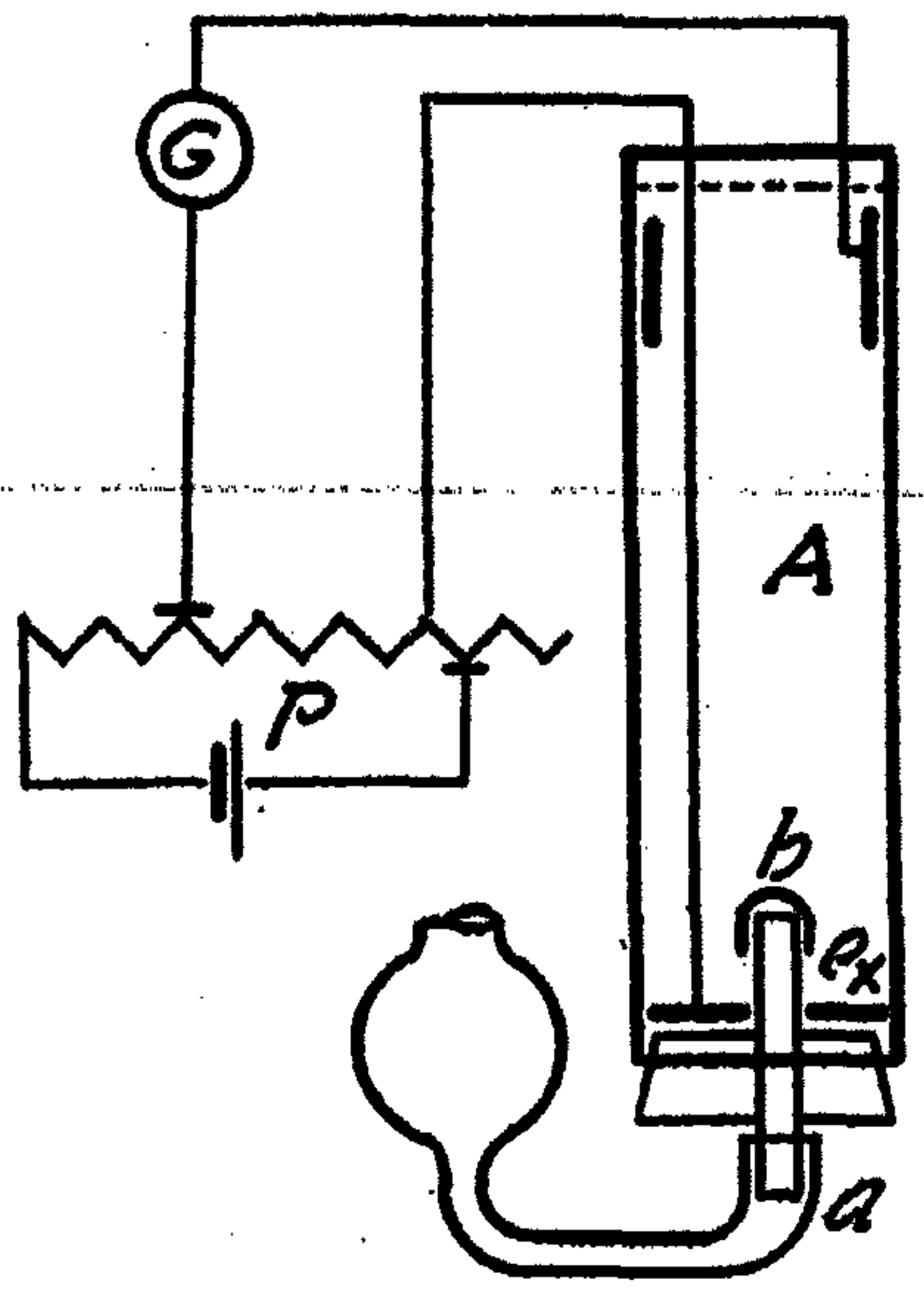

FIG. 1

The direction of the e.m.f. generated along the path of the bubbles was measured by two electrodes e_1 and e_2 connected to a galvanometer G. The electrode e_1 usually consisted of a cylinder of metal and the electrode e_2 of a circular plate perforated by a hole in its center. When the electrodes were of platinum they consisted of two half cylinders.

As is well known air bubbled through a liquid carries an electric charge away with it and leaves the liquid oppositely charged. To prevent this effect from influencing our results the electrode e_1 was connected to earth. It was found, however, that this precaution was scarcely necessary since it did not affect the results.

The agitation of the solution near the top electrode caused by the rising bubbles may give rise to a disturbing effect. Thus if the agitation gets transferred to the immediate vicinity of the electrode it will disturb and partly remove the electrical layer furthest away from the electrode and give rise to a corresponding change in the difference of potential between the two electrodes. This effect was obviated by using a concentrated central stream of small bubbles, which would give rise to little agitation, and the result obtained was checked in some cases by lowering a wax paper cylinder some distance into the tube, which cut off the agitation, but reduced the sensitiveness of the experiment. It was found that the change in potential along the path of the bubble was greater with small bubbles than with larger ones. The smaller bubbles rose more slowly than the larger ones, of course, but more surface came into play in the case of the smaller bubbles. Since large bubbles would produce more agitation near the top electrode than small ones, this variation of size afforded another method of making sure that the results obtained were not seriously affected by the agitation produced.

The difference of potential between two electrodes of the same metal in a solution, though small, would give rise to a considerable galvanometer deflection, which was often off the scale. This difference of potential was counterbalanced by a potentiometer arrangement P in Fig. 1, which requires no explanation. This potential would also show considerable variations in magnitude, which, however, would gradually become smaller with time and after some time would practically disappear. It was usually necessary, therefore, to wait for some time before taking readings, occasionally several hours, and in this way the experiments consumed a good deal of time.

In all cases possible a pair of electrodes of the same substance as the base of the salt of the solution was used initially, and then a pair of platinum electrodes. In those cases in which this was not possible, platinum electrodes alone were used.

Table I, in the third column, gives the sign of the electrical layer furthest from the surface of a solution as determined in the manner described for a number of solutions of various salts and acids. Whenever possible or feasible a result was checked by using two sets of electrodes in succession as described. The first column of the table gives the name and chemical formula of the salt used, and the percentage in weight of the salt contained in the solution.

These does not seem to be any simple connection between the nature of the salt used and the corresponding sign of the electrical layer under consideration. It may be noted that for the copper and cobalt salts used, the sign of the layer is positive in each case; but similar compounds of other substances do not in general fall into line with this result. In fact there is a greater tendency for the sign of the layer to be negative than positive, which in the present experiments is indicated by the ratio of 33 to 25. It may be noted that the sign of the layer for a solution of ferric sulphate is negative, while it is positive in the case of ferrous sulphate. A double sign appears in the table in the case of zinc nitrate and of potassium bromide. In these cases the galvanometer showed, on bubbling, first a deflection in one direction, rapidly followed by a much larger deflection in the opposite direction. This probably indicates that in both cases the electrification surrounding each bubble consisted of at least two double layers. The layer furthest from the liquid surface is negative and was 'peeled off' during the initial stages of the motion of the bubbles and the corresponding positive charges shedded further ahead. But the reconstruction of the disturbed electrical layers was not sufficiently rapid to counteract this shedding of electrical charges, and a stage was ultimately reached when positive electricity belonging to the second double layer was initially peeled off, and the corresponding negative charge shedded further ahead. Thus the fall of potential along the tube would change sign with time of bubbling.

TABLE I

Nature of solution		Nature of electrodes	Sign of electrical layer furthest from air surface	Sign of electrical layer furthest from metal surface
2% copper sulphate	$Cu SO_4$	Cu or Pt	+	–
1% copper nitrate	$Cu(N O_3)_2$	Cu	+	–
1% copper nitrate	$Cu(NO_3)_2$	Pt	+	+
1/2 cupric chloride	$Cu Cl_2$	Cu or Pt	+	–
1% cupric acetate	$Cu (C_2H_3O_2)_2$	Cu	+	–
2% cupric bromide	$Cu Br_2$	Cu or Pt	+	–
2% zinc sulphate	$Zn SO_4$	Zn	+	–
2% zinc nitrate	$Zn (NO_3)_2$	Zn	+ –	–
2% zinc chloride	$Zn Cl_2$	Zn	–	–
1% zinc acetate	$Zn (C_2H_3O_2)_2$	Zn	+	–
1% zinc acetate	$Zn (C_2H_3O_2)_2$	Pt	+	+
Sat. zinc phosphate	$Zn_3(P O_4)_2$	Zn	+	–
Sat. zinc phosphate	$Zn_3(P O_4)_2$	Pt	+	+
2% ferric sulphate	$Fe_2(SO_4)_3$	Fe	–	–
2% ferric sulphate	$Fe_2(SO_4)_3$	Pt	–	+
1% ferrous sulphate	$Fe SO_4$	Fe	+	–
1% ferrous sulphate	$Fe SO_4$	Pt	+	+
1% ferrous ammonium sulphate	$(NH_4)_2 Fe (SO_4)_2$	Fe	+	–
1% ferrous ammonium sulphate	$(NH_4)_2 Fe(SO_4)_2$	Pt	+	+
1% ferric chloride	$Fe Cl_3$	Fe	–	–
1% ferric chloride	$Fe Cl_3$	Pt	–	+
2% aluminum sulphate	$Al_2(SO_4)_3$	Al	–	–
2% aluminum sulphate	$Al_2(SO_4)_3$	Pt	–	+
2% aluminum potassium sulphate	$Al K (SO_4)_2$	Al	+	–
2% aluminum potassium sulphate	$Al K (SO_4)_2$	Pt	+	+
1% aluminum nitrate	$Al(NO_3)_3$	Al	–	–
1% " "	$Al(NO_3)_3$	Pt	–	+
1% aluminum chloride	$Al_2 Cl_6$	Al or Pt	–	–
1/2% aluminum sodium chloride	$Al_2 Cl_6 2NaCl$	Al or Pt	–	–
1% aluminum chlorate	$Al(Cl O_3)_3$	Al or Pt	–	–

TABLE I (Continued)

Nature of solution		Nature of electrodes	Sign of electrical layer furthest from air surface	Sign of electrical layer furthest from metal surface
2% cobalt sulphate	$Co_2(SO_4)_3$	Pt	+	−
2% cobalt nitrate	$Co(NO_3)_2$	Pt	+	−
2% cobalt chloride	$Co\,Cl_2$	Pt	+	−
2% cadmium sulphate	$CdSO_4$	Cd	−	−
2% cadmium sulphate	$CdSO_4$	Pt	−	+
1.5% cadmium nitrate	$Cd(NO_3)_2$	Cd	+	−
1.5% cadmium nitrate	$Cd(NO_3)_2$	Pt	+	+
2% cadmium chloride	$CdCl_2$	Cd or Pt	−	−
2% cadmium iodide	CdI_2	Cd or Pt	+	−
1/2 lead nitrate	$Pb(NO_3)_2$	Pb	−	−
1/2% " "	$Pb(NO_3)_2$	Pt	−	+
1% mercuric nitrate	$Hg(NO_3)_2$	Pt	+	+
1% barium nitrate	$Ba(NO_3)_2$	Pt	−	+
2% barium chloride	$Ba\,Cl_2$	Pt	−	−
2% barium hydroxide	$Ba\,(OH)_2$	Pt	+	+
2% potassium chloride	KCl	Pt	−	−
2% potassium bromide	KBr	Pt	+ −	+
2% potassium permanganate	$KMnO_4$	Pt	−	+
1% potassium hydroxide	KOH	Pt	−	+
2% sodium chloride	$Na\,Cl$	Pt	−	−
1-3/4 " bicarbonate	$H\,Na\,CO_3$	Pt	+	+
1% sodium hydroxide	$Na\,OH$	Pt	−	+

TABLE I (Continued)

Nature of solution		Nature of electrodes	Sign of electrical layer furthest from air surface	Sign of electrical layer furthest from metal surface
2% magnesium chloride	$MgCl_2$	Pt	–	–
2% magnesium sulphate	$MgSO_4$	Pt	+	–
1% magnanese chloride	$MnCl_2$	Pt	+	–
1% manganese sulphate	$Mn_2(SO_4)_3$	Pt	–	+
1% ammonium nitrate	NH_4NO_3	Pt	–	–
1% ammonium chloride	NH_4Cl	Pt	–	–
2% ammonium carbonate	$(NH_4)_2CO_3H_2O$	Pt	+	+
1% ammonium oxalate	$(NH_4)_2C_2O_4H_2O$	Pt	–	+
1% ammonium tartrate	$(NH_4)C_4H_4O_2$	Pt	+	+
1% ammonium iodide	NH_4I	Pt	+	–
1% ammonium fluoride	NH_4F	Pt	–	+
2% sulphuric acid	H_2SO_4	Pt	+	–
2% nitric acid	HNO_3	Pt	–	–
2% hydrochloric acid	HCl	Pt	–	–

II. Solution in Contact with a Metal

The sign of the electrical layer furthest away from the surface of a metal, we have seen, can be determined by giving a motion to the metal and measuring the direction of the change in potential along its path. But this may also be accomplished with the experimental arrangement shown in Fig. 1, by giving a motion to the liquid near the top electrode, parallel to its surface and noting the direction of deflection of the galvanometer. This motion would evidently have the effect of numerically increasing the potential difference between the solution and the electrode, since this is equivalent to increasing the distance of separation between two charges of opposite sign. The reconstruction of the disturbed electrical layers will have the effect of further increasing numerically this change in potential. Large effects were usually obtained. Therefore in order to make sure that these effects corresponded to a peeling off of the outermost layer of electricity only, the motion given to the liquid was not greater than necessary to give an easily measurable deflection, and was continued only for a short time,—a fraction of a second.

The fourth column of Table I gives the results obtained in this way. It will be seen that in each of the cases examined the sign of the outermost layer of electricity associated with a metal immersed in a solution of its salt is negative. This result seems to be quite general.

A comparison of this result with the difference of potential between a metal plate and a solution in which it is immersed gives some interesting information in connection with the number of electrical double layers associated with the boundary of the metal and solution. For example, the difference of potential between a zinc plate immersed in a solution of zinc sulphate, zinc chloride, or zinc nitrate, is in each case negative, taking the potential of the solution as zero.[1] It does not definitely follow from this that the zinc plate in each case is negatively charged, which, it should be noted, corresponds to the sign of the electrical layer nearest to the plate. However, let us make the assumption that the plates are negatively charged. Now, in order that this may harmonize with the result that the outer most layer of electricity is negative, two electrical double layers, (− +) (+ −) should be associated with each zinc plate in the solutions mentioned. Besides, in order that the difference of potential between solution and plate may be negative, the difference of potential associated with the double layer nearest to the zinc must be larger than that associated with the other double layer.

If we make the assumption that the charge on the zinc plate is positive in each case, three double layers, (+ −) (− +) (+ −) would be associated with the boundary between metal and solution. The difference of potential of the middle double layer would in that case be greater than the sum of the difference of potential of the two remaining layers.

The difference of potential between a solution of cadmium sulphate, or cadmium chloride, and a cadmium plate, is negative, and the same remarks will therefore apply to these combinations.

The difference of potential between a solution of copper sulphate or a solution of copper nitrate, and a plate of copper, is positive in each case. Therefore, if the charge on the copper plate is positive one double layer only would be associated with the liquid metal boundary. On the other hand, if the charge on the plate is negative, two electrical double layers, (− +) (+ −), will be associated with the boundary in each case.

A set of similar experiments were carried out on the nature of the electrical layer furthest from a metal plate in distilled water, using a number of different metals. The results obtained are given in the second and fifth columns of Table II. The third and sixth columns in the Table give the charge on the metal plate obtained in previous experiments.[2] A comparison of these results

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[1] Watson's Physics. First ed. p. 815.

[2] Kleeman and Fredrickson: Phys. Rev. (2) 24, 134-136 (1923).

shows that in the case of the metals Mg, Zn, Pt, Ni, and Al, the metal water boundary is associated in each case with two double layers of the nature (− +) (+ −).

It appears from these results that several electrical double layers may be associated with the boundary of a metal plate and a solution. The sign of the charge on the metal cannot therefore be definitely inferred from the difference of potential between the metal and solution. It is evidently necessary, therefore, in order to obtain definite information about the minimum number of these layers that may exist in a given case, to know the sign of the charge assumed by the metal. This is not definitely known, except in the case of some metals immersed in water. The method by means of which these results were obtained—measuring the deflection of a thin wire of a metal in a solution by an electric current—was tried using solutions of salts, but it is difficult to get reliable results in that case, because the deflections in a given time are small in comparison with those obtained with distilled water, probably owing to a smaller fall of potential for a given current being obtained with solutions. If a large current is used the electrolysis distorts the shape of the wire. A reliable method of determining the charge on the metal would therefore be desirable.

TABLE II

Metal	Sign of layer furthest from metal surface	Sign of charge on metal	Metal	Sign of layer furthest from metal surface	Sign of charge on metal
Mg	−	−	Mo	+	−
Al	−	−	Cd	−	+
Fe	−	+	Sn	+	−
Ni	−	−	W	+	−
Cu	+	−	Pt	−	−
Zn	−	−	Pb	−	+

Some of the apparatus and chemicals used in these experiments were purchased out of a grant from the Bache Fund of the National Academy of Science; most of the other chemicals used were contributed by the Chemistry Department of Union College and the Research Laboratory of the General Electric Company. We desire to express in this connection our appreciation and thanks.

Summary

Sign of electrical layer furthest away from surface of solution.

1. *In contact with air.* Small bubbles of air were produced at the bottom of a vertical glass tube containing a solution of a salt or an acid. The motion of the bubbles up the tube gave rise to a fall of potential along the tube whose direction was measured by two electrodes connected to a galvanometer. The fall of potential was assumed to be produced by a 'peeling off' of electrical charges

from the electrical double layers associated with the liquid surfaces of the bubbles, which would give rise to an excess of charge of one sign at the beginning of the path of the bubbles, and an excess of the opposite kind at the end of the path. The sign of the charge in excess at the beginning of the path would be the same as that furthest away from the liquid surface. Over fifty solutions were examined. No simple relation seemed to exist between nature of solution and sign of this layer.

2. *In contact with a metal plate.* A tangential motion given to the liquid near one of the electrodes would tend to 'peel off' the outermost layer of electricity, and set up a corresponding difference of potential between the electrodes, from which the sign of the layer furthest from the metal could be determined. The layer was found to be always negative when the solution consisted of a salt of the same metal as the electrodes. For platinum electrodes the sign was sometimes positive, sometimes negative; no simple relation to composition was observed. With distilled water, the sign was usually negative, the exceptions being Cu, Sn, Mo and W.

On comparing these results with the known values of the difference of potential between a metal and a solution it appears that in the case of zinc in a solution of zinc sulphate, chloride, or nitrate, the double layers have the arrangement of either (− +) (+ −) or (+−) (− +) (+ −). This also holds for cadmium in a solution of cadmium sulphate or chloride. A comparison of the sign of the outermost layer of metals in distilled water with the sign of the charge on the metal given by previous experiments (Kleeman and Fredrickson: Phys. Rev. (2) 24, 134-136, (1923) shows that the layers associated with the metals Mg, Zn, Pt, Ni, Al, have the arrangement (− +) (+ −).

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ON THE STABILITY OF COLLOIDAL SOLUTIONS III.

THE INFLUENCE OF NEGATIVE IONS, THE EFFECT OF DILUTION AND AGEING AND THE INFLUENCE OF CAPILLARY ACTIVE NON-ELECTROLYTES ON THE COAGULATION OF COPPER FERROCYANIDE SOL

BY K. C. SEN

In the first part of this series of papers[1] it has been shown that the stability of a colloidal solution or suspension depends to a great extent on the amount of impurity present and also on the concentration of the sol. Thus with a sol of ferric hydroxide, the stability gradually increases with the increase in the hydrochloric acid content. With a suspension of aluminium hydroxide, the stability also increases with the increase in the concentration of the peptising acid and in both the cases, the stability ultimately reaches a maximum. This fact has been explained by the view that the first stabilisation is due mainly to the adsorption of $H^\cdot$ ions from the acid, but gradually with the increase in the concentration of the acid, the concentration of the negative ion in the solution increases and exerts a coagulating effect. Also the adsorption of $H^\cdot$ ion by the particles of the suspension has been found to reach a maximum, and hence owing to the balancing of these factors, a maximum in stability soon occurs. In the second part of this series, it has been found that the same relations hold in the case of a chromium hydroxide sol. With the gradual addition of hydrochloric acid, colloidal chromium hydroxide becomes more and more stabilised towards KCl, K_2SO_4 and $K_2C_2O_4$, but in the last two cases the stability soon reaches a maximum. With a mixture of the electrolytes K_2SO_4 and $K_2C_2O_4$, no stabilising influence of any one of the electrolytes was observed. With all these three hydroxides, it has been found that dilution of the colloid makes it less stable towards all electrolytes irrespective of the valency of the precipitating ions. It has further been shown that the gradual addition of potassium ferrocyanide to a sol of copper ferrocyanide made it more stable towards both monovalent and bivalent precipitating ions, but the stability soon reaches a maximum also. While experimenting on this sol, it was observed that the negative ions had a marked effect on the precipitating values of different electrolytes having the same cation. The effect of dilution of the sol and that of ageing were also in some respects anomalous. It was therefore considered advisable to take up a detailed study on the coagulation of this colloid, and the present paper contains some of the results obtained.

The coagulation of copper ferrocyanide sol has been studied by Pappadà[2] and he has shown that the Schulze-Hardy law is applicable to this colloid. He however, did not study the stability relations of this colloid in detail and

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[1] J. Phys. Chem. 28, 1029 (1924).

[2] Kolloid-Z., 9, 136 (1911)

his results are more or less qualitative in nature. It is well known that colloidal ferrocyanides are negatively charged owing to the adsorption of ferrocyanide ions and it is not possible to free either prussian blue or copper ferrocyanide from adsorbed potassium ferrocyanide. In the present investigation about 3% solution of copper chloride was mixed with a slight excess of potassium ferrocyanide and the precipitate of copper ferrocyanide was filtered off. On washing with distilled water several times, the excess of potassium ferrocyanide was removed, and the precipitate began to pass through the filter paper as a colloidal solution. The first hundred cubic centimeters was rejected, and then a sufficient amount of the pure colloid for this investigation was collected by continual washing with distilled water. This colloidal solution was then dialysed for a month in a parchment dialyser. The resulting sol was fairly stable, but, owing to the method of preparation, somewhat dilute. The concentration of this sol was 0.8 gr. copper ferrocyanide per litre. The method of determining the precipitation values was to take 5 cc of the sol in one test tube and in another test tube suitable amounts of electrolytes made up to 5 cc with pure water, and then the contents of the two tubes were mixed rapidly several times. In every case, the total volume was 10 cc and one hour was allowed for the flocculation to take place. In the course of the experiments it was found that in many cases, specially with dilute sols, complete settling of the colloid was not a true measure of the precipitation value of the colloid and the points at which clots were just perceived were found to give reproducible values. It was further observed that ageing had a distinct effect on the sol which will be referred to in the sequel. In Table I some results are given showing that the sol is almost normal so far as the Schulze-Hardy law is concerned.

TABLE I

Electrolyte		Amount required to coagulate in cc	Precipitation value: milli-gram equivalent per litre of the final mixture.
KCl	N/8	2.85	35.6
NaCl	N/2	1.85	92.5
$BaCl_2$	N/200	1.83	0.915
$SrCl_2$	N/200	2.15	1.075
$MgSO_4$	N/200	3.05	1.52
$Al_2(SO_4)_3$	N/2000	3.5	0.175
$Ce(NO_3)_3$	N/2000	2.05	0.102
$Th(NO_3)_4$	N/1000	1.5	0.15

It will be observed from Table I that the valency rule holds in practically every case except thorium nitrate which comes between cerium and aluminum ions. The exceptional behaviour of thorium nitrate is however well known in the case of arsenious sulphide and antimony sulphide sols, and in a previous paper[1] I have shown that, in the coagulation of negatively charged chromium

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[1] Kolloid-Z. 34, 262 (1924).

hydroxide sol, the precipitation value of the thorium ions comes nearly equal to that of a bivalent ion. It seems therefore that the sol of copper ferrocyanide follows the Schulze-Hardy law and shows a normal behaviour with regard to the valency of the precipitating ion.

The Effect of the Negative Ions on the Coagulation of the Negatively Charged Copper Ferrocyanide Sol

In two previous papers[1] I have studied the effect of negative ions on the coagulation of negatively charged ferric hydroxide and chromium hydroxide sols. It has been found that when different anions are used with the same precipitating ion, the difference in the precipitation values is quite marked and cannot be due to any experimental error. In Table II the results obtained with these two sols are summarised.

TABLE II

Negative ferric hydroxide sol		Negative chromium hydroxide sol	
Electrolyte	Precipitation value	Electrolyte	Precipitation value
KCl	15.4	KCl	225.0
KBr	7.57	KBr	225.0
KI	8.25	KI	225.0
		KNO_3	275.0
		K_2SO_4	375.0
		K_3 Cit	No coagulation

It will be seen from Table II that the negative ion has a marked influence on the precipitation value of an electrolyte. This is quite evident in the case of negative ferric hydroxide sol, where the difference between the precipitation values of KCl and KBr or KI is about 200%. In the case of chromium hydroxide sol, there appears to be no effect of Cl′, Br′ or I′ ions but NO_3' and SO_4'' ions have a marked effect, the sulphate having the greatest precipitation value. It should be noted also that with anions such as citrate, phosphate, etc., it is practically impossible to coagulate a negatively charged sol of say ferric hydroxide or chromium hydroxide due to the great peptising effect of these ions. In the previous paper also, a summary of the existing literature on the influence of negative ions in the coagulation of negatively charged sols was given. From the experimental results it was observed that greater the valency of the negative ion, the greater is the stabilising effect on a negatively charged sol of arsenious sulphide. The precipitation values of different potassium salts, according to Schulze, are in the order

$$Fe(CN)_6'''' > SO_4'' > C_2O_4'' > \text{tartrate}'' > NO_3' > I' > Cl' > ClO_3' > Br'$$

beginning with the greatest precipitation value. If however a bivalent or trivalent ion be chosen as the coagulating ion, the precipitation values do not differ much. It has already been shown that in the case of mono-valent potassium, the actual difference in the precipitation values of the foregoing salts

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[1] J. Phys. Chem. 28, 313 (1924); Kolloid-Z. (loc. cit.)

comes to about 20 percent from the average whereas, if calcium be taken as the precipitating ion, the difference comes to about one percent from the average. With trivalent aluminum as the coagulating ion, the difference in the precipitation values of the sulphate, nitrate and the chloride is only slight. Similar results were also obtained by Odén[1] with his sulphur sol.

In a recent paper Mukherjee and Chaudhuri[2] have studied the influence of anions on the coagulation of negatively charged arsenious sulphide and gold sols and have come to the conclusion that, in the precipitation of arsenious sulphide sol, the anion, unless it has a complex chemical composition, has little effect; and the valency, the mobility and the concentration of the cation generally determine the rate of coagulation. They have shown that the chlorides, bromides, nitrates, and sulphates of sodium and potassium, and the corresponding acids coagulate arsenious sulphide sols at a definite concentration of the respective cations. The influence of the anions is thus very small in these cases. Comparing their actual results it is found that at the same concentration of KCl, KI, and almost equal concentration of K_2SO_4 the times required for coagulation are respectively 7 minutes 29 seconds, 27 minutes, and 25 minutes 20 seconds.

TABLE III

Electrolyte	Precipitation value Millimole per litre.
KCl	49.5
KNO_3	50.0
$\frac{1}{2}$ K_2SO_4	65.5
K acetate	110.0
K formate	86.0
$\frac{1}{3}$ K_3 citrate	>240.0

The conclusion of these authors therefore seem to be at variance with other published results on the coagulation of arsenious sulphide sols. Even leaving aside the older results of Schulze[3], those obtained by Freundlich[4] show much difference. Thus with a particular As_2S_3 sol he obtained the following results. Without considering the case of organic anions for the present, it is apparent from these results that the difference between the coagulating powers of KCl and K_2SO_4 is appreciable. Recently Weiser and Nicholas[5] have also shown that there is a marked difference between the precipitating power of KCl and K_2SO_4 on arsenious sulphide sol, the actual precipitating values being 33.2 and 43.5 respectively expressed in milli-equivalents per litre. The experiments were carried out with unusual care and hence the difference cannot be due to any experimental error. It is therefore not possible to discuss the results of

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[1] "Der kolloide Schwefel", 156 (1912)

[2] J. Chem. Soc. 125, 794 (1924)

[3] J. prakt. Chem. 1882, 1883, 1884.

[4] "Kapillarchemie", 576 (1922)

[5] J. Phys. Chem. 25, 742 (1921)

Mukherjee and Chaudhuri without knowing which authors are in the wrong[1]. In discussing their results, these authors further remark "We do not think that our results support the conclusions of Weiser regarding adsorption of the anion in the precipitation of the arsenious sulphide sol. The conclusion that the adsorption of anions by negatively charged surface is small, as long as the anion is not of great complexity, and the fact that there is no valency effect are significant if we consider the specific nature of adsorption. We do not think that there is much justification for considering the adsorption of the anion by a negatively charged surface to be comparable with that of a positively charged ion."

"In the precipitation of negatively charged hydrosols the anions in many cases play a subsidiary part and the concentration of the cation determines the coagulation. When the anion is complex, for example, benzoate or sulphosalicylate, specific influence of the anion is observed. When the ions and the colloidal surface are oppositely charged, we observe the characteristic effect of the valency and the mobility of the ion. In many cases the adsorption of an ion of the same sign by a charged surface is scarcely noticeable."

"As stated above in the case of the chloride, bromide, iodide, and sulphate ions, the adsorption of the anion is either identical or, what seems more probable, negligible. We think Weiser is not correct in assuming that both cations and anions are equally adsorbed."

It will be noticed from this extract, that Mukherjee and Chaudhuri do not consider the adsorption of anions by negatively charged surfaces, to be probable. In a previous paper[2] I have however shown that hydrated manganese dioxide which is slightly negatively charged in presence of water, adsorbs both the positive and the negative ions, and the adsorption of negatives ion is appreciable. I have also found that hydrated ferric oxide, aluminum oxide and chromium oxide which are good adsorbent for acids, also adsorb alkali to a fairly great extent. In these cases therefore we are dealing with the adsorption of both the ions by the same substance. Ghosh and Dhar[3] have also shown that barium sulphate in course of precipitation adsorbs both the cations and anions, but the latter to a greater extent. Ghosh[4] has recently carried out some measurements of adsorption by arsenious sulphide sol, and one result is given below.

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[1] In this connection attention may be drawn to a recent paper by Henry and Morris: Trans. Faraday Soc. 20, 30 (1924) on the effect of anions in the coagulation of a gold sol. These authors find that anions have appreciable stabilising effects, the order of the stabilising powers being oxalate $> HPO_4'' > CO_3'' > OH'$, citrate $> HCO_3' > Br', I'$, acetate, valerate $>$ butyrate, $CNS' > SO_4'' > Cl'$, benzoate. Though the order is very peculiar, it cannot be doubted that the anions exert an appreciable effect in the coagulation of negative gold sol.

[2] J. Phys. Chem. 28, 469 (1924)

[3] Kolloid-Z. 35, 144 (1924)

[4] Unpublished work.

TABLE IV

Adsorption of Potassium Chloride by As_2S_3 sol
Amount of precipitated As_2S_3 = 0.4508 gr.
Total volume = 100 cc

Original concentration gr. ion per litre	Final concentration gr. ion per litre	Percentage adsorption	Ratio $\frac{K^{\cdot}}{Cl'}$
0.05997 $K^{\cdot}$	0.05790 $K^{\cdot}$	3.3	2.06
0.05997 Cl'	0.05900 Cl'	1.6	

It will be observed from this result that the precipitated arsenious sulphide carries down a large amount of Cl' ions, and the extent of this adsorption is quite comparable to that of the $K^{\cdot}$ ion. Hence these results support the conclusion of Weiser and Nicholas and also that advanced by us. Very recently Frankert and Wilkinson[1] have published an investigation on the adsorption of electrolytes by copper ferrocyanide sol. This paper has a special interest in connection with my experimental work and will be taken up later on. It may be mentioned however that with the suspension of the negatively charged copper ferrocyanide, considerable adsorption of negative ions was observed. In Table V the results obtained with our sol are given.

TABLE V

Electrolyte		amount required in c. cm.	Precipitation value
KCl	N/8	2.85	35.6
KBr	N/8	2.2	27.5
KI	N/4	4.0	100.0
KNO_3	N/8	2.3	28.7
KNO_2	N/2	1.58	79.0
K_2SO_4	N/2	0.95	47.5
K_2HPO_4	N/2	0.95	47.5
K_2CrO_4	N/2	1.6	80.0
$K_2C_2O_4$	N/2	3.4	170.0
K_2 tartrate	N/2	1.9	95.0
$K_3Fe(CN)_6$	N	2.05	205.0
$K_4Fe(CN)_6$	N	2.6	260.0

In Table V the influence of the anion when the coagulating ion is monovalent has been given. In Tables VI and VII the effect of anions with bivalent and trivalent coagulating ions is shown.

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[1] J. Phys. Chem. 28, 651 (1924)

TABLE VI

Electrolyte		Amount required in cc	Precipitation value
$BaCl_2$	N/200	1.83	0.915
$Ba(NO_3)_2$	N/200	1.78	0.89
Ba acetate	N/200	1.78	0.89
$MgSO_4$	N/200	3.05	1.52
$MgCl_2$	N/200	3.0	1.50

TABLE VII

$Al_2(SO_4)_3$	N/2000	3.5	0.175
$Al(NO_3)_3$	N/2000	3.5	0.175

From an examination of the foregoing results, it will be found that the anions have the greatest effect when the coagulating ion is monovalent. Thus the order of the different potassium salts is

$$K_4Fe(CN)_6 > K_3Fe(CN)_6 > K_2C_2O_4 > KI > K_2 \text{ tartrate} > K_2CrO_4 > KNO_2 > K_2SO_4, K_2HPO_4 > KCl > KNO_3 > KBr,$$

beginning with the greatest precipitation value. It will further be observed that the precipitation values differ considerably even in the case of chloride, bromide, iodide, nitrate, and sulphate, where there is usually no possibility of complex formation. It is interesting to note that the effect of the anions is in the same direction as their valencies, namely the greater the valency of the anion, the greater is the stabilising effect on the negative sol. There are however some exceptions, specially in the case of KI and KNO_2, where more of the salt is required to coagulate the sol than is the case with other monovalent anions. If the effect of organic ions is also considered, it will be seen that the difference in the precipitation values of the different potassium salts comes to more than one hundred percent from the average in some cases. When however the case of bivalent coagulating ions is considered, it is seen that the extreme difference in the case of the barium salts is about three percent from the average, and in the case of $MgSO_4$ and $MgCl_2$ one percent from the average. In the case of trivalent aluminum, the sulphate and nitrate have equal coagulating power. These results entirely confirm my conclusions drawn from the results of Schulze, Linder and Picton, and Freundlich and given in my previous paper[1]. When the coagulating ion is monovalent, the electrolyte has to be used in rather high concentrations, and the effects of the negative ions are consequently marked in these cases. When the coagulating ion is however bivalent or trivalent, the concentration of the negative ion is very small and hence its adsorption which is usually small, becomes negligible. Hence in these cases the effect of the negative ions does not become appreciable. Thus though organic anions are said to have considerable stabilising effect, barium acetate and nitrate have equal coagulating power. These results therefore do not corroborate the views expressed by Mukherjee and Chaudhuri. It has

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[1] Kolloid-Z. 34, 266 (1924)

already been pointed out that the stabilising effect of the anions is more marked the greater the valency of the stabilising ion. It would otherwise be difficult to explain the fact that $K_4Fe(CN)_6$ has usually the greatest precipitation value on negative sols. It appears probable that if the Schulze-Hardy law, that is, greater the valency the greater is the coagulating power of an ion, be true, then the converse of the Schulze-Hardy law, namely, the greater the valency of an ion the greater is its stabilising influence on a sol having the same charge, is also true. Just as the Schulze-Hardy law has many exceptions, so this generalisation will have undoubtedly some exceptions. Weiser and Nicholas have also come to the same conclusion. Some recent experiments of Loeb[1] seem also to support this conclusion. Working with a sol of gelatine-coated collodion particles, he showed that it could be stabilised into a suspension at the isoelectric point pH = 4.7 of gelatine by some salts. The minimum concentrations of $Na_4Fe(CN)_6$, Na_2SO_4 and NaCl required were respectively M/1000,000, M/16,000, and M/12. The collodion particles are negatively charged and hence the data show the remarkable effect of negative ions of different valencies on the stabilisation of a negatively charged suspension.[2] Mukherjee and Chaudhuri have cited the work of Michaelis and Hirabayashi on a sol of congorubin and mastic in support of their conclusion that negative ions unless of complex composition, have practically no effect on negative charged sols. It will be seen however from their data on mastic sol that the NO_3 ion behaves abnormally. Ostwald[3] made a series of quantitative experiments on the coagulation of congorubin sol. When his results are expressed in milligram equivalents per litre the following series beginning with the highest precipitation value is obtained:

$$K_2SO_4 > KNO_3 > KCl > KBr > KI$$

This shows that negative ions which are not much active in complex formation, show fairly appreciable differences.

There are two other points which should be discussed in connection with coagulation by different potassium salts, namely the degree of dissociation of the salt and its hydrogen ion concentration. Many years ago, Linder and Picton[4] showed that, generally, the coagulating power of a salt is greater the greater its degree of dissociation. It is well known that the degree of dissociation of potassium tartrate or potassium citrate is less than that of KCl and hence KCl should be a better coagulant. That this view alone can not explain the results obtained in this paper is evident, for the chloride, bromide, and nitrate are almost equally dissociated at the dilution studied, but still have different precipitation values. Arranging some of the salts in decreasing order of their equivalent conductivity of N/32 solution, the following order is obtained.

$$KNO_2 > KBr > KI > KCl > K_3Fe(CN)_6 > K_2CrO_4 > KNO_3 > K_2SO_4 > K_4Fe(CN)_6$$

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[1] J. Gen. Physiol. 5, 479-504 (1923)

[2] Kolloid-Z. 29, 154 (1921); 30, 209 (1922)

[3] Kolloidchem. Beihefte 10, 209 (1919).

[4] J. Chem. Soc. 67, 69 (1895).

This shows that it is not possible to correlate the behaviour of these salts with the equivalent conductivity shown by them.

The second point of importance is the concentration of the hydrogen ion in the salt solutions. It has been found that with negatively charged suspensions some free alkali usually increases the stability of the sol towards electrolytes, and this also happens with colloidal copper ferrocyanide. It is of interest here to notice the relative difference in the pH of these salt solutions. In a recent paper Bartell and Miller[1] have carried out some measurements of the Sörensen pH values of several salt solutions by means of the Clark and Lubs series of indicators. With N/50 solutions the following results were obtained.

TABLE VIII

Salt	pH	Salt	pH
KNO_3	6.8	$K_4Fe(CN)_6$	7.0
KBr	7.0	K_2HPO_4	4.4
KI	7.0		

It will be apparent from these approximate results that the stabilising influence of several ions can not be ascribed to the liberation of OH′ ions in solution. According to these values, the pH of KBr, KI and $K_4Fe(CN)_6$ is the same, and hence these salts should coagulate in equal concentrations. It is not therefore possible to explain away the stabilising influence of some anions by considering only the decreased dissociation and different pH values of their salt solutions though in some cases their effect may become undoubtedly appreciable. I am therefore inclined to the view that the valency of the anion is an important factor in the stabilisation of the sols. It is also peculiar that these higher valent ions have also great residual chemical affinity by which they go in for complex formation. There is no doubt that negative ions are adsorbed by negatively charged colloids to a more or less extent depending on the nature of the anion, and some times this adsorption may become appreciable or even greater than that of the positive ion. In the latter case the solutions become distinctly alkaline. An illustration of this will be given later on in the case of copper ferrocyanide. The mechanism of this adsorption is however obscure, and it is probable that some sort of quasi-chemical attraction in the Langmuir sense becomes operative.

Influence of the Dilution of the Sol on its Coagulation by Electrolytes

I have already shown in several previous papers[2] that the effect of the concentration of the sol on its coagulation by electrolytes is considerable, and for comparative studies the strength of the sol must be taken account of. It has been found that as a general rule, the greater the concentration of the sol the

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[1] J. Am. Chem. Soc. 45, 111 (1923).

[2] J. Phys. Chem. 28, 313 (1924); Kolloid-Z. 34, 262 (1924).

greater is the amount of electrolyte necessary for its coagulation irrespective of the valency of the precipitating ion. There are however some exceptional cases namely sulphides of arsenic and antimony and mastic sol. In these cases, with monovalent coagulating ions dilution increases the stability. In view of these facts some experiments on the dilution effect on copper ferrocyanide sol were carried out and has been given in the foregoing papers. The results obtained are reproduced below. The sol was prepared in the same way as described in this paper, its concentration being 1.31 gr. per litre.

TABLE IX

Electrolyte	KCl N/4	$K_4Fe(CN)_2$ N/2	$BaCl_2$ N/500	$Al_2(SO_4)_3$ N/800
Original sol	1.6cc	2.8	1.9	1.35
4/5 diluted sol	2.0	—	—	0.95
1/2 diluted sol	2.2	3.1	2.1	0.85
1/4 diluted sol	—	4.2	2.45	—

These results showed that with both mono- and bivalent coagulating ions, dilution increases the stability of the sol. When however the effect of dilution was studied with the sol used in the present investigation, it was observed that KCl gave anomalous results, in the way that the effect of dilution with this salt appeared to be practically nil. In order to find out the source of error in the previous experiment, a comparative study of both the sol and their analysis was made. It was found out that in the previous sol, a considerable amount of potassium ferrocyanide was present, but practically no trace of potassium chloride could be detected. On coagulating a portion by KCl, the supernatant liquid became distinctly yellow, showing the presence of $K_4Fe(CN)_6$. When however the present sol was examined, very little of free ferrocyanide could be obtained. On coagulation, the supernatant liquid did not show any yellow colouration; but this sol was found to contain appreciable amount of potassium chloride. It appeared therefore probable that the presence of this electrolyte has somehow masked the effect of dilution of the sol. It was therefore thought advisable to study the dilution effect with electrolytes other than KCl, and the results are shown in Tables X-XII.

TABLE X

Monovalent Coagulating Ions

Electrolyte	KCl N/8 in cc	NaCl N/2 in cc
Original sol	2.85	1.85
1/2 diluted sol	2.85	2.4
1/4 diluted sol	2.90	2.8

TABLE XI

Bivalent Coagulating Ions

Electrolyte	$BaCl_2$ N/200	$SrCl_2$ N/200	$MgSO_4$ N/200
Original sol	1.85	2.15	3.05
1/2 diluted sol	2.2	2.5	3.8
1/4 diluted sol	2.6	3.1	4.3

TABLE XII

Trivalent Coagulating Ions

Electrolyte	$Al_2(SO_4)_3$ N/2000	$Ce(NO_3)_3$ N/2000
Original sol	3.5	2.05
1/2 diluted sol	2.6	1.65
1/4 diluted sol	1.7	1.3

TABLE XIII

Quadrivalent Coagulating Ion

Electrolyte	$Th(NO_3)_4$ N/1000
Original sol	1.5
1/2 diluted sol	1.15
1/4 diluted sol	1.0

It will be observed from these tables that excepting the case of KCl, the other monovalent and bivalent coagulating ions show the same behaviour as was obtained in the case of the previous sol. The effect of dilution in these cases was to stabilise the sol towards mono- and bivalent precipitating ions. Potassium chloride behaves in an anomalous way in that its precipitation concentration remains practically constant. That this fact is connected with the presence of electrolytes in the sol seems probable from my previous observation on the analysis of the two sols. I believe therefore that the presence of impurities in the sol may affect the stabilisation of a sol in such a way that the effect of dilution may become masked for some particular electrolytes. It appears probable that this may be one of the reasons for some anomalous results found in the literature. Thus it is well known that a sol of arsenic sulphide requires more of an univalent electrolyte for coagulation when diluted than when concentrated. Kruyt and Spek[1] however found that the precipitation values of KCl with As_2S_3 sol were exactly the same with two widely different concentrations of the colloid. Weiser and Nicholas (loc. cit.) showed some three years back that with dilution of a prussian blue sol, the precipitation value of KCl became less. In a recent paper Ghosh and Dhar (unpublished work) however find that dilution increases the stability of the prussian blue sol towards KCl. The difference between the two sols seems to be that in the sol used by Weiser and Nicholas some free potassium ferrocyanide was present whereas in the sol of Ghosh and Dhar there was no free ferrocyanide. In some preliminary experiments I used a sol of prussian blue peptised by means of oxalic acid. The sol was dialysed and was quite free from ferrocyanide and oxalic acid. On making some precipitation experiments, it was observed that dilution had practically no effect on the precipitation value of KCl. I am therefore inclined to believe that both Weiser and Nicholas and Ghosh and Dhar are correct so far as their experimental results are concerned. The difference is most probably due to the amount of electrolyte content and the purity of the sols studied.

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[1] Kolloid-Z. 25, 11 (1919).

One important fact that has come out in course of these dilution experiments is that complete settling is not a true measure of the coagulation of these sols. This has already been emphasised by Mukherjee and Sen[1] in the case of As_2S_3, HgS and CuS sols. It has been observed that when dilute sols of either copper ferrocyanide or prussian blue are used no settling takes place for hours even if slight excess of electrolytes is added. With prussian blue the results are more peculiar. If an already coagulated mass of prussian blue is shaken up with little water, the precipitate is at once redispersed as a colloidal solution, and if a large amount of water is used the newly formed sol becomes very stable. Since simply water can act as a dispersing agent it is evident that dilution will have an effect on the stabilisation of these ferrocyanide sols. Consequently we observe the anomalous behaviour with mono- and bivalent coagulating ions, where the anions have considerable effect. With tri- and quadrivalent ions however the normal behaviour is shown, for in these cases the anion effect is negligible and it appears probable that the effect of distance becomes only appreciable when anions have also some effect.

It is interesting to note in this connection that when copper ferrocyanide sol is precipitated by different electrolytes, the nature of the substance precipitated is not always the same. Thus when KCl is used, the precipitate is very fine and passes through filter papers. When however salts like $BaCl_2$, $SrCl_2$, $Al_2(SO_4)_3$, etc., are used, the precipitate is much coarser and is retained by the filter paper. A similar behaviour has been noticed by Weiser in the case of $Fe(OH)_3$ and $Cr(OH)_3$ sols. I have also noticed that when $Cr(OH)_3$ sol is coagulated by KCl, the precipitate is very fine and does not settle soon unless large excess of electrolyte is used. On filtering through ordinary papers, a portion of the precipitate passes out, but the particles can be distinctly recognised. When however salts like K_2SO_4 or $K_2C_2O_4$ are used, the precipitate is more coarse grained, settles down rapidly and does not pass through filter papers. These results seem therefore to be analogous to those described by Odén[2] in the case of sulphur sol. He found that the physical properties of sulphur precipitated from colloidal solution varied very markedly with the electrolyte used for precipitation. It came down as a hard precipitate with potassium salts, fine-grained with copper sulphate, plastic with barium salts, fluid with hydrochloric acid, and slimy with other salts. Thus the nature of the precipitating electrolyte on the physical property of the coagulated mass is of considerable importance.

Effect of some Non-Electrolytes on the Coagulation of Copper Ferrocyanide Sol

In a previous paper I have drawn attention to the effect of some non-electrolytes on the stability of arsenious sulphide sol and their possible mechanism. The main work in this line has been carried out on arsenious sulphide sol, ferric hydroxide sol, and kaolin suspension. Thus Freundlich and Rona[3] found that

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[1] J. Chem. Soc. 115, 461-472 (1919).

[2] "Der kolloide Schwefel", 134, 157 (1912).

[3] Biochem. Z. 81, 87 (1917).

a ferric hydroxide sol was made more sensitive to precipitation by electrolytes on the addition of camphor, thymol and the urethanes. Kruyt and Duin[1] noted that isoamyl alcohol increased the sensitivity of an arsenious sulphide sol to mono and trivalent coagulating ions but protected it for divalent ions, whilst Rona and György[2] obtained an actual precipitation of kaolin suspensions on the addition of camphor and thymol. It will therefore be evident that a good deal of qualitative work has been done in this line. I have observed that a sol of copper ferrocyanide can not be coagulated by adding either ethyl or propyl alcohol. These substances however sensitise the sol considerably towards monovalent and bivalent and to a less extent trivalent coagulating ions. With cane sugar however different results were obtained. With KCl cane sugar had no effect on the stability of the sol. With $BaCl_2$ sugar acted as a great sensitiser and with $Al_2(SO_4)_3$ the sol was only slightly sensitised. The effect of adding varying quantities of the alcohols was studied by adding a definite quantity of the salt and noting the time required for coagulation in each case. In the following table the results with mono- and bivalent salts are shown.

TABLE XIV

Electrolyte NaCl N/2 1.9 cc

Amount of alcohol 98% in cc	0.5	0.4	0.3	0.2	0.1	0.0
Time in minutes for coagulation	19.0	25.0	30.0	35.0	44.0	55.0

Electrolyte $SrCl_2$ N/200 2.2 cc

Amount of alcohol	0.5	0.4	0.3	0.2	0.0
Time for coagulation	15.0	21.0	21.0	28.0	55.0

These results show that with the gradual addition of alcohol, the stability of the colloid towards electrolytes decreases. But in the absence of any electrolyte, no coagulation occurs even if a fairly large quantity of the alcohols are added. The mechanism of the effect of the non-electrolytes is however obscure, and no satisfactory explanation has yet been given. In a previous paper I have suggested that the protective action of the protective colloids like gelatin, gums, etc., can be explained by assuming that when these substances are adsorbed by the colloid particles, the surface of the particles is changed in the sense that it shows a different Hofmeister series of ion adsorption from the original surface. The stability is therefore due to a rearrangement of the atoms on the surface and their comparative inactivation towards certain ions owing to a pseudo-chemical combination with the atoms or molecules of the protective colloids, which are usually amphoteric in nature. This sort of explanation is not however quite satisfactory in the case of alcohols. Freundlich and Rona (loc. cit.) suggested that the non-electrolytes are adsorbed at the surface of the colloid particles. Since the dielectric constants of these non-electrolytes are less than that of water they diminish the density of the charge on

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[1] Kolloidchem. Beihefte, 5, 287 (1914).

[2] Biochem. Z. 105, 133 (1920).

the surface. Hence the sol becomes sensitised. Along with this it was observed that an addition of 5 millimoles of camphor decreased the mobility of a colloidal ferric hydroxide in an electric field from 0.4×10^{-4} into 0.2×10^{-4} cms. per second. In a discussion of these results[1] however has recently pointed out that the hypothesis of Freundlich is evidently untenable since a concentration of 5 millimoles of camphor per litre of water of $K = 81$ corresponds to a dilution of only one part in 10,000 of a substance of $K = 10$, and a scarcely perceptible alteration in the K of the medium would result. In discussing the action of non-electrolytes and specially alcohol, there is another possibility to be kept in view. The researches of Born[2], Kossel[3] and others make it probable that hydration is the result of electrical polarisation, and it seems likely that the hydration of a colloidal particle or a colloidal surface is intimately connected with the density of the electrical charge on the surface. The greater the density, the greater is the thickness of the layer of hydration. The electrocapillary attractions between particles are also probably dependent on the thickness of the hydration layer. The greater the thickness, the less the attraction between the particles. A diminution in the thickness of the hydration layer means an increased electrocapillary attraction, and hence if the added non-electrolytes can decrease the extent of hydration, then the colloid will become less stable. Incidentally it may be pointed out that my results with cane sugar do not support the views of Anderson[4] that it is not the ionic concentration but the activity of potassium ion which determines the precipitation value of KCl. Since the activity of potassium ion is increased in presence of sugar, KCl ought to show a lower precipitation value on copper ferrocyanide sol in presence of this substance. But no such stabilisation is actually observed.

Effect of Ageing

In a previous paper[5] it has been shown that a sol of Sb_2S_3 becomes unstable in course of time, and less of precipitating electrolytes are required for coagulation of an old sol than that of a new one. A similar phenomenon is also known in the case of As_2S_3 where the sol is sensitised in course of time. What happens is not exactly known but in the case of Sb_2S_3 sol, mould formation has been observed. Most probably the sols are decomposed partially on standing for some time. When however the effect of ageing on copper ferrocyanide sol was investigated, it was observed that the sol behaved in a peculiar way inasmuch as it was stabilised on standing instead of being sensitised towards electrolytes. This stabilisation was very marked for the first fifteen days after which the effect of ageing became gradually less. Thus after five days of the preparation of the sol, 5 cc of the sol required 1.80 cc of N/8 KCl for coagulation whereas after a month the amount required was 2.85 cc and

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[1] Proc. Camb. Phil. Soc. **22**, 102 (1924).
[2] Z. Physik, **1**, 45, 221 (1920).
[3] Ann. Physik, (4) **49**, 314 (1916).
[4] Trans. Faraday. Soc. **19**, 635 (1924).
[5] J. Phys. Chem. **28**, 328 (1924).

after two months 3 cc. The effect of ageing was observed not only with monovalent coagulating ions, but also with bi- and trivalent ions, and the same stabilisation was observed. In order to minimise the error due to this fact, the results given in Tables V, VI and VII were obtained on the one month old sol and the series with potassium were completed within three days. This could be done by first determining the precipitation values accurately in the ordinary way, and then determining the change if any, within these three days. Often different salts of potassium were added to the colloid in different test tubes on the same day side by side and the precipitation values were determined. The values were quite reproducible within three days and are absolutely comparative, the limit of error being 0.025 cc. The precipitation values of salts containing bivalent and trivalent coagulating ions were also determined and compared with one another in the same way.

The reason for the increased stability of the copper ferrocyanide sol on ageing seems to be that a portion of the substance undergoes slow hydrolysis with the liberation of some free hydroferrocyanic acid and it will be shown later on that a little amount of free ferrocyanide stabilises the sol considerably. It has also been observed that if the sol is allowed to stand for a very long time, a portion eventually coagulates. This becomes more rapid if the sol is exposed to strong sunlight. In this connection the so-called acclimatisation effect observed in the case of arsenious sulphide sol has also been found to take place in the case of copper ferrocyanide sol. Thus greater amounts of electrolytes are required for coagulation if added by portions at a time than when they are added all at once. Copper ferrocyanide sol is thus comparable to arsenious sulphide sol in many respects.

Effect of Stabilising Electrolytes and the Coagulation of Colloids by Mixtures of Salts

It has already been stated that some free ferrocyanide stabilises the sol considerably towards coagulation by electrolytes. In a previous paper a detailed study of the effect of acid, alkali and different salts has been made. It has been found that alkali has a stabilising effect whereas acids make the sol more sensitive towards electrolytes. In recent years the coagulation of colloids by mixtures of electrolytes has received much attention. The importance of these studies immediately reveals itself when we consider that colloids are usually stabilised by the preferential adsorption of one ion, and hence in all coagulation experiments where an electrolyte is added to a sol, the effect which is observed is really the joint effect of the adsorbed ion and the ions of the added electrolyte. As my results on the effect of the addition of acids on iron, aluminium and chromium hydroxide sols and that of alkali and potassium ferrocyanide on copper ferrocyanide sol on their stability towards electrolytes throw considerable light on the mechanism of coagulation by mixture of electrolytes it is intended to give a discussion on the experimental results obtained with copper ferrocyanide sol.

The first experiment with mixtures of electrolytes on an inorganic colloid seems to be that of Linder and Picton[1] who showed that with colloidal arsenious sulphide and a mixture of KCl and $SrCl_2$, the precipitation value of the mixed electrolytes was not the algebraic sum of the precipitation values of each separately, but considerably greater quantity of $SrCl_2$ was necessary when KCl was already present in the arsenious sulphide sol. With the increase in the addition of KCl, the amount of $SrCl_2$ gradually reached a maximum, and then became less. Linder and Picton also made some experiments with mixtures of salts containing bivalent precipitating ions and showed that in this case no stabilisation of the sol occurs and the precipitation values are approximately the sum of each electrolyte. Weiser[2] studied the precipitation values of several mixtures of electrolytes such as KCl + $K_2C_2O_4$ and K_2SO_4 + $K_2C_2O_4$ on a sol of positively charged ferric hydroxide and pairs of such salts as KCl + $SrCl_2$ and $BaCl_2$ + $SrCl_2$ on a negatively charged sol of arsenious sulphide. His results show that with As_2S_3 sol, the results of Linder and Picton are quire correct, that is, more of $SrCl_2$ is necessary to coagulate a fixed amount of As_2S_3 sol in presence of KCl than when it is absent. On making adsorption experiments, it was found that the presence of potassium ion markedly decreased the adsorption of $Ba^{\cdot\cdot}$ ion, and Weiser explained the stability of As_2S_3 sols in presence of KCl as due to the cutting down of the adsorption of the coagulating $Ba^{\cdot\cdot}$ ions. With the mixture $SrCl_2$ + $BaCl_2$ where both the precipitating ions are bivalent, the precipitation values showed an additive relation and in this also Linder and Picton's result was corroborated. In the case of ferric hydroxide colloid, no stabilisation was observed in any case and along with it, the presence of KCl did not affect the adsorption of oxalate ion. A year later Freundlich and Scholz[3] published an investigation in which they studied the effect of mixture of electrolytes on Odén's[4] sulphur sol, von Weimarn's[5] sulphur sol, Donau's[6] gold sol and an arsenious sulphide sol. The authors confirmed the results of Odén, to the effect that the coagulating properties of a salt are diminished or destroyed by the presence of a second salt, but in contradistinction to Odén they also found that the reduction is not due to the diminution of cation action by the anion but rather to an antagonism between the cations. The antagonistic action was measured by mixing Odén's sulphur sol with a quantity of an electrolyte insufficient to cause flocculation and then determining the quantity of a second electrolyte necessary to effect this change. The ion pairs magnesium + lithium and magnesium + hydrogen showed strong antagonistic effect. The anions had also an influence in the diminution of the coagulation value in the order citrate > sulphate > chloride. Definitely hydrophobic sols, such as Weimarn's sulphur sol and Donau's gold sol, did not exhibit the antagonistic phenomena. In these cases the coagula-

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[1] J. Chem. Soc. 67, 67 (1895).

[2] J. Phys. Chem. 25, 665 (1921).

[3] Kolloidchem. Beihefte, 16, 267 (1922).

[4] "Der kolloide Schwefel", (1912).

[5] Kolloid-Z., 8, 214 (1911).

[6] Monatsheft, 26, 525 (1905).

tion values of sols containing electrolytes were always less than those of the pure sols; that is, the action of the two electrolytes was additive. Freundlich and Scholz believed that the behaviour of Odén's sulphur sol was probably to be connected with its distinct hydrophilic character; that is, with the hydration of the micellae. In the case of arsenic sulphide sol a certain antagonism was observed for salts such as lithium chloride and magnesium chloride, and hence this sol was also considered by these authors to be hydrophilic.

In a recent paper Weiser[1] has again studied the precipitation of hydrous chromium oxide, stannic oxide and arsenious sulphide sol by various mixtures of electrolytes, and has come to the conclusion that the explanation of Freundlich and Scholz is untenable. Several well known hydrophilic sols such as hydrous ferric oxide, chromium oxide, stannic oxide, etc., show no antagonistic effect when they are coagulated by pairs of different electrolytes. On the other hand a strong antagonistic action is observed when As_2S_3 sol is coagulated by such pairs as $HCl + MgCl_2$, $LiCl + BaCl_2$ and $LiCl + MgCl_2$. Weiser therefore considers that hydration of a sol is not an important factor in producing such phenomena, and it is more possible that the antagonistic action is due to the effect of one cation upon the adsorption of the other by the colloid particles. This view is supported by the fact that the adsorption of $Ba^{\cdot\cdot}$ ion by As_2S_3 sol is decreased to a marked extent by the presence of lithium ion below the precipitation concentration of the chlorides of the metals. The adsorption of $Li^{\cdot}$ ion is also influenced by the presence of $Ba^{\cdot\cdot}$ ion. This cationic antagonism according to Weiser, is the important factor in raising the precipitation values of certain mixtures above the additive values.

The importance of this subject of coagulation of colloids by mixtures of electrolytes has also been perceived in some biological studies, and Freundlich and Scholz have cited the works of Neuschloss, J. Loeb, and R. S. Lillie. Specially interesting in this connection is the coagulation of egg white by mixtures of salts. Wo. Pauli[2] determined the effect of mixtures of two salts and found that the coagulating action of salts upon proteins is additive, that is the precipitating power of the mixture is the algebraic sum of the separate effects exerted by its components except when the two salts have a common ion and so diminish each other's degree of dissociation. Later on he found that a number of salts which will not coagulate egg white by themselves will do so or will increase the coagulating power of other salts when mixed with them, while others markedly diminish the coagulating power of salts which in their absence, readily coagulate egg albumin. These cases are therefore in line with those already cited.

About ten years ago, Bender[3] published an interesting paper, which has however not received much attention, on the coagulation of mastic sol by mixtures of two salts. In most cases he used HCl as one of the electrolytes and his results show that, in general, the substitution of an equimolar quantity of a

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[1] J. Phys. Chem. **28**, 232 (1924).

[2] Beitr. chem. Physiol. Pathol. 3, 225 (1903).

[3] Kolloid-Z. **14**, 255 (1914).

metallic ion causes no appreciable change in the coagulating power of the acid. This relation holds only in the case of mono- and bivalent metals. In the case of trivalent metal ions a slight stabilisation was observed. Thus $Al_2(SO_4)_3$ + HCl do not show any additive relation with regard to their precipitation values on mastic sol. This behaviour is not, however, noticed when NaCl is substituted for HCl. Also pairs of electrolytes like $MgSO_4$ + HCl, $BaCl_2$ + HCl, LiCl + HCl, $Ce(NO_3)_3$ + HCl, $CdSO_4$ + HCl do not show any antagonistic effect but a mixture of $AuCl_3$ + HCl, and $HgCl_2$ + HCl show this behaviour. Since colloidal mastic is usually negatively charged it was expected that in presence of OH′ ions the stability would be increased. This was found to be true by Bender who observed that in presence of NaOH and $Ba(OH)_2$ more of NaCl was required to coagulate the colloid. A similar effect was observed in the case of the pair of electrolytes KCN + NaCl where the stabilisation is undoubtedly due to the OH′ ions set free by the hydrolysis of the KCN. In Tables XV-XVI the results obtained with the previous copper ferrocyanide sol is shown.

TABLE XV

Electrolytes $K_4Fe(CN)_6$ + KCl

Amount of $K_4Fe(CN)_6$ N/2 taken in c.c.	Amount of KCl N/4 reqd. for coagulation		Difference
	observed	calculated	
0.0	1.6		
0.1	2.05	1.54	0.51
0.5	2.0	1.31	0.69
1.0	1.75	1.03	0.72
1.5	1.4	0.745	0.655
2.0	0.95	0.46	0.49
2.8	0.0		

TABLE XVI

Electrolytes $K_4Fe(CN)_6$ + $BaCl_2$

Amount of $K_4Fe(CN)_6$ N/2 taken	Amount of $BaCl_2$ N/500 for coagulation		Difference
	observed	calculated	
0.0	1.9		
0.3	2.2	1.69	0.51
0.5	2.5	1.56	0.96
0.8	2.8	1.36	1.44
1.0	3.1	1.22	1.89
2.0	3.0	0.54	2.46
2.2	2.7	0.41	2.2
2.8	0.0		

The precipitation concentrations were determined by the same method as Weiser has used and the total volume in every case was 10 cc. It is apparent that the stabilisation reaches a maximum with the addition of potassium ferrocyanide and then falls off. Similar results are also obtained with such mixtures as KOH + KCl and KOH + $BaCl_2$. When curves are drawn with the results of Linder and Picton, of Weiser and those obtained by me, plotting the amount of KCl, LiCl, HCl or $K_4Fe(CN)_6$ taken as the abscissa and the amount of $SrCl_2$, $BaCl_2$, $MgCl_2$, KCl, etc., required for coagulation as the ordinate, it is seen that the nature of all the curves are very similar. Thus in every case, the curves reach a maximum and then fall off. This denotes that the nature of the action exerted by the different stabilising agent is probably the same. Thus the action of $K_4Fe(CN)_6$ in stabilising a sol of copper ferrocyanide appears to be of the same nature as the action of KCl or HCl on arsenious sulphide sol. Now it is well known that the stabilising action of $K_4Fe(CN)_6$ is due to the great adsorption of the ferrocyanide ion by copper ferrocyanide, for Duclaux[1] has shown that when copper ferrocyanide is precipitated, a great deal of potassium ferrocyanide is also taken up, and it is practically impossible to free copper ferrocyanide from adsorbed potassium ferrocyanide. This stabilisation in presence of mixtures of salts can not be explained on the basis that the addition of $K_4Fe(CN)_6$ decreases the dissociation of KCl, for though the dissociation of KCl may be decreased, the amount of the coagulating ion potassium actually increases very much on the addition of $K_4Fe(CN)_6$. Again a mixture of $K_4Fe(CN)_6$ and $BaCl_2$ shows similar stabilisation and here no decrease in the dissociation of $BaCl_2$ can take place, there being no common ion in the added electrolyte. The stabilisation therefore is undoubtedly due to the ferrocyanide ion. Similar results happen in the case of alkali, and it has been observed that the presence of OH' ions stabilises the negatively charged sol of copper ferrocyanide to a certain extent. It has already been stated that a mastic sol is also stabilised by alkali. Mukherjee and Sen (loc. cit.) have shown that colloidal solutions of cupric, mercuric and arsenious sulphides are stabilised by solutions of potassium and sodium sulphides. This stabilising influence has been found for ammonium, potassium, barium and strontium chlorides and aluminium sulphate. With a trace of pure alkali, sols rich in sulphide are prepared and the OH' ions largely increase the stability of these colloids. It is clear therefore that in these cases, the negative ion is the real stabiliser, and the so-called antagonistic effect is really due to the negative ions of the electrolytes. As a matter of fact, there can not be any cationic antagonistic action when the mixture $K_4Fe(CN)_6$ + KCl is used for coagulation, since both electrolytes contain the same cation, and hence in these cases it must be recognised that the antagonistic effect has been mainly due to anion of potassium ferrocyanide.

Since the precipitation value of an electrolyte for a colloid is that concentration which results in sufficient adsorption of the precipitating ion to neutralise the combined adsorption of the original stabilising ion and the stabilising ion added with the electrolyte, it is evident that any ion present in the solution which can either decrease the adsorption of the coagulating ion, or, by being itself adsorbed by the colloid particles increases the charge and hence the stability of the colloid, will act as a stabiliser of the sol towards that par-

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[1] J. Chim. phys. 7, 405-446 (1909).

ticular coagulating ion. It is probable that anions act in the latter way on negatively charged sols, and H$^{\cdot}$ ions also do the same thing on positively charged sols. There is therefore practically no difference in the nature of the stabilising action exerted by acids on iron, chromium and aluminium hydroxide sols and potassium ferrocyanide, alkali, etc., on negatively charged sols. We can therefore predict that easily hydrolysable salts such as $FeCl_3$, $Fe(NO_3)_3$, $Al(NO_3)_3$, etc., which give acid reaction in water will also stabilise a sol of ferric hydroxide, and mixtures like $FeCl_3 + KCl$ will show considerable antagonistic action. Again with arsenious sulphide sol, a mixture like potassium benzoate + KCl or potassium ferrocyanide + KCl will also probably show antagonistic behaviour. It seems therefore that the opinion held by Weiser that only cations which have highly different coagulating powers can affect each other's precipitation values can not be correct. For in that case, the antagonistic action showed by the mixture $K_4Fe(CN)_6 + KCl$ can not be explained. If however the presence of a cation can decrease the adsorption of another coagulating cation, then also the sol may be stabilised. In this case the antagonistic effect will be really cationic. In no case, however, has it been definitely proved that the antagonistic action is only cationic. Thus with the mixture $LiCl + BaCl_2$ and As_2S_3 sol, it has been shown by Weiser (loc. cit.) that the amount of adsorption of either of the ions Li$^{\cdot}$ or Ba$^{\cdot\cdot}$ is decreased in presence of each other. But this does not necessarily mean that the sol becomes stable towards Ba$^{\cdot\cdot}$ ions on the addition of Li$^{\cdot}$ ions. Though the adsorption of each is separately diminished, the total adsorption of both the ions may be equivalent to the adsorption of either Li$^{\cdot}$ or Ba$^{\cdot\cdot}$ when only one is present at the coagulating concentration. Since the coagulation of a colloid depends primarily upon the charge neutralisation of the colloid, equivalent amounts of Li$^{\cdot}$ or Ba$^{\cdot\cdot}$ ions will be necessary to discharge the colloid particles. Hence when the sum total of the adsorption of Li$^{\cdot}$ or Ba$^{\cdot\cdot}$ ions separately expressed in electrochemical equivalents reaches a certain limit, the colloid will be coagulated irrespective of whether the original point of adsorption of Ba$^{\cdot\cdot}$ ion when it was present alone to coagulate the sol, has been reached or not. In order to support this explanation of the antagonistic action between the ions Li$^{\cdot}$ and Ba$^{\cdot\cdot}$, it will have to be shown that though one of these ions is not appreciably adsorbed, simply by its presence the adsorption of the other ion is diminished considerably. Also along with this fact it must be observed that by the addition of LiCl to $BaCl_2$ solution, the degree of ionisation of both the electrolytes are thrown back and the concentration of the Cl$'$ ions is proportionately increased. The increase in the concentration of the Cl$'$ ions will mean a stabilisation of the colloid and hence the antagonistic effect which is observed will be the sum of the cationic and anionic effects. This seems also to be the case with such mixtures as $HCl + MgCl_2$, $KCl + SrCl_2$ and $LiCl + MgCl_2$.

It has already been stated that the continual addition of the stabilising agent does not stabilise the colloid to an infinite extent. This is evident from all the results given in the previous paper as well as in this paper, where the stabilisation is found to reach a maximum soon. This is due to the fact as has been already stated that positive ion of the stabilising agent in the case of negative sols, begins to exert a coagulating effect at higher concentrations of the stabilising electrolyte. This view is extremely well supported by a recently published investigation on the adsorption of electrolytes by colloidal copper ferrocyanide. It has been found by Frankert and Wilkinson (loc. cit.) that with pure copper ferrocyanide different potassium salts show a gradual change from developing a small amount of acidity with the chloride to large amounts of alkalinity with the ferrocyanide. When the ferrocyanide concentration is gradually increased, the alkalinity which is developed first, gradually changes to acid. On the principle of selective adsorption, the explanation of this phenomenon is that the ferrocyanide ion is strongly adsorbed and the resulting solution thus becomes alkaline. In a particular case, working with 2 gr. of copper ferrocyanide and 2 N $K_4Fe(CN)_6$ solution, the total alkalinity developed was equivalent to 200 cc of .01 N KOH solution. With the ferrocyanide solution also, a similar behaviour is observed. The solution is first alkaline due to the adsorption of $Fe(CN)_6''''$ ions, leaving an equivalent amount of KOH in solution. Soon however, the $K^{\cdot}$ ions become effective and cut down the adsorption and hence the alkalinity due to the $Fe(CN)_6''''$ ion and finally overcome it entirely and the solution becomes acid. The experimental curve is therefore the resultant or the difference between the two because one of them tends to develop acid and the other base. This shows that each ion has its own adsorption curve and when several ions are present in the solution, the experimental curve will be the resultant of all the curves.

In the foregoing pages it has been shown that the antagonistic effect between pairs of salts, or the stabilisation of a sol by means of an electrolyte, is in the majority of cases due to the influence of the ion carrying the same charge as the colloid particles themselves possess. It has also been stated that the stabilisation of some sols on dilution towards certain electrolytes may also be explained on the assumption that the stability is due to the adsorption of the ion charged oppositely to the precipitating ion. These phenomena seem therefore to be related to each other. It is also very probable, as Ghosh and Dhar (private communication) suggest, that the phenomenon of "acclimatisation" of colloids may be brought in line with these two cases. Since in the phenomenon of acclimatisation more electrolyte is necessary to coagulate a colloid when it is added slowly than when it is added rapidly, it is probable that below the precipitation value of the electrolyte, comparatively more of the ions having the same charge as the colloid particles may be adsorbed, and thus the stability of the suspension may be proportionately increased. This view will explain the "acclimatisation" shown by As_2S_3 sol and copper ferrocyanide sol. It seems therefore that the stabilisation of a colloid in presence of an electrolyte, the stabilisation of some sols on dilution towards certain electrolytes, and the acclimatisation of sols, may be all explained by the same theory, and in all these cases, the importance of the ion having the same charge as that on the colloid particles, will in all probability, have to be recognised as one of the primary factors.

The general results of this paper may be summarised as follows:

(1) The coagulation of copper ferrocyanide sol by electrolytes has been studied under different conditions. It is shown that the colloid obeys the Schulze-Hardy law.

(2) When the coagulating ion is monovalent potassium, the negative ions have an appreciable effect on the precipitation values of different salts. This effect can not be ascribed simply to the decreased degree of dissociation and changed pH values of the salt solutions. The generalisation has been drawn that greater the valency of the negative ion, the greater is its stabilising power on a sol having the same charge.

(3) With the increase in the valency of the precipitating ions, the precipitation values being very small, the concentration of the negative ions becomes also very small and hence their effect is not appreciable.

(4) Dilution of the sol makes it more stable towards mono- and bivalent coagulating ions and less stable towards tri and quadrivalent ions. It has been observed also that the presence or absence of some impurities in the sol may affect the stability of the sol on dilution.

(5) The effect of cane sugar and of ethyl and propyl alcohols on the coagulation of copper ferrocyanide sol has been studied and it has been found that sugar has no effect when KCl is used as the coagulant, but makes the sol unstable towards $BaCl_2$. The other two non-electrolytes considerably sensitise the sol towards mono-, bi- and trivalent ions.

(6) It has been suggested that the sensitising effect of the alcohols may be due to their diminishing the layer of hydration round the colloid particles. This means that the electrocapillary attraction between the colloid particles is increased and consequently the sol becomes unstable.

(7) The effect of ageing in the case of copper ferrocyanide sol is considerable and the sol becomes more stable towards all electrolytes on standing. The explanation of this behaviour is that some free ferrocyanide ion is liberated owing to a slow hydrolysis of the substance, and this stabilises the sol.

(8) The effect of adding varying amounts of $K_4Fe(CN)_6$ on the stability of the sol towards KCl and $BaCl_2$ has been studied. It has been found that the stability reaches a maximum and then decreases.

(9) It has been shown that the nature of the stabilisation observed in the case of copper ferrocyanide sol in presence of $K_4Fe(CN)_6$ is similar to that observed by other investigators in the case of As_2S_3 sol and KCl, LiCl or HCl. This is also the case with mastic, As_2S_3, HgS and CuS sols in presence of OH′ ions, and $Fe(OH)_3$, $Al(OH)_3$, and $Cr(OH)_3$ sols in presence of acids.

(10) The view has been put forward, that in the majority of cases studied, the antagonistic effect between pairs of salts is really due to the stabilising effect of the ions charged oppositely to that of the precipitating ion. In no case has it been definitely proved that the antagonistic action is purely cation-

ic, but it is probable that in some cases, a joint action of the anionic and cationic effect may have been observed. It has also been suggested that salt pairs like $FeCl_3$ + KCl etc., and $K_4Fe(CN)_6$ + KCl etc., will show an antagonistic action with sols of $Fe(OH)_3$ and As_2S_3 respectively.

(11) It seems probable that the stabilisation of some colloids on dilution, the antagonistic action between pairs of some electrolytes on several colloids, and the phenomenon of acclimatisation of sols, may all be explained by the same theory, and in all these cases, the influence of ions with the same charge as on the colloid particles, will have to be recognised as of primary importance.

My thanks are due to Mr. M. R. Mehrotra, M. Sc., for his assistance in the early part of the investigation.

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SORPTION OF NITROUS OXIDE AND SULPHUR DIOXIDE BY GLASS

D. H. BANGHAM AND F. P. BURT

In a previous paper[1] experiments on the sorption of ammonia and carbon dioxide by a glass surface at 0° C. were described, and the time and pressure relationships were discussed. Similar experiments have been carried out with nitrous oxide at 0° C., using the same tube of glass wool as sorbent[2]; and the results confirm substantially the conclusions arrived at from the carbon dioxide series.

Nitrous oxide as supplied for anaesthetic purposes(that is, practically free from other oxides of nitrogen) was collected in a gas-holder over aqueous potash. After drying over calcium chloride and phosphoric oxide it was solidified at liquid air temperature and freed from permanent gas by means of the mercury pump. After fractional distillation a product was obtained which had a melting-pressure of 662 mm.

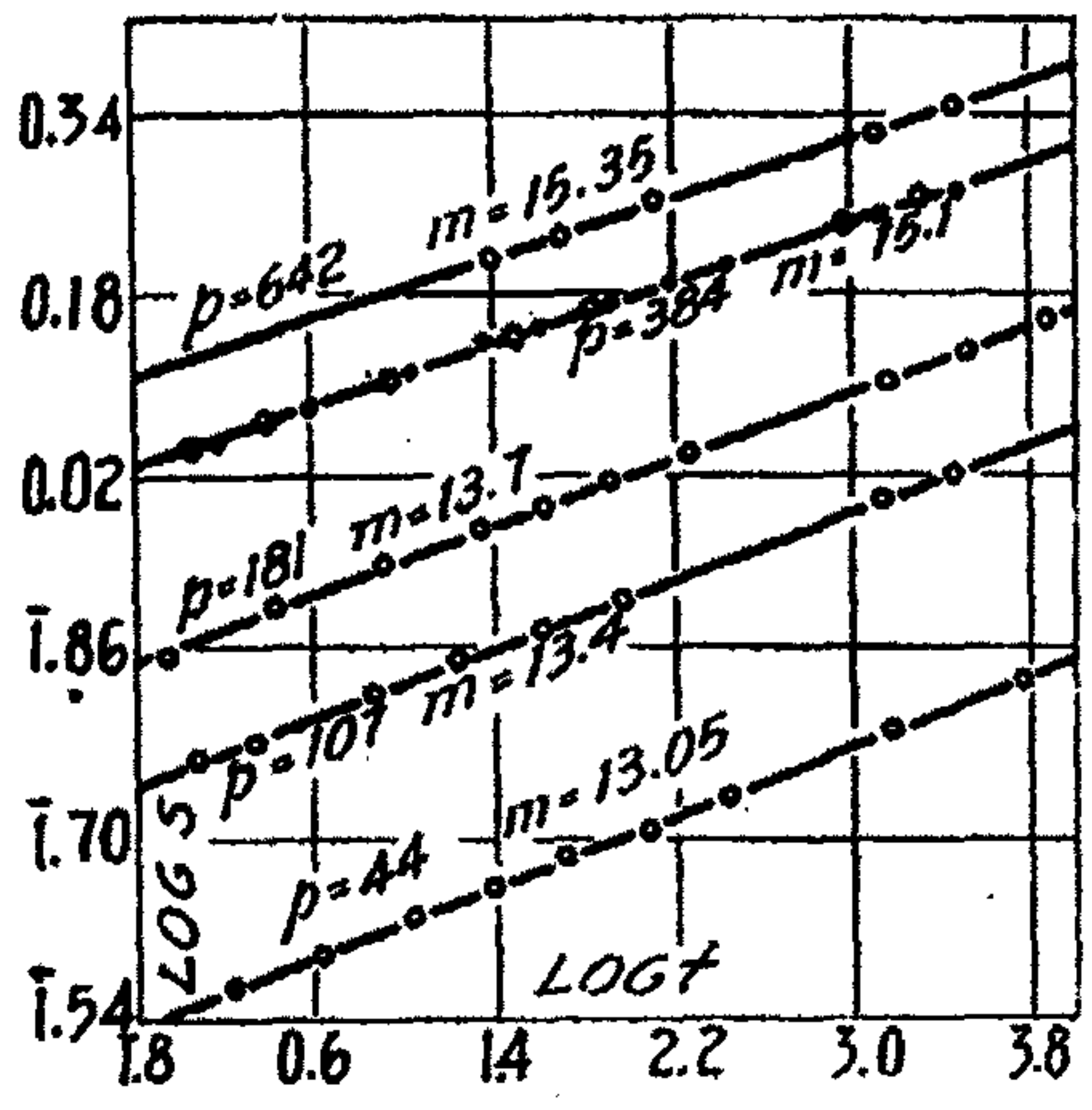

Fig. 1

With this gas sorption experiments were carried out at a series of pressures ranging from 44 mm. to 640 mm. Every effort was made to obtain as large a time-range as possible, and in one case the observations extended from 52 seconds to 5 days. The sorption values and times together with the momentary pressures are given in Table I, and the log s, log t graphs derived therefrom are shown in Fig. 1. For corresponding times and pressures the sorption values for nitrous oxide are invariably smaller than for carbon dioxide. Two

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[1] J. Phys. Chem. 29, 113 (1925)

[2] The surface of the sorbent was very nearly 3 square metres.

TABLE I

Nitrous oxide.

Time-sorption measurements

24. July 1922
(2nd Exp.)

Time (mins)	p (mm. of Hg)	s (cc. @ N.T.P)
25	640.67	1.625
35	640.52	1.656
50	640.29	1.689
65	639.98	1.722
85	639.67	1.752
131	639.37	1.809
195	638.80	1.855
1225	636.81	2.085
1510	636.63	2.119
2655	635.97	2.200

19. July 1922
(1st Exp)

Time (mins)	p (mm. of Hg)	s (cc. @ N.T.P)
1.5	382.40	1.117
4	381.65	1.196
7	381.18	1.251
11	380.85	1.287
14	380.59	1.314
17	380.40	1.332
23	380.06	1.371
28	380.04	1.372
31	379.89	1.389
35	379.80	1.401
40	379.73	1.411
50	379.61	1.424
65	379.40	1.450
85	379.17	1.479
113	378.90	1.506
148	378.72	1.525
268	377.88	1.587
1290	376.17	1.760
1655	376.29	1.790
2742	375.46	1.847

19. Oct. 1922
(5th Exp.)

Time (mins)	p (mm. of Hg)	s (cc. @ N.T.P)
1.96	386.74	1.154
7	385.77	1.254
10	385.52	1.281
13	385.24	1.313
16	385.14	1.324
19	384.95	1.346
24	384.80	1.362
29	384.62	1.378
34	384.54	1.389
39	384.39	1.406
49	384.13	1.433
59	384.02	1.446
79	383.73	1.472
119	383.32	1.514
1470	380.63	1.792
2819	379.87	1.872

11. Oct. 1922
(4th Exp)

Time (mins)	p (mm. of Hg)	s (cc. @ N.T.P)
0.86	180.73	0.723
2.65	179.90	0.800
4.7	179.53	0.832
8	179.06	0.877
11	178.90	0.891
16	178.60	0.920
21	178.40	0.938
31	178.17	0.959
41	177.94	0.980
60	177.62	1.010
80	177.41	1.027
140	176.96	1.069
173	176.78	1.085
1400	174.79	1.262
2920	174.09	1.336
4225	173.75	1.370
7150	173.23	1.419

TABLE I (Continued)

Time (mins)	p (mm. of Hg)	s (cc. @ N.T.P)	Time (mins)	p (mm. of Hg)	s (cc. @ N.T.P)
	26. Sept. 1922 (3rd Exp.)			30th Oct. 1922 (6th Exp.)	
1.17	106.59	0.590	1.67	43.93	0.368
2.17	106.38	0.608	4.25	43.63	0.392
4.50	105.97	0.644	7.60	43.35	0.416
7.25	105.67	0.670	10.75	43.23	0.425
9.1	105.45	0.685	14	43.15	0.432
14.2	105.23	0.709	19	42.96	0.447
17.3	105.12	0.717	24	42.90	0.452
23	105.00	0.728	29	42.84	0.458
30	104.85	0.741	39	42.69	0.469
40	104.60	0.762	49	42.54	0.482
60	104.32	0.786	59	42.44	0.490
90	104.04	0.810	79	42.37	0.495
128	103.85	0.827	119	42.22	0.507
132	103.81	0.830	186	41.96	0.529
1325	101.98	0.987	264	41.76	0.544
2660	101.33	1.042	1400	40.86	0.617
			4205	40.21	0.671
			5640	40.04	0.685

experiments were performed at about ½-atmosphere pressure; namely, the first experiment of the series where the initial pressure was 382.4 mm., and the fifth experiment where the initial pressure was 386.7 mm. The excellent agreement between these two precludes the possibility of any serious fatigue effects having occurred in the interval. In the graph, a single log s, log t straight line is drawn to represent the course of sorption at an average pressure.

As in the case of carbon dioxide the slopes of the log s, log t lines vary with the pressure. A table of "experimental" reciprocal slopes is given below (Table II.) together with the "corrected" values deduced for sorption under constant pressure. These last were arrived at by applying the same methods of correction for falling pressure as were used and described under carbon dioxide[1]. For such "corrected" times and sorption values the symbols t_c and s_c are used.

The Pressure-Sorption-Time Relationships for Nitrous Oxide

The pressure-sorption relations for nitrous oxide are represented in Fig. 2. The heavily-drawn curves are derived from the experimental sorption- and pressure-values for t = 1 min. and t = 3000 mins., respectively (black circles). The corrected sorption values for t_c = 10, 100, 1000 and 3000 mins. are de-

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[1] J. Phys. Chem. 29, 113 (1925)

TABLE II

Values of $m = \dfrac{\delta \log t}{\delta \log s}$

Initial Pressure (mm. of Hg)	$m = \frac{\delta \log s}{\delta \log t}$ from experimental log s, log t graphs	$m = \left(\frac{\delta \log t_c}{\delta \log s_c}\right)_P$ from corrected log s, log t graphs.
641.9	15.35	15.35
384.6	15.1	15.1
180.7	13.7	13.4
106.6	13.4	12.95
43.9	13.05	12.4

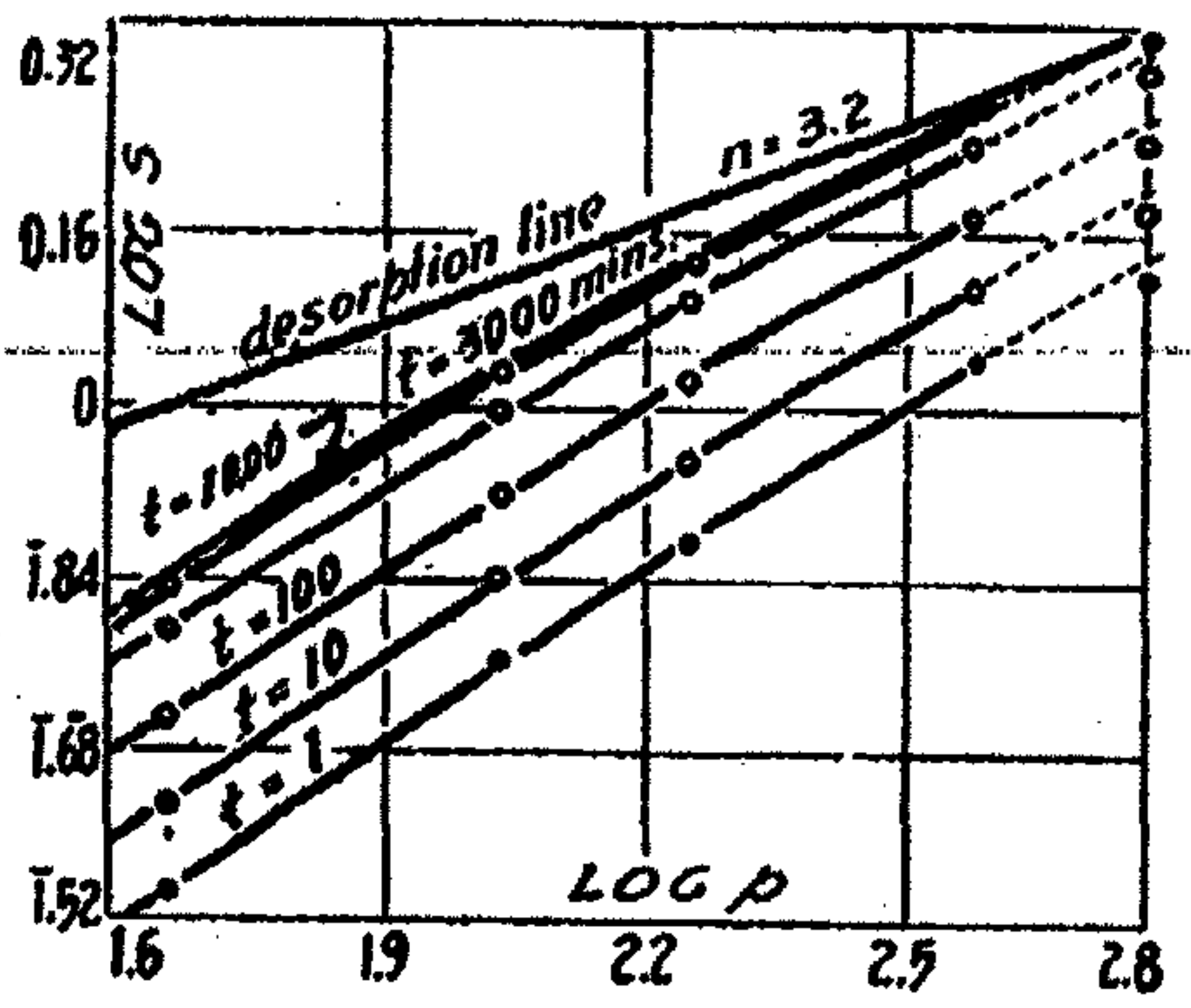

FIG. 2

noted by white circles through which fine lines are drawn to indicate the course of the "corrected" log s_0, log p curves. For t = 1 min., corrected and experimental curves coincide, and the differences are very small even for t = 3000 mins.

It was realized when too late to repeat it that the experiment at 642 mm. had yielded results somewhat at variance with the others: thus, in Fig. 2, the highest-pressure points fall considerably below any reasonably-shaped curves drawn through the remainder. Since the neighbouring ½-atmosphere points are the results of two separate experiments in excellent agreement, it seems probable that a gross error of some 90 cmm. (such as would have resulted from misreading a millimetre division on the scale) was made in the measurement of the gas introduced, in this experiment. The value of the index *m* (15.35) also points to an error having been made, since it represents a disproportionately small increase on the ½-atmosphere value (15.1).

The remainder of the points in Fig. 2 lie very satisfactorily. Table III gives data derived from the log s_0, log p curves: in compiling it the pressure region beyond the well-substantiated ½-atmosphere points has been neglected. In column (1) are given selected ordinate values, and in columns (2) to (6)

TABLE III

Nitrous oxide. Data from corrected log s_c, log p curves.

(1) log s_c	(2)	(3)	(4) log p	(5)	(6)	(7)	(8)	(9) Δ log p (horizontal intercepts between pairs of curves)	(10)
	$t_c = 1$	$t_c = 10$	$t_c = 100$	$t_c = 1000$	$t_c = 3000$	$t_c = 10$ to $t_c = 1$	$t^0 = 100$ to $t_c = 10$	$t_c = 1000$ to $t_c = 100$	$t_c = 3000$ to $t_c = 1000$
0.26	——	——	——	2.625	2.553	——	——	——	0.072
0.16	——	——	2.547	2.390	2.320	——	——	0.157	0.070
0.06	2.620	2.475	2.325	2.173	2.098	0.145	0.150	0.152	0.075
$\bar{1}.96$	2.418	2.270	2.115	1.965	1.890	0.148	0.155	0.150	0.075
$\bar{1}.86$	2.225	2.077	1.922	1.770	1.700	0.148	0.155	0.152	0.070
$\bar{1}.76$	2.035	1.887	1.735	——	——	0.148	0.152	——	——
$\bar{1}.66$	1.850	1.702	——	——	——	0.148	——	——	——
$\bar{1}.56$	1.670	——	——	——	——	——	——	——	——
					Mean Δ log p	0.147	0.153	0.153	0.072
					whence $\left(\frac{\Delta \log t_c}{\Delta \log p}\right)_{s_c} =$	6.8	6.5	6.5	6.6

For over-all range from $t_c = 1$ to $t_c = 3000$,

$$\left(\frac{\Delta \log t_c}{\log p\Delta}\right)_{s_c} = \frac{3.477}{0.525} = 6.6$$

corresponding abscissa values, for log t_c = 0.0, 1.0, 2.0, 3.0 and 3.477 respectively, while columns (7) to (10) show the values of the horizontal intercepts between adjacent curves. These intercepts are sensibly constant in each vertical column, and, as in the case of carbon dioxide, are almost exactly proportional to the corresponding differences in log t_c. For the over-all range, the value of the constant $\left(\frac{\Delta \log t_c}{\Delta \log p}\right)_{s_c}$, which may be regarded as the quotient

$$\left(\frac{\delta \log s_c}{\delta \log p}\right)_t \Big/ \left(\frac{\delta \log s_c}{\delta \log t_c}\right)_p, \text{ is } 6.6.$$

As in the case of carbon dioxide, this relationship makes it possible to express log s (derived from the different sorption experiments) as a single-valued function of the complex variable $5.6 \log p_t + \log \int_0^t p.dt$. The continuous line obtained on plotting these variables shows only slight curvature over a large range of sorption values.

Desorption Experiment with Nitrous Oxide

Some of the results of this experiment (performed by reducing the pressure in successive stages, following protracted sorption at a higher pressure) have already been published[1]. It was found that if sufficient time[2] was allowed for desorption at each stage, the residual sorption values were related to the corresponding pressures by the Freundlich equation $s^n = k'p$, n having the value of 3.2.

Time-desorption measurements with nitrous oxide confirmed the conclusion previously arrived at[3] that sorption and desorption follow similar time equations. In Fig. 3 the logarithms of the quantities of gas disengaged are plotted against the logarithms of the times reckoned from the moment of each pressure reduction. Early readings were taken in only one or two instances but, where the observations were few, the slopes could be gauged from those of the neighbouring lines. The coefficient r of the equation $r \log \zeta = \log t +$ constant, (where ζ is the quantity of gas desorbed in time t) appears to decrease considerably in the later stages of desorption.

All the gases so far investigated have yielded s, p values obeying Freundlich's equation under the conditions of our desorption experiment. It still remains doubtful, however, whether this fact is indicative of a near approach to equilibrium conditions, or whether we are dealing with a fictitious regularity conditioned by the procedure adopted. While the rate of desorption was practically undetectable after 24 hours, it is noteworthy that at the end of the *first* desorption step the s value passed through a minimum and began to increase at a very small but measurable rate.

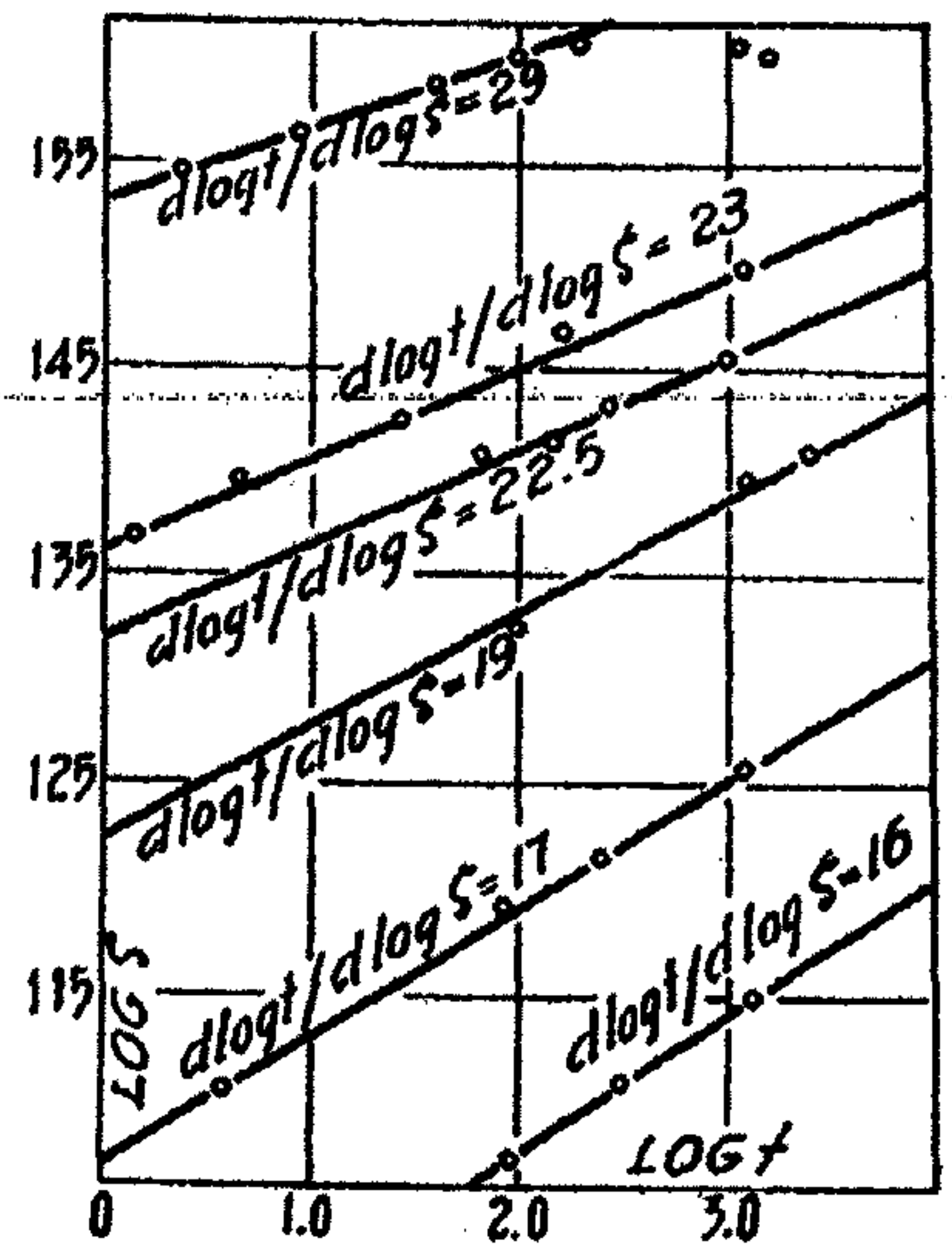

Fig. 3

With the hope of throwing some light on this question, the pressure, which at the end of the desorption experiment had been reduced to 9.86 mm. was suddenly raised to 38.7 mm. by the introduction of more gas, and the progress of the renewed sorption was followed over a period of 3 days. The results are shown in Table IV.

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[1] Proc. Roy. Soc. 105A, 487 (1924).

[2] The usual time interval allowed between successive pressure reductions was 24 hours, but on two occasions the system was allowed to stand over the week-end. This treatment had no apparent effect on the regularity of the results.

[3] J. Phys. Chem. 29, 113 (1925).

In Fig. 4 the values of log (sorption increment) are plotted against log t (time being measured from the moment of increasing the pressure). Not only are the early points seen to be closely linear, but the line drawn through them has a reciprocal slope of 13.7, in fair agreement with the value 13.05, found for the 43.9 mm. sorption experiment, starting with gas-free wool. In contrast, however, to the latter experiment, the line becomes practically parallel to the log t axis after one day's sorption. The fact that the sorption appears to be tending to a limit in the immediate neighbourhood of the value assessed on the basis of the desorption results, using the Freundlich equation as an interpolation formula, (0.938 cc.), suggests that the applicability of the equation is not a fortuitous concomitant of the conditions imposed.

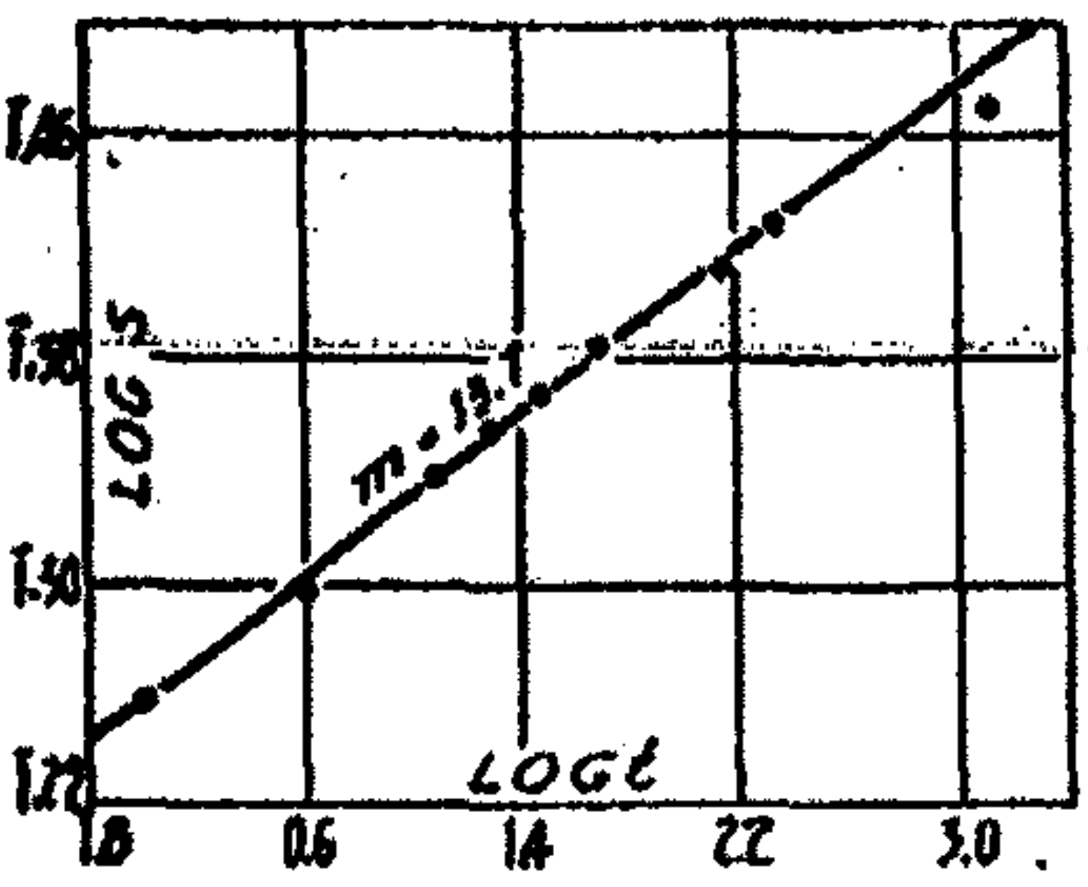

Fig. 4

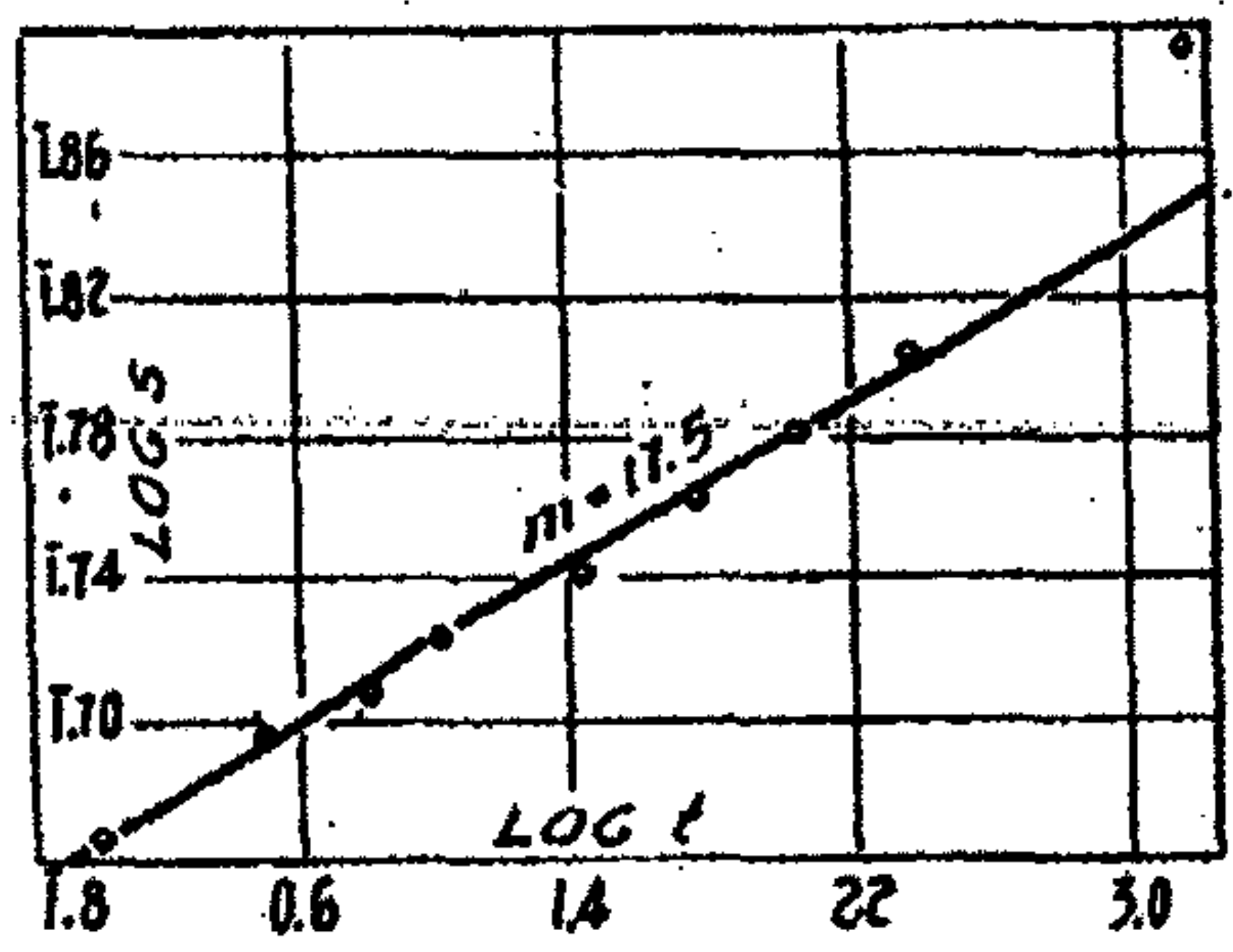

Fig. 5

TABLE IV

Time from moment of increase of pressure (mins)	p (mm. of Hg)	s (total) (cc. @ N. T. P)	s (increment) (cc. @ N. T. P)
0	9.87	0.627	—
1	38.72	0.808	0.181
4	38.50	0.825	0.198
9	38.27	0.844	0.217
12	38.26	0.845	0.218
15	38.21	0.849	0.222
19	38.17	0.853	0.226
24	38.13	0.855	0.228
30	38.07	0.860	0.233
48	37.96	0.869	0.242
81	37.82	0.881	0.254
142	37.77	0.885	0.258
217	37.64	0.892	0.265
1310	37.30	0.922	0.295
4370	37.11	0.924	0.297

(Freundlich equation interpolation value = 0.938 for p = 37.1)

The results of this experiment stand in contrast to one performed with carbon dioxide and discussed in our previous paper. In the latter the pressure was increased at a moment when sorption was still progressing at a measureable rate. Under these conditions the values of log (sorption increment) and log t yielded a graph initially very straight but afterwards becoming *convex* to the log t axis. This is shown in Fig. 5. The direction of the departure of the later points from the linear appears, therefore, to depend on whether the rate of sorption, ds/dt, was positive or negative at the moment of pressure increase. An analogous conclusion was reached in the case of desorption[1].

Experiments with Sulphur Dioxide

This gas was obtained from a syphon of liquid sulphur dioxide in which the chief impurity is air. After passage over phosphoric oxide the gas was solidified in a fractionating vessel cooled in liquid air. The accumulating permanent gas was removed at intervals by a mercury pump. The solidified gas was then sublimed into a second vessel, a further quantity of permanent gas being evolved during the process. Continued repetition of this treatment was required to remove the last traces of permanent gas which are very obstinately retained. The solid was then allowed to liquefy and further purified by fractional distillation. A middle fraction was introduced into an evacuated storage bulb. The melting-pressure of this was gas 13.2 mm.

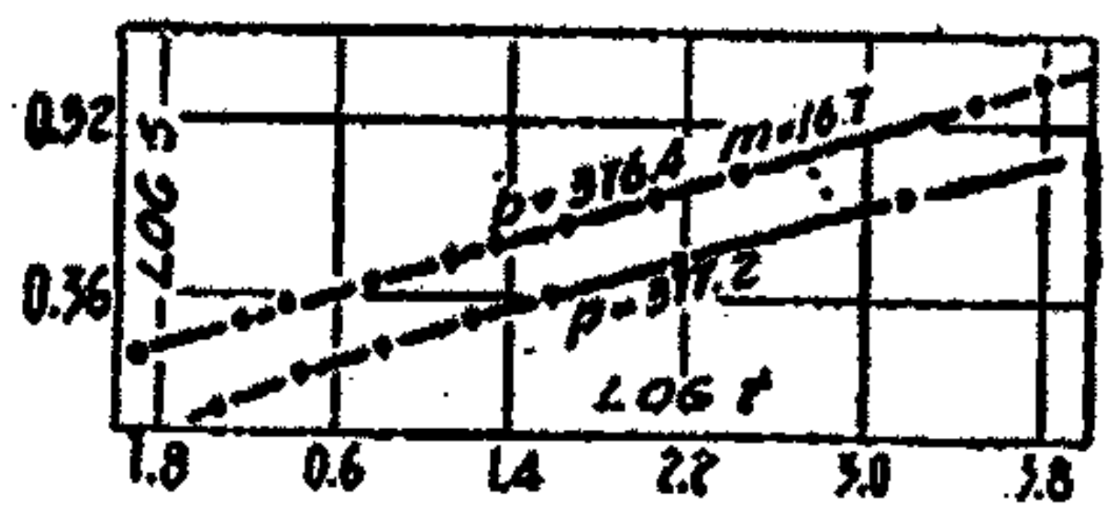

FIG. 6

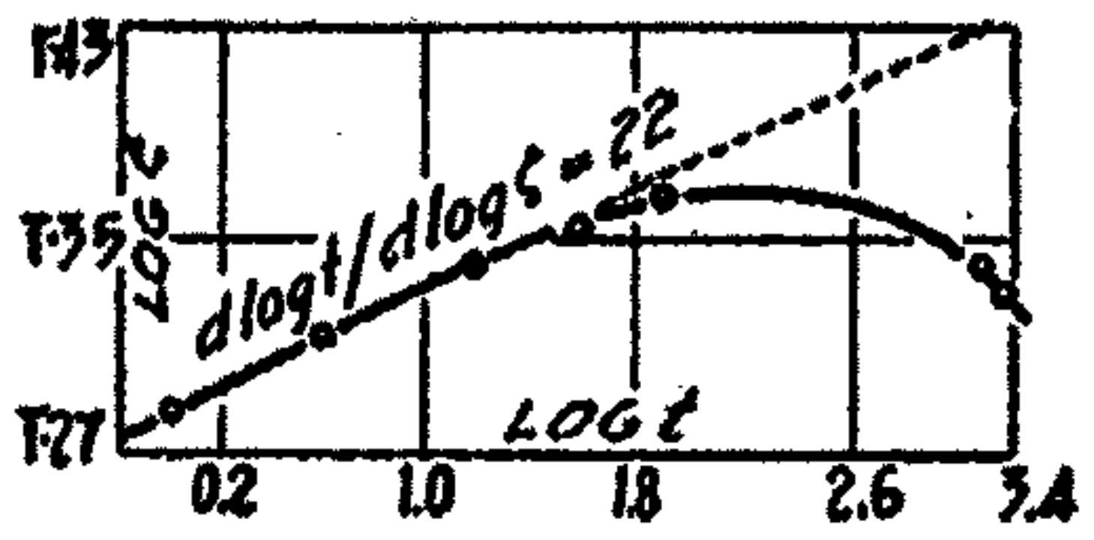

FIG. 7

The first experiment with sulphhr dioxide, performed at an initial pressure of 376 mm., gave results quite in keeping with those for other gases, the log s, log t graph being strictly linear over the whole time range from t = ½-minute to t = 4 days. This graph is represented by the upper line in Fig. 6, while the corresponding s, t values, together with the momentary pressures are given in Table V. (experiment 1). The reciprocal slope of the log s, log t graph is 16.7, a somewhat higher value than that found for the gases previously examined.

At the end of four days, the pressure was suddenly reduced by about one half, and very careful time-desorption observations were taken. The graph in Fig. 7, where log ζ (ζ = quantity of gas desorbed) is plotted against log t (t = time from moment of reducing pressure), illustrates clearly the passage of the sorption value through a minimum (over-night). The straight line joining the three early points has a reciprocal slope of 22: (compare values ranging from 29 to 16 in the case of other gases).

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[1] Proc. Roy. Soc. 105A, 487 (1924).

Further pressure reductions were subsequently made but no more time observations were taken. The final s, p values obtained for each step have already been published[1]. They show close agreement with the Freundlich equation, the value of the index n being 10.7.

A repetition of the ½-atmosphere sorption experiment brought to light a conspicuous difference in the behaviour of sulphur dioxide from that of any gas previously tested. The results showed that the routine treatment adopted for out-gassing the glass wool (3 hours heating in vacuo at a temperature of 200 °C.) had, for the first time, proved inadequate. Not only did the points obtained fail to yield a linear graph, but the sorption values differed so widely from those of the first experiment that the conclusion that the sorbent still contained a residue of gas was unavoidable. Continued heating at the same temperature, though effecting the removal of some small further quantities of gas (circa 150 cmm), led to no material improvement in the results. We were reluctant at this stage of the work to increase the out-gassing temperature for fear of altering the condition of the sorbent.

TABLE V

Sulphur Dioxide

Time-sorption measurements.

Exp. 1.			Exp. 2.		
Time (mins)	p (mm. of Hg)	s (cc. @ N. T. P)	Time (mins)	p (mm. of Hg)	s (cc. @ N. T. P)
0.50	376.35	2.032	1.10	377.21	1.830
1.37	374.99	2.177	1.67	376.60	1.898
2.27	374.21	2.264	2.67	375.96	1.968
3.55	373.70	2.319	4.09	375.39	2.032
5.47	373.28	2.370	6.17	374.92	2.083
8.95	372.63	2.443	11	374.21	2.164
12.5	372.17	2.491	16	373.78	2.211
16	371.89	2.526	26	373.17	2.279
21	371.50	2.565	36	372.78	2.317
26	371.21	2.595	76	371.75	2.423
31	370.94	2.627	136	371.00	2.498
41	370.53	2.667	182	370.55	2.539
56	370.00	2.722	1450	367.88	2.850
76	369.54	2.766			
106	368.94	2.827			
167	368.29	2.904			
255	367.62	2.977			
2884	363.06	3.456			
5795	361.76	3.605			

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[1] Proc. Roy. Soc. 105A, 487 (1924).

Attempt to remove Sulphur Dioxide

As a less objectionable alternative we endeavoured to attain the same result by introducing ammonia to the glass wool and subsequently out-gassing at the usual temperature. Advantage was taken of this opportunity to examine the rate of sorption of ammonia by a glass surface known to be contaminated with another gas. Ammonia was introduced to a pressure of about half an atmosphere and the observations recorded show well marked points of difference from our earlier experiments with gas-free sorbent 7. In the first place, the sorption values for similar times and pressures were noticeably smaller: in the second place, the log s, log t graph, while strictly linear for the first few hours, became thereafter *convex* to the log t axis, indicating that in these later stages the rate of sorption was greater than that required by the normal equation, $s^m = kt$. The value of *m* derived from the linear portion of the graph was about 13, as compared with 12 in the earlier experiments. The conclusion that the presence of an impurity in the sorbent may depress the rate of sorption in the earlier stages while accentuating it in the later, appears to be well established[1]. When the impurity is the same as the gas being sorbed the behaviour is very different. This is indicated by the lower graph in Fig. 6, which represents our second sorption experiment with sulphur dioxide, the corresponding s, t values being given in Table V, (Experiment 2.). Further sorption experiments with ammonia, both at ½-atmosphere and at lower pressures, shewed the same characteristics, indicating that the attempt to wash out sulphur dioxide had been unsuccessful.

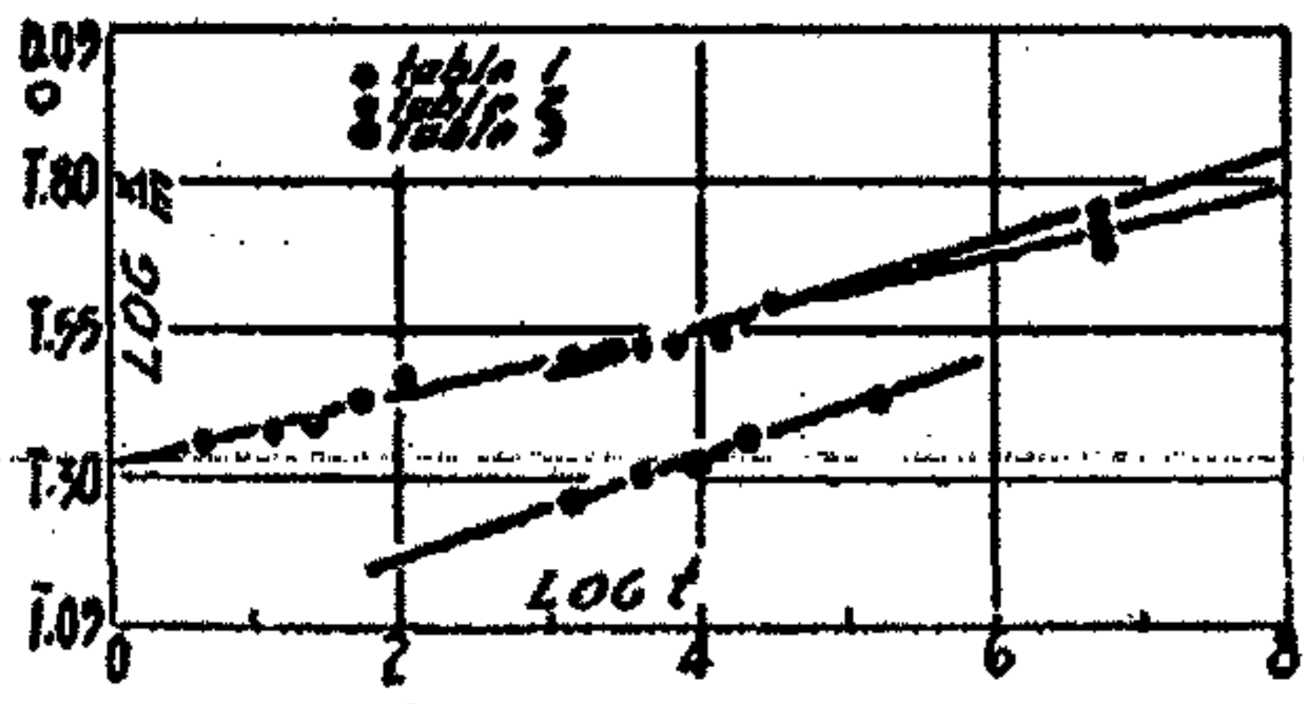

FIG. 8

As was remarked in our first paper, the relationship between log s and log t has been found to be a linear one within the limits of experimental error over a wide range of sorption data. Thus McBain and Davis[2] examined the sorption of iodine from various solvents by very finely powdered charcoal. The results are shown in Fig. 8, plotting as absicssae value of log t, and as ordinates values of log (x/m), where x/m is the amount of iodine sorbed per gram of charcoal. The three graphs reproduced refer to data from Tables I, II and III respectively, in the paper quoted. The results are tabulated below:—

TABLE VI

Exp.	Sorbent	Solvent	range of time covered by experiment	$d \log t / d \log\left(\frac{x}{m}\right)$
1.	animal charcoal	toluene	5 mins to 11 years	17.5
2.	" "	benzene	3 days to 11 years	13.4
3.	" "	benzene	1 day to 120 days	12.0

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[1] Trans. Am. Electrochem. Soc. **36**, 153 (1919).

[2] Trans. Faraday Soc. **14**, 202 (1919).

It is noteworthy that the value of the coefficient (which appears to vary with the solvent) is of the same order as yielded by our various experiments with glass.

Mention may also be made of F. Bergter's experiments on the sorption of air by cocoa-nut charcoal[1], as some of these accord very closely with the linear formula. Thus, an experiment carried out at 735.6 mm. yields the graph depicted in Fig. 9. With the exception of the first observation ($t = 0.75$ mins.), all the points lie closely about a straight line having a reciprocal slope of 18.5.

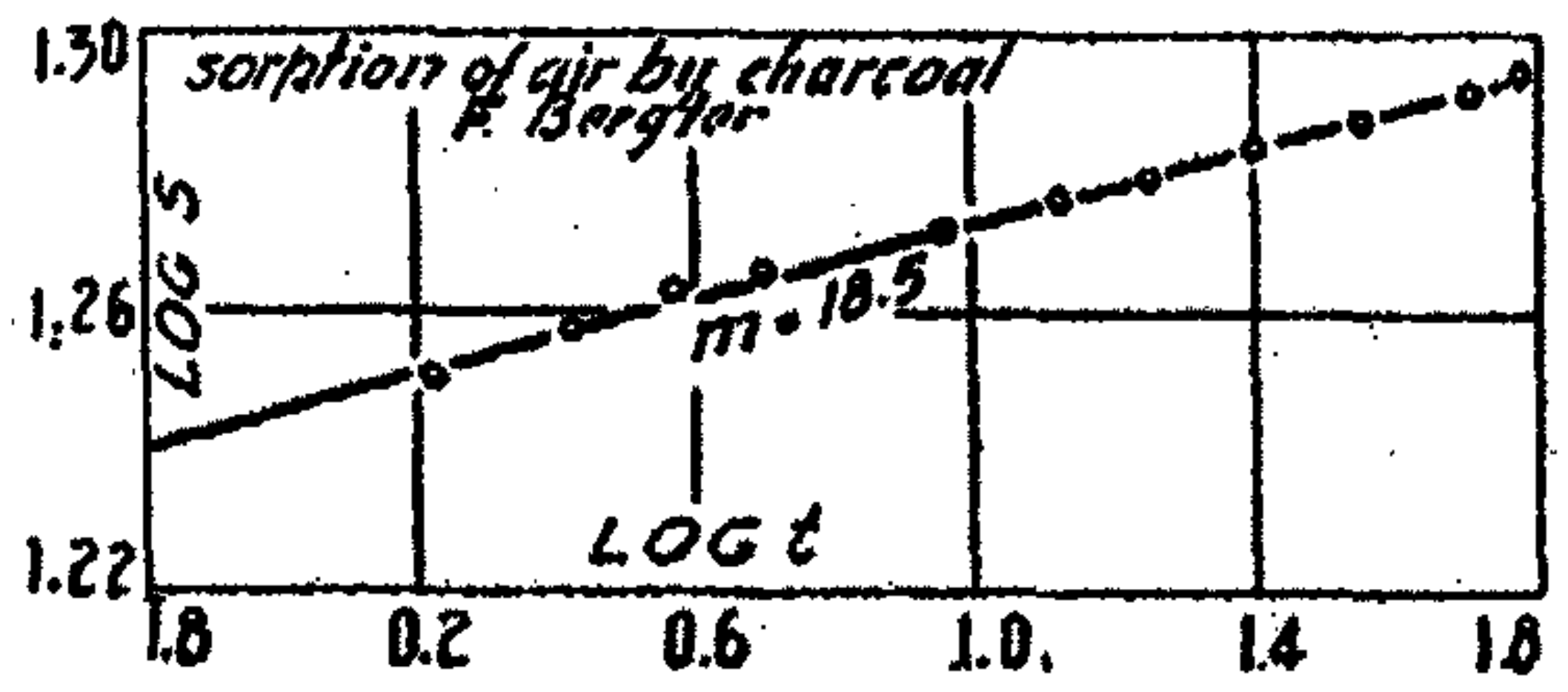

Fig. 9

Summary

The sorption of nitrous oxide by glass reproduces the essential characteristics observed with carbon dioxide. Considering any series of constant-pressure experiments, log (sorption) appears to be a single-valued function of log ($p^{0.6}t$), the relationship approximating more closely to the linear than in the case of carbon dioxide.

Sulphur dioxide also follows the linear log s, log t law, but as we did not succeed in out-gassing the sorbent we were unable to examine the pressure exponent.

We wish to acknowledge here the receipt of grants from the Royal Society Committee and from the Brunner Mond Research Fund, which partly defrayed the expenses of this investigation.

Chemistry Department,
University of Manchester.

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[1] Ann. Physik, (4) 37, 498 (1912).

TECHNIC FOR MEASURING THE HYDROGEN ION CONCENTRATION OF DISTILLED WATER AND UNBUFFERED SOLUTIONS NOT IN EQUILIBRIUM WITH CARBON DIOXIDE OF THE AIR

BY LOUIS E. DAWSON

At times, in various hydrogen ion investigations, the investigator obtains inconsistent results with variations which are, at the time, unexplainable. When, however, the influence of contact with air on the materials studied is considered, these inconsistencies are often found to be caused by a constituent of the air. This condition has most often occurred in the purification or handling of various pure substances. It is hoped that this paper will demonstrate the large effect of a small amount of carbon dioxide on purified distilled water and unbuffered solutions which are not in equilibrium with the air.

TABLE I

Date	Investigator	Method	$K_W \times 10^{14}$	$C_H \times 10^7$	pH
1893	S. Arrhenius[1]	Hydrolysis of sodium acetate	1.21	1.1	6.96
1893	J. J. Wijs[2]	Hydrolysis of methyl acetate	1.44	1.2	6.92
1907	C. W. Kanolt[3]	Hydrolysis of NH_4 salts of diketotetrahydrathiozole	.82	.906	7.04
1907	H. Lunden[4]	Hydrolysis of trimethylpyridin $(\alpha\alpha\gamma)$p-nitrophenolate	1.05	1.025	6.99
1909	A. Heydweiller[5]	Recalculation of conductivity data of pure water[6]	1.04	1.02	6.99
1909	C. S. Hudson[7]	Mutarotation of glucose by acids and alkalis	1.0	1.0	7.00
1909	R. Lorenz & A. Böhi[8]	Acid-alkali chain	1.21	1.1	6.96
1914	L. Michaelis[9]	" " "	1.27	1.127	6.95
1917	G. N. Lewis, T. B. Brighton, and R. L. Sebastian[10].	" " "	1.012	1.006	7.00

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[1] Z. physik. Chem. 1, 631 (1887); 11, 823 (1893).

[2] Z. physik., Chem. 11, 492; 12, 253, 514 (1893); 14, 189 (1894).

[3] J. Am. Chem. Soc. 29, 1414 (1907).

[4] J. Chim. phys. 5, 589 (1907).

[5] Ann. Physik, (4) 28, 511, (1909).

[6] F. Kohlrausch and A. Heydweiller: Wied. Ann. 53, 234 (1894); Z. physik. Chem. 14, 330 (1894).

[7] J. Am. Chem. Soc. 31, 1136-8; Bur. Chem. Circular 45 (1909).

[8] Z. physik. Chem. 66, 748 (1909)

[9] "Die Wasserstoffionenkonzentration" (1914).

[10] J. Am. Chem. Soc. 39, 2260 (1917).

TABLE II

	Numbers referring to original Investigator in Table I.
W. M. Clark[1]	2, 3, 5, 6, 8, 9, 10.
Landolt-Börnstein, 4th Ed.[2]	(1?), (2), 3, 4, 5, 8, 10.
Landolt-Börnstein, 5th ed.[3]	(1?), 3, 4, 5, 8, 10.
W. McC. Lewis[4]	1, 2, 3, 5, 6, 7.
L. Michaelis[5]	1, 2, 4, 6, 9, 10.

The values for the dissociation constant of water (K_w) at 25° given in Table I were compiled from the most reliable figures given by the investigators listed in Table II. The average of the values recognized as reliable by Landolt-Börnstein, Fifth Edition, is $K_w = 1.026 \times 10^{-14}$, from which $C_H = 1.013 \times 10^{-7}$ and $pH = 6.99$. The average of all values in Table I is $K_w = 1.117 \times 10^{-14}$, from which $C_H = 1.057 \times 10^{-7}$ and $pH = 6.98$.

From the values obtained by L. Michaelis[6] for the dissociation constant of water at different temperatures, it may be concluded that for the interval 16–26°, the temperature coefficient of K_w is -0.340 (equivalent to $pH = -0.017$), which agrees well with the theoretical value -0.0349 (equivalent to $pH = 0.0175$). From the foregoing data it may be concluded that pure water should have a pH of 7.0 at practically 25°C.

Since the purest distilled water of the laboratory is a saturated solution of carbon dioxide under the existing atmospheric conditions[7], and since carbon dioxide is the only constituent of the normal air which confers conductivity on water[8], carbon dioxide is the substance to be eliminated from the laboratory distilled water to give neutral water, and also to be kept from again contaminating the neutral water being stored, tested, and used in making up unbuffered solutions. It is assumed here that the distilled water regularly obtainable in any chemical laboratory is free from such other substances as ammonia, chlorine, and fatty acids. The presence of any one of these in the distilled water is due to an unsatisfactory water supply or to an improper method of treatment and distillation.[9]

Some claimed that it was impossible to prepare water having a value of pH 7.0. H. A. Fales and J. M. Nelson[10] found that the distilled water in their

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[1] "Determination of Hydrogen Ions". Second Edition, 27-29 (1922).

[2] "Physikalisch-Chemische Tabellen". Fourth Edition, 1187 (1912).

[3] "Physikalisch-Chemische Tabellen". Fifth Edition, 1164 (1923).

[4] "A System of Physical Chemistry". Second Edition, 1, 269-274 (1918).

[5] "Die Wasserstoffionenkonzentration". Second Edition, 21-25 (1922).

[6] "Die Wasserstoffionenkonzentration", (1922). Data partly reproduced in W. M. Clark "Determination of Hydrogen Ions", 29, (1922).

[7] J. Kendall: J. Am. Chem. Soc., 38, 1480-97 (1916).

[8] J. Walker and W. Cormack: J. Chem. Soc. 77, 5-21 (1900); confirmed by J. Kendall: loc. cit.

[9] See W. M. Booth: Trans. Am. Inst. Chem. Eng., 10, 247-330 (1917), for a survey of methods of treatment and distillation and of impurities which may be found in poor distilled water.

[10] J. Am. Chem. Soc., 37, 2769-86 (1915).

laboratory had a fairly constant pH of about 6.2 and when this was redistilled in three different ways the pH was 5.8 in each case. They used p-nitrophenol as an indicator and mixtures of citrate solution and 0.1 molar NaOH as the comparison standards. According to J. Kendall[1], a saturated solution of carbonic acid under atmospheric conditions at 25° has a calculated hydrogen ion concentration of 2.05×10^{-6}, or pH = 5.7. This value agrees very closely with the value observed by Fales and Nelson of pH = 5.8.

H. T. Beans and E. T. Oakes[2] attempted to determine the hydrogen ion concentration in pure water by a method for measuring the electromotive force of concentration cells of high internal resistance. Their earlier readings made under less carefully controlled conditions of distillation of the water gave pH values from 4.44 to 6.24 and they reported as their most accurate value a pH of 7.91. W. M. Clark[3] stated that it is almost impossible to make an accurate electrometric determination of the pH of solutions unless buffered to some extent. This with the results reported by Beans and Oakes, would exclude the electrometric method from use for our purpose. It may, of course, be used to standardize buffer solutions, with which the colorimetric standards are compared.

Others have found it possible to prepare water which is neutral. L. Tribondeau[4] gave a method for redistilling water to obtain neutral water for microscopic staining; he depended mainly upon the coloration of blood to which the water is added as an index of its neutrality. S. P. L. Sörensen[5] proposed a method of preparing and preserving neutral water. The distilled water was heated in a tinned copper flask to free it from CO_2 and the water was siphoned into flasks previously filled with CO_2-free air. He transferred the water from one vessel to another by means of two glass tubes through a rubber stopper, one long tube extending to the bottom of the flask through which the water was siphoned without contact with outside air containing CO_2. According to W. Olszewski[6], the small tube should be connected to a soda-lime tube. W. M. Booth[7] stated that at least one-third of the water must be evaporated to completely remove the CO_2. W. Olszewski[8] gave evidence that he had neutral water in that he tested it with alcoholic bromthymol blue solution, using 100cc. of water samples.

As may be seen later, probably the reason that Olszewski could get pH = 7 tests was because of the large sample he used, which, in the interval of time for the test would not have become sufficiently contaminated with CO_2 to cause noticeable error.

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[1] J. Am. Chem. Soc., **38**, 2460-6 (1916).

[2] J. Am. Chem. Soc., **42**, 2116-31 (1920).

[3] "Determination of Hydrogen Ions", 44 (1922).

[4] Compt. rend. Soc. Biol., **80**, 388-9, (1917).

[5] Biochem. Zeit. **21**, 131-304, (1909). (See pages 167-8).

[6] Pharm. Zentralhalle, **65**, 129-30 (1924).

[7] Trans. Am. Inst. Chem. Eng. **10**, 247-330 (1917)

[8] loc. cit.

J. R. Williams and M. Swett[1] have made hydrogen ion concentration studies on distilled water. Judging from their results, they succeeded in obtaining water of pH = 6.9, but some inconsistencies in their values would indicate that they had not completely eliminated errors in their method or technic of measuring the pH of their samples under storage. For example, out of six storage experiments four showed one abnormal value, an increase in pH, when the other figures in the experiments were decreasing with the time of standing. They concluded that the practical preparation of distilled water at the theoretical pH, 7.0, is difficult, and to store or keep it for any length of time by ordinary means is quite impossible.

As a result of an investigation of this problem, the author has concluded that the difficulty of obtaining neutral distilled water, and preserving it without change, is not so much in the method of preparing it as in the technic of determining the pH of the water.

Experimental

The container in which the neutral water is to be prepared, stored, tested, or otherwise used, may be a source of contamination if care is not taken to see that it is always perfectly clean and made of material which is not dissolved. The nature of the material is especially important if the water is to be in contact with it any length of time or is to be heated in contact with it. Pyrex glassware has been used wherever possible and has been cleaned in the usual manner, then thoroughly rinsed several times with distilled water and allowed to dry before using.

Preparation of Neutral Water

The preparation of neutral water does not occupy much of the worker's time and requires no special apparatus or arrangement of apparatus.

More than twice the quantity of distilled water desired was boiled in a pyrex flask[2] until less than two-thirds remained. The boiled water was transferred while still hot to smaller pyrex flasks. The flasks were filled to the brim and covered with an inverted pyrex beaker a little larger in diameter than the mouth of the flask. They were then placed under a stream of cold water and brought to the room temperature.

Method of pH Measurement

With the foregoing technic for preparing and handling the water and the following technic for determining its pH value, the author obtained repeatedly pH 7.0 with both indicators used.

Hatfield's[3] modification of the Gillespie colorimetric method of determining pH was used. The author measured by pipettes rather than by counting the drops in making up his comparison standards and in adding his indicators,

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[1] J. Am. Med. Assoc. 78, 1024-6 (1922); Proc. Soc. Exp. Biol. Med., 19, 266-9 (1922).

[2] For long boiling, a tinned copper flask, as used by S. P. L. Sörensen (Biochem. Z., 21, 131-304 (1909) (see pages 167-8) might be preferable.

[3] W. D. Hatfield: J. Am. Chem. Soc., 45, 940-3 (1923).

finding that this procedure gave more consistent checks. The indicators bromthymol blue and bromcresol purple were used. The standards were compared with buffer solutions, which were in turn checked electrometrically. With distilled water, purified from CO_2 as described above, the author obtained values from pH 6.4 to pH 6.6 when making pH tests in the regular way, and afterwards with water from the same flask obtained $pH = 7.0$ with the technic described below. When the test tube was not previously rinsed out with distilled water and dried, values as high as 7.4 were obtained. This was probably due to the presence of salts from the tap water which had been used to wash the test tubes.

Technic

The water or solution was contained in a completely filled vessel or in a vessel so arranged that the liquid was covered with CO_2-free air. A sample was obtained by withdrawing it into a 5 cc. pipette and transferring to a clean test tube of the same diameter as that of the tubes containing colorimetric standards. If through lack of dry test tubes it is desired to use a test tube just rinsed out and not dried, it should finally be completely filled with *neutral* water and this poured off immediately before introducing the pipette full of sample. In transferring the sample, the tip of the pipette was placed at the bottom of the test tube and held so that the stream of sample did not pass through air. The required quantity of indicator was added and the test tube agitated without mixing with the air. The tube was then compared with the standards.

Unless the foregoing precautions to minimize the amount and duration of contact with atmospheric air are taken, it will be impossible to get readings of $pH = 7$ with the small sample. The following strikingly demonstrates the effect of such contact with air. A sample of neutral water, with indicator which showed color indicating $pH = 7.0$, was shaken with the air in the test tube (equivalent to twice the volume of solution) and when compared with the standards read $pH = 6.5$.

Storing Neutral Water

The author believes that the experiments of Williams and Sweet[1], aside from the inconsistent results pointed out above, if properly carried out would have shown more nearly the same values from time to time on the same sample. The second probable source of error in their experiments to show an increase in acidity in samples on standing may be due to the manner of removing samples from the flask at the different periods of time, allowing the entrance of more air containing CO_2.

No study was made on the keeping of neutral water. However, the following procedure may be found more convenient and more reliable than any method of storing.

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[1] J. Am. Med. Assn., **78**, 1024-6 (1922); Proc. Soc. Exp. Biol. Med., **19**, 266-8 (1922).

If neutral water is needed during the day, distilled water in a large vessel may be started to boiling and over one-third of it evaporated. Then the vessel is loosely covered to minimize further evaporation and kept over a small flame. Whenever any is needed the desired quantity is poured into the smaller flask for cooling as directed.

A more convenient but less reliable arrangement may be the well known method of bubbling CO_2-free air through distilled water. This method requires no attention other than occasional renewal of soda-lime, used for removal of CO_2 from the air, and of water to replace that removed for use. It may be allowed to go day and night, thus providing a supply of neutral water for use at any moment. This method is less reliable because of the uncertainty as to the amount of air required to remove all the CO_2 from a certain volume of water and because of variations from time to time in the efficiency of the soda-lime for removing the CO_2 from the air. With this method, the water should be tested for neutrality every time it is used. With the boiling method, this may be unnecessary, provided the operator is sure that at least one-third of the volume of water has been evaporated.

The technic for preparing, handling, and testing neutral distilled water given in this paper may be used for preparing, handling and testing neutral unbuffered solutions. Also the technic for handling and testing neutral distilled water may be used for unbuffered solutions not in equilibrium with the CO_2 of the air. For example, refined sugar solutions may be made up by weighing the desired quantity of sugar into a flask of suitable size and the flask filled up almost to the brim with hot, freshly boiled water and cooled in the manner described above. This is the procedure used by Paine, Badollet and Keane[1] of this laboratory in a study of the pH values of different grades of granulated sugar.

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[1] Ind. Eng. Chem., **16**, 1252-8 (1924).

"THE BEHAVIOR OF SILVER IODIDE IN THE PHOTO-VOLTAIC CELL." A CRITICISM[1]

BY T. SLATER PRICE

In a paper on the subject named in the title, Garrison[2] describes a number of important experiments and gives a theoretical discussion of the same. In view of the fact that he states (p. 341) that he is proceeding to a quantitative investigation of the influence of optical and chemical sensitisers such as are used with the photographic plate, the following considerations may be of interest.

In the first series of experiments given by Garrison the potential of a polished silver electrode against a tenth-normal solution of potassium iodide, saturated with silver iodide, was measured both in the light and in the dark. Successive thin coatings of silver iodide were then put on the electrode by electrochemical means and the dark and light potentials measured, with the results given in the following table, where the first column gives the initial dark potential of the electrode, the second column the negative photo-effect, the third column the succeeding positive photo-effect and the last column the dark potential after exposure. The first result is for a pure silver electrode, the following ones being for successive coatings of silver iodide.

TABLE I

	$\pi_{Ag\text{-}cal.}$	$d\pi(-)$	$d\pi(+)$	$\pi'_{Ag\text{-}cal.}$
(1)	−0.4327	none	trace	−0.4327
(2)	−0.4315	none	+.0015	−0.4320
(3)	−0.4296	none	+.0031	−0.4300
(4)	−0.4275	trace	+.0031	−0.4282
(5)	−0.4273	−0.0005	+.0032	−0.4280
(6)	−0.4270	−0.0012	+.0030	−0.4280

Garrison gives an explanation of these results, but criticism is made somewhat difficult by the fact that no statements are made, or figures given from which an idea of the thickness of any of the coatings can be formed. However, he points out later that the negative photo-effects may be made larger and less transient by decreasing the concentration of the potassium iodide in the solution; further, that the photo-potential may be made either positive or negative by varying the ratio of the silver to the iodide ions in the saturated silver solution. The results of experiments are then given in which the concentrations of ions in the electrolyte were altered by adding either silver nitrate or potassium iodide to an electrolyte of dilute sodium sulphate solution saturated with silver iodide. The concentration of the sodium sulphate is not given nor

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[1] Communication No. 43 from the British Photographic Research Association Laboratories.

[2] J. Phys. Chem. 28, 333 (1924).

the reason for its use. There must also have been free alkali halide present, in order to account for the concentration of the ions given.

In the first three series of experiments given in Table II the same electrode was used and was coated "with a moderately thick layer of iodide corresponding approximately to electrode No. 3 in Table I." In the table the first column contains the dark potential with respect to the normal calomel electrode, the second and third the concentrations of the silver and iodide ions respectively and the fourth the alteration in potential of the electrode on exposure.

TABLE II

	$\pi_{Ag\text{-}cal.}$	[Ag˙]	[I′]	dπ
(I)	−0.2705	0.757 × 10^{-12}	1.42 × 10^{-4}	−0.0030
	−0.2400	2.42 " "	.412 " "	−0.0085
	−0.2200	5.24 " "	.190 " "	−0.0140
	−0.2120	7.07 " "	.141 " "	−0.0160
	−0.2050	10.7 " "	0.093 " "	−0.0262
(II)	−0.2330	3.16 × 10^{-12}	0.316 × 10^{-4}	−0.0125
	−0.3200	0.112 " "	8.91 " "	+0.0023
	−0.3320	0.0707 " "	14.1 " "	+0.0032
(III)	−0.2332	3.16 × 10^{-12}	0.316 × 10^{-4}	−0.0036
	−0.1771	27.1 " "	0.0368 " "	−0.0124
	−0.1560	61.0 " "	0.0164 " "	−0.0120

In the following experiments thicker coatings were used, that in (V) corresponding with electrode 6 in Table I.

(IV)	−0.2201	5.24 × 10^{-12}	0.190 × 10^{-4}	−0.0195
	−0.1189	17.4 " "	0.0575 " "	−0.0261
(V)	−0.4270	1.86 × 10^{-14}	0.00547*	−0.001 to + 0.003
	−0.3455	4.22 " "	0.0023	−0.0260

* The paper gives 0.0547.

In commenting on these results Garrison sometimes assumes that the electrode is functioning as a silver electrode and at other times as an iodine electrode. From the dark potentials and the concentrations of silver ion given, it is possible to decide whether the electrode is functioning as a silver electrode or not, by making use of the relation:

$$\pi = \pi_0 + RT/F \ln \frac{[Ag^{\cdot}]}{[Ag]} \qquad (1)$$

From any two values of π and the corresponding two values of [Ag˙] it is possible to calculate the value of RT/F, since, if the electrode is functioning as a silver one, π_0 and [Ag] will be constant. The following table shows the results obtained by such calculations:

TABLE III

Series	Dark Potentials	$[Ag^{\cdot}] \times 10^{12}$	RT/F
I	−.2705	0.757	0.0604
	−.2400	2.42	
	−.2705	0.757	0.0601
	−.2200	5.24	
	−.2705	0.757	0.0603
	−.2120	7.07	
	−.2705	0.757	[0.0569]
	−.2050	10.7	
	−.2400	2.42	0.0601
	−.2120	7.07	
II	−.3320	.0707	0.0600
	−.2330	3.16	
III	−.2332	3.16	0.0601
	−.1771	27.1	
	−.2332	3.16	0.0601
	−.1560	61.0	
IV	−.2201	5.24	0.0598
	−.1889	17.4	
I and IV	−.2705	0.757	0.0601
	−.2201	5.24	
V	−.4270	1.86×10^{-3}	[0.229]
	−.3455	4.22×10^{-2}	
I and V	−.2705	1.86×10^{-2}	[0.0972]
	−.2705	0.757	

With the exception of the last measurement in I, it will be seen that the same values for RT/F are obtained in the series I to IV. Moreover, the average value, 0.0601, agrees very well with the calculated value, 0.0596, for the temperature, 27°C, at which the measurements were made. It follows, therefore, that in I to IV the electrode is acting as a silver electrode. In series V, however, the iodide coating has obviously become so thick that the electrode no longer functions as a silver one; it may possibly be acting as an iodine electrode, but this cannot be tested by calculation, since the concentration of free iodine cannot be taken as constant in the different experiments.

Having shown that in Series I to IV the electrode functions as a silver one, and that RT/F is constant in these series, it follows that the concentration, [Ag], of the silver remains constant, and assuming this, that any explanation (neglecting any possible photo-electric one) must depend on alterations in the concentration of the silver ions, $[Ag^{\cdot}]$. Garrison assumes that the action of light is to make the silver iodide more soluble, that is, to increase its solubility product. Since in all cases the concentration of the I-ion is much greater than that of the Ag-ion (of the order of 10^{-4} against 10^{-12}), it follows that any increased solubility of the silver iodide will increase appreciably the concentration, $[Ag^{\cdot}]$, of the silver ion only. The photo-effect should therefore be an increase in the positive, that is, a decrease in the negative potential. Only in two cases in series I to IV, where the I-ion concentration is considerably increased relatively to that of the Ag-ion concentration, does this hold. In other cases there is an increased negative potential, which cannot be explained in this way if the electrode still functions as a silver electrode.

What, then, can be the explanation of the negative photo-potential? On exposure it is known that silver iodide is decomposed, so that iodine is set free. It is then possible that, under the action of light the electrode changes temporarily to an iodine electrode, the potential of which is regulated by the equilibrium $I_2 + 2\odot \rightleftarrows 2\,I'$, and given by the equation:

$$\pi = \pi_0 + \frac{RT}{2F} \ln \frac{[I_2]}{[I']^2} \qquad (2)$$

If this potential happens to be more negative than the silver potential the negative photo-potential would be explained. It should then follow, however, that with increasing I-ion concentration, whereby π becomes less positive, the negative photo-potential should be increased; a further negative increase would also be occasioned by the fact that with increasing I-ion concentration the concentration of the free iodine, $[I_2]$, is diminished in accordance with the equilibrium $I' + I_2 \rightleftarrows I_3'$. Actually, however, the facts are just the opposite to what the theory leads one to expect.

It follows from the above that some other explanation of the results in series I to IV must be found. Such an explanation may be as follows:—On exposure, the silver iodide is decomposed, with the formation of photo-iodide, that is, of colloidal silver, which will have, at all events just after it is formed, a higher solution pressure than massive silver. The concentration, [Ag], is therefore increased, that is, the positive potential of the silver electrode is diminished and therefore there is a negative photo-effect. As stated by Garrison, this decomposition on exposure is all the more marked the higher the concentration of Ag-ions and the lesser that of the I-ions and the negative photo-effect should therefore increase with increasing concentration of Ag-ions, as is the case. When, however, the concentration of I-ions is sufficiently great, the photo-decomposition, as proved by experiment by Garrison and others, is inhibited and then only the positive effect, due to increased solubility of the silver iodide can occur. It must further be assumed either that on keeping the electrode in the dark, the colloidal silver will coagulate to massive silver and the electrode return to its original condition, or what is more probable, that recombination of the silver and iodine takes place.

The increased solubility of a silver iodide when exposed to light has been mentioned in the preceding, and is also postulated by Garrison so that it is necessary to see if there is any basis for the assumption. It has been shown by Lüppo-Cramer[1] that silver iodide is disintegrated when illuminated. Since solubility is a question of the size of particles it is quite possible for the disintegrated iodide to be more soluble than the original substance. It may be

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[1] "Das latente Bild" (1911) and other publications.

mentioned that others have assumed that the silver halides become more soluble on exposure to light; for example, Baur[1] makes this assumption when discussing Sichling's paper[2] on photo-voltaic cells containing photo-chloride.

There remain to be discussed the two experiments in series V, in which the electrode no longer functions as a silver electrode. Unfortunately the results cannot be compared with those in series I to IV, since the concentrations of Ag-ions are much less, and those of the I-ions much greater. It has also to be borne in mind that the photo-potential is negative, whereas in the first experiments done by Garrison, (Table I), using electrodes with a similar thick coating of iodide, and an N/10 solution of potassium iodide

$$([I'] = 0.1 = 1000 \times 10^{-4})$$

the photo-potential was first negative and then positive.

If the electrode is acting as an iodine electrode (as assumed by Garrison with thick coatings) the effect of illumination would conceivably be as follows. The silver iodide would be decomposed, thus increasing the concentration of the free iodine and there should be a positive photo-effect. Even if it is assumed that the solubility of the silver iodide is increased, this cannot affect appreciably the concentration of the I-ions, since these are already present in appreciable concentration; there will thus be no negative effect due to this cause. The negative photo-effect cannot therefore be explained in this way, although Garrison seems to imagine that it can.

Before considering this question further, we may now return to a consideration of the results given in Table I. Since in the series I to III (Table II) the electrode has been proved to act as a silver electrode, it follows that this is also the case with electrodes 2 and 3 in Table I, since that used in I to III is stated to be approximately the same as No. 3. Also, in series IV, Table II, the electrode used has a thicker coating of silver iodide than that of the electrode used in series I to III, and yet it gives the same silver potential. It may therefore be reasonably assumed, although Garrison gives no figures with respect to the thickness of the coatings, that electrode 4 in Table I acts similarly to the electrode used in series IV, Table II, and therefore that the electrodes 2, 3 and 4 in Table I all act as silver electrodes. It follows that Garrison's explanation that the gradual decrease in the negative dark potential as the thickness of the coating is increased is due to the silver of the electrode becoming more completely covered with iodide at each coating, whereby the solution tension, [Ag], of the silver is diminished, cannot be correct.

Comparing the results for electrodes 2, 3 and 4 in Table I with those for series I to IV in Table II, it is noticeable that there are two very marked differences. In Table I the electrode, after exposure, does not regain the original dark potential, whereas in Table II it does, since the calculations of RT/F give agreeing results.[3] Also, for the same sets of electrodes, in Table I the photo-

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[1] Z. physik. Chem. 77, 58 (1911).

[2] Z. physik. Chem. 77, 1 (1911).

[3] The fifth experiment in series I is an exception; this may be due to an error or else to the electrode behaving as in Table I.

potential is positive, whereas in Table II it is negative. Since the only difference in the systems used lies in the relative concentrations of the Ag- and I-ions the observed differences in the photo-effect must be due to a change in the composition of the electrolyte. As far as the photo-potentials are concerned a possible explanation of the observed differences can be given. In Table I the concentration of the Ag-ion is much less than in Table II, the solution being tenth-normal with respect to potassium iodide. Photo-decomposition is inhibited by the excess of iodide and exposure brings about increased solubility of the iodide whereby the Ag-ion concentration is increased and hence a positive photo-potential produced. In Table II, however, in series I to IV, there is a much greater relative concentration of silver ion, to iodide-ion, except in the two cases where there is a positive photo-potential, and photo-decomposition is possible with the production of colloidal silver, which, as explained previously will give rise to a negative photo-potential.

In order to explain the fact that, after illumination, the electrode in Table I, did not return to its original dark potential, but became more negative, Garrison assumes that a partial destruction of the layer of iodide occurred during illumination, thus increasing the concentration of the silver. This cannot be correct, at all events for the electrodes 2, 3 and 4, since they are acting as silver electrodes, and therefore some other explanation must be found. Such an explanation may be based on the increased solubility on illumination and the consequent Ostwald ripening which then takes place in the dark, whereby larger crystals of silver iodide are formed than those deposited electrolytically in making the electrode; these larger crystals mean a lesser solubility, and therefore a diminished Ag-ion concentration and more negative potential. Sichling[1] has postulated a similar effect with silver chloride electrodes.

It has been shown that the electrode used in series V, Table II, no longer appeared to act as a silver electrode,[2] the coating of silver iodide apparently being sufficient to cover the silver. Electrode 6, Table I, is stated to have been very similar, and thus was probably the same for electrode 5, since the decrease in the negative dark potential for the last coating was only 0.3 millivolt, and therefore probably within the error of experiment. Exposure to light makes these two electrodes more negative at first, and then the positive effect follows. It has been pointed out that neither increased solubility due to the exposure, nor the assumption that the electrode acts as an iodine electrode, can explain the negative effect, so that some other reason must be found. If, in spite of the thick coating of iodide, the electrode acts as a silver electrode with a diminished solution tension of silver, it is possible that the increased negative charge may be due to disintegration of the silver iodide coating by the light (cf. Lüppo-Cramer's experiments), whereby more silver is exposed and its solution tension increased. It is not probable that the increased solution tension is due to formation of colloidal silver, since I-ion is present in large excess and prevents the photo-decomposition of the silver iodide.

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[1] Z. physik. Chem. 77, 1 (1911).

[2] If it still functioned as a silver electrode it would mean that the solution tension of the silver had been very much reduced from what it was in series I to IV.

The succeeding positive effect could be accounted for by an increase in the solubility of the silver iodide on exposure, the increased solubility being due to the disintegration by light. There would probably be a lag in this effect, and this would afford an explanation of why the negative effect is the one which is first evident with thickly coated electrodes. It is, however, difficult to make a satisfactory criticism since Garrison does not give sufficient experimental details. It would have been advantageous if he had given figures or curves showing the relation between the photo-potential and time, as other investigators have done. Some of the statements seem to be contradictory; for example, for electrodes 5 and 6 in Table I, where thick coatings are used and the concentration of Ag-ion is very small, a primary negative effect with a positive recoil is obtained, whilst on pp. 337-338 he writes: "In the case of electrodes with thick coatings in solutions where the silver ions were reduced negative effects could be obtained which were more permanent. There was practically no recoil in the positive direction in this case, the photo-chemical decomposition being retarded."

The data given for Table III in Garrison's paper are still more incomplete than in other cases, so that there is no advantage in discussing them, although they can be explained qualitatively in the light of the considerations given above, as also can the results obtained showing the relation between photo-effect and the intensity of illumination.

It seems to the writer that Garrison has been working with two different kinds of electrodes without differentiating between them in a way which could have been made more exact by further experiment. Undoubtedly most of the electrodes acted as reversible silver electrodes, but those on which there was a thick coating of silver iodide did not satisfy the criteria of reversibility given by Sichling (*loc. cit.*), since any iodine liberated on exposure could react with the silver of the electrode.

Dec. 28, 1924.

METALLIC LUSTER. II

BY WILDER D. BANCROFT AND R. P. ALLEN[1]

The first paper[2] was necessarily devoted chiefly to destructive criticism; this one gives our attempt at constructive work. The sensation of metallic luster may be obtained with metals; with many sulphides, phosphides, silicides, selenides, tellurides, and arsenides of the heavy metals; with selective reflection, as in the case of solid magenta; with oil films and with the iridescent feathers of birds, the Impeyan or Monaul pheasant being a very striking case; with exfoliated mica sheets; with total reflection; with moonlight on the water or the setting sun reflected from windowpanes; and with stereoscopic luster. It is of course theoretically possible that there are several different types of metallic luster, in which case we shall have to find some method of arranging these different cases in two or more groups. If there is only one type of metallic luster, there must be some characteristic common to all these cases.

There is not much help to be got from the psychologist. Kirschmann[3] says that Wundt proved that all luster involves parallax and Kirschmann considers that metallic luster is due to the parallax of indirect vision, which is distinctly not helpful. As a matter of fact, Wundt[4] did not study metallic luster at all, so far as we can learn. We have repeated Wundt's experiments in which he got the sensation of luster when he saw one surface through another. One does get luster under these conditions; but it is always vitreous luster.

The failure to distinguish between different types of luster is not uncommon. Silliman[5] says that although luster "is not peculiar to the metals, it is possessed by them in a most eminent degree, as is beautifully exhibited in clean mercury, in burnished silver and gold, and in polished steel. It is true that mica or isinglass, several of the feld-spars, and some other earthy compounds exhibit, in their natural state, a considerable degree of brilliancy, and the marbles, the gems and most very hard stones, can be made, by polishing, to assume it in a high degree; but if a furrow be made by scratching any brilliant body, which is not metallic, it will appear dull; on the contrary if a bright metal (not an ore) be scratched, the furrow is equally as brilliant as the original surface. Mica is sometimes mistaken for a metal; but it may always be distinguished in this way, and by its inferior weight."

If one asks a physicist to what metallic luster is due, he is very apt to talk about free electrons; and this sort of thing is not always confined to physicists.

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[1] The experiments on which this article is based were made under a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[2] Bancroft and Allen: J. Phys. Chem. 28, 588 (1924).

[3] Archiv. ges. Psychologie, 41, 97 (1921).

[4] Pogg. Ann. 116, 627 (1862); Physiologische Psychologie, 4, 625 (1902); 12, 672 (1910).

[5] "Elements of Chemistry," 2, 103 (1831).

Ryschkewitsch[1] says that "the atomic configuration of graphite is characterized, like that of the metals, by the presence of free electrons which make it a good conductor of heat and electricity and confer on it its metallic lustre." Irvine Masson[2] is even more definite. "Finally, the physical and the chemical characters, of metals are interestingly correlated; for a piece of metal is now known to be not an assemblage of atoms merely, but an assemblage of positively-electrified atoms, the ions of that metal; and interwoven with these are the compensating units of negative electricity, the electrons, none of them fixedly attached to any special atom, but capable of being independent. The ions are positive because they are atoms, initially neutral, which have lost these negative electrons. The lustre of a metal is the lustre of the electronic web; its power of allowing electricity so freely to pass is due to the freedom with which the dotted tracery of electrons can move through the interstices of the coarsely-grained ionic fabric, which itself remains immobile; it is these negative electrons which are shot forth when ultra-violet light falls on a metal and leave it positively electrified; and, lastly, the chemical ability of a metal to dissolve in an acid and form a salt depends on the fact that the acid provides something positive (hydrogen ions) which can pair with these negative electrons and so leave the residual stack of metallic ions free to fall to pieces and pass as such into the liquid."

The inadequacy of this is obvious when we consider that the interference colors of thin films are rather more strikingly metallic than the metals themselves although an oil or a nitrocellulose film does not conduct electricity and contains no more free electrons than anything else. Like almost everybody, Drude[3] recognizes that total reflection at an air surface looks exactly like a metallically lustrous mercury surface. Here again the conception of metallic luster as due to electrons is singularly inappropriate.

We believe that all the cases of metallic luster can be included under one heading and we will therefore give the conclusion that we have reached and then show how it applies in the different cases. We get the sensation of metallic luster when there is sufficient reflection from practically one surface, with suitable variations in intensity either in space or time.

Metals are very opaque and consequently the light that comes to the eye is reflected practically completely from the surface, thus satisfying the first criterion. A crystalline or a hammered surface is more metallic than a more nearly smooth one. A perfectly burnished surface would be a perfect mirror and one would not see the surface at all. That is a limiting case and actually one usually sees the surface with metal plates though not in the case of good mirrors. Nobody calls the reflection from a mirror metallic.

The sulphides, phosphides, silicides, selenides, tellurides, arsenides, and some oxides of the heavy metals are usually more or less metallic when crystalline. They are all opaque and are more metallic the more opaque they are.

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[1] Mellor: "Treatise on Inorganic and Theoretical Chemistry," 5, 759 (1924).

[2] Armstrong: "Chemistry in the Twentieth Century," 41 (1924).

[3] Kirschmann: Archiv ges. Psychologie, 41, 99 (1921).

This has been recognized for a long time. Spring[1] compressed powders in a steel cylinder with polished inner walls. "The powders were always very fine and, so far as possible, they were prepared by chemical precipitation. This was always so for the sulphides, oxides, and carbonates, and usually so for the salts and substances soluble in water. Some of the substances have formed cylinders with more or less marked metallic luster, even when the powder was not that of a metal; others, however, formed cylinders having surfaces showing a glassy luster which was more or less perfect, depending on the degree of agglomeration. For instance, bismuth sulphide, copper sulphide, and manganese dioxide showed a metallic luster while zinc sulphide, mercuric oxide, copper carbonate, etc., appeared to be varnished on the surface. If the fine powders of substances belonging in these two categories are examined under the microscope by transmitted light, it is easy to see what is the controlling physical factor. Without exception the substances which show metallic luster when compressed are opaque when powdered or at least appear so under the conditions of the experiment, while the substances belonging to the other class are more or less transparent in the form of fine powder."

In order to show how extremely metallic some of these compounds are, we call attention to the fact that the phosphide of iron is so much like a metal that it has twice been mistaken for a new element.[2] "In 1781 Meyer published the results of an investigation concerning a "white earth" which he had discovered in cast-iron made from "bog iron-ores." He found that the solution of this iron in dilute sulphuric acid deposited a white precipitate, which is the earth in question. By heating this *per se* in a crucible made out of a solid piece of charcoal, he procured a "very beautiful button," hollow in the interior and containing prismatic metallic crystals. The metal was extremely brittle, easily pulverizable, very fusible, and not attracted by the magnet. He made numerous experiments upon it; he melted it with twice its weight of lead, and obtained a very uneven button, which could be hammered somewhat and cut; its fracture was granular; before the blow-pipe it gave a semivitreous slag, and a metallic bead attractable by the magnet. Meyer concluded that it was a metal, or rather semi-metal, and that it caused the great fusibility of the cast-iron from bog iron-ore. He published a second series of experiments on this supposed new metal and proposed for it the name *Wassereisen* or Hydrosiderum. He gave a summary of its characters which leaves no doubt that it was phosphide of iron. Its specific gravity was 6.710. It was very slowly dissolved by the three mineral acids, but most rapidly (?) by oil of vitriol, and with this and hydrochloric acid it yielded crystals. In 1784 Meyer announced that his pretended new metal was only iron containing phosphoric acid; he begins his announcement with the confession that "to err in chemistry, is alas! too easy", and ends it with an expression of evident satisfaction that Bergmann had committed the same blunder. In the collected works of this distinguished Swedish chemist, which appeared in 1783, is a chapter on the cause of cold-

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[1] Bull. Acad. roy. Belg. (2) 11, 9 (1880).

[2] Percy's Metallurgy: Iron and Steel, 64 (1864).

shortness of iron, containing the following information:— A "white calx" was slowly deposited from the filtered solution of cast-iron made from bog iron-ores in oil of vitriol. This "calx" heated with charcoal yielded a metal (or rather semi-metal, *regulus*, then termed) of the specific gravity 6.700; it was white, dull, and granular in fracture, with no sign of fibre, very brittle, easily fusible, and difficultly attacked by acids. He regarded it as a new metal, and called it Siderum. It is singular that the German and Swedish chemists should have been led at about the same time to the same conclusion as to the cause of cold-shortness in iron, and should both have proposed the same term, Siderum, for the supposed new metal. In 1785, after the decease of Bergmann, his illustrious countryman, Scheele, published an excellent paper on the subject, which, like all the contributions to chemical science of this acute investigator, will ever be deserving of study. He proved in the clearest manner that Siderum was only phosphide of iron."

Ephraim[1] points out that the crystallized sulphides of lead, iron, antimony, vanadium, rhodium, palladium, titanium, nickel, molybdenum, bismuth, copper, silver, and manganese show metallic luster while the sulphides of mercury and zinc do not. Iron pyrites is often called "fools' gold", which shows that it has metallic luster. Roscoe and Schorlemmer[2] say in regard to bismuth that "the word *marcasite*, by which, up to the recent times, the metal bismuth was often designated, is found in the authors of the thirteenth century. Hence it has been supposed that this metal was known at that time. This is, however, not the case, for the name marcasite had in those days and even at a much later period, a very indefinite meaning, being given to any ore which had a metallic appearance, and especially to those ores which are now classed as pyrites."

Ephraim states that the selenides and tellurides are more metallic looking than the sulphides. Tin selenide is metallic but cadmium telluride is not. In fact Ephraim suggests that selenides and tellurides might perhaps be considered as alloys. He believes that the phosphides, arsenides, and antimonides are alloys,[3] in which case of course their metallic luster does not have to be accounted for. Mellor[4] disagrees definitely with this view-point so far as phosphides are concerned, is non-committal in regard to arsenides, and considers antimonides as alloys.

Ephraim[5] states that all the silicides show metallic luster, even lithium silicide having an indigo-blue luster while the silicides of the alkaline earths are lead-gray to silver gray and those of the heavy metals are exactly like metals. Most of the borides also show metallic luster, even including aluminum boride.

From our point of view it is immaterial whether one classes the antimonides, arsenides, phosphides, borides, etc., as alloys or as salts. They have metallic luster because they are opaque. It is admittedly a very interesting problem and one which we hope to take up some day, why the sulphides, to take

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[1] "Anorganische Chemie," 410 (1923).

[2] "Treatise on Chemistry," 2, 1031 (1923).

[3] "Anorganische Chemie," 500 (1923).

[4] "Modern Inorganic Chemistry," 582, 604, 606 (1912).

[5] "Anorganische Chemie," 673 (1923).

up a single group, are so much like metals; but that is, fortunately, not essential to the psychological problem, of what characteristics are essential to the sensation of metallic luster.

Among the oxides Roscoe and Schorlemmer[1] mention cupric oxide, manganese dioxide, calcium ferrite, ruthenium dioxide, and rhodium monoxide as having metallic luster, while magnetite is said to have an iron-black color and a more or less strong metallic luster. There is some doubt about the oxides of iron. Percy[2] says that, when crystallized, magnetite has a metallic luster; but elsewhere it is said to have a sub-metallic luster.[3] Ferric oxide is said to have a steely luster when crystallized. Percy[4] reports that when what he calls tribasic silicate is heated with air, oxidation occurs and the product, which is known as "bulldog," has a bright luster strongly inclining to metallic. This would seem to refer to ferric silicate; but Percy does not believe in the existence of this compound and considers that bulldog is an intimate mixture of ferric oxide and silica, in which case the metallic luster must be due to ferric oxide.

According to Roscoe and Schorlemmer[5] titanium tetra-iodide and bismuth tri-iodide have metallic luster. Without ever having seen them, it seems probable from the description that they owe the metallic luster to their opacity. The metallic luster of certain graphites is unquestionably due to opacity. Some people question the metallic luster of graphite; but the situation seems to be covered by Mellor.[6] "Thin laminae of graphite are opaque. The luster may be dull and earthy, or bright and metallic with intermediate varieties." By allowing a very smoky flame to play against white-hot, glazed porcelain, Luzi[7] obtained on the porcelain a light, lustrous deposit hardly to be distinguished from a silver mirror.

All solid substances which show selective reflection at the surface have metallic luster. A large number of the organic dyes, such as magenta, methyl violet, etc., belong in this class. Magenta is a greenish gold by reflected light and purple-red by transmitted light. Since these substances show intensely strong absorption for the rays which they reflect selectively, the light which is reflected selectively comes practically from a single surface and therefore gives the sensation of metallic luster. As with metals, the metallic effect is increased by slight irregularities in the surface.

It has been recognized for a long time that there was a close connection between the intense absorption and the metallic luster of the light reflected selectively. Stokes[8] says in regard to metallic reflection by non-metallic substances that "my attention was first directed to this subject while engaged in some ob-

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[1] "Treatise on Chemistry," 2, 1266 (1923).

[2] "Metallurgy: Iron and Steel," 20 (1864).

[3] Thorpe's "Dictionary of Applied Chemistry," 3, 677 (1922).

[4] "Metallurgy: Iron and Steel," 100 (1864).

[5] "Treatise on Chemistry," 844, 1041 (1923).

[6] "Treatise on Inorganic and Theoretical Chemistry," 5, 755 (1924).

[7] J. Chem. Soc. 62, 565 (1892).

[8] "Mathematical and Physical Papers," 4, 39, 45, 261 (1909).

servations on safflower-red (carthamine), which I was led to examine with reference to its fluorescence. In following out the connection which I had observed to exist between the absorbing power of a medium and its fluorescence, I was induced to notice particularly the composition of the light transmitted by the powder; and I found that the medium, while it acted powerfully on all the more refrangible rays of the visible spectrum, absorbed green light with remarkable energy. I need not now describe the mode of absorption more particularly. During these experiments I was struck with the metallic yellowish-green reflexion which this substance exhibits. It occurred to me that the almost metallic opacity of the medium with respect to light was connected with the reflexion of a greenish light with a metallic aspect.

"I will here mention another instance of the connexion between metallic reflexion and intense absorption. I choose this instance because a different explanation from that which I am about to offer has been given of a certain phenomenon observed in the substance. The instance I allude to is specular iron [ferric oxide]. As it is already known that various metallic oxides and sulphurets possess the optical properties of metals, there is nothing new in bringing forward this particular mineral as a substance of this kind.

"An excellent example of the intimate connexion between metallic reflexion and intense absorption is afforded by crystals of permanganate of potash. These crystals exhibit a green metallic reflexion, and, when crushed, yield a powder of an intense purple colour by transmitted light."

In view of these quotations it will be sufficient to give one reference to what Kirschmann[1] says. "The metal-like luster on the surface of many strongly-absorbing dyes like fuchsine, carthamine, indigo, and cyamine must not be overlooked. This luster is due to the fact that light is reflected from different depths. The difference in depth of the different components is probably much less than in the real metallic luster, which is why the effect is less intense. On account of the very strong absorption, the reflection is very weak in comparison with that of metals." The light is not reflected from different depths. There is no evidence to show that there is any difference in depth for these dyes and the metals. The effect is not less intense with the dyes than with the metals; in fact it is rather the other way round. The absorption does not make the reflection very weak in comparison with that of metals for the rays which are reflected selectively. The essential difference between the sulphides and these dyes is that the sulphides are opaque to all the visible spectrum and the dyes only to portions thereof.

There are a number of cases outside the dyes where we have metallic luster due to selective reflection. Magnesium platinocyanide[2] shows a brilliant green metallic luster on the sides of the prismatic crystals and a deep violet metallic luster on the ends of the prisms. Ephraim[3] agrees with Stokes in saying that potassium permanganate crystals show metallic luster due to selective reflection; but Stokes makes the color green and Ephraim calls it that of the gold

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[1] J. Phys. Chem. 28, 609 (1924).

[2] Wood: "Physical Optics," 560 (1911).

[3] "Anorganische Chemie," 364 (1923).

beetle, which is presumably golden. Roscoe and Schorlemmer[1] add to the confusion by saying that the crystals, when freshly prepared possess a green metallic luster, which, however, on exposure to the air becomes of a steel-blue tint without any further alteration in the salt taking place.

Anhydrous chromic bromide is green by transmitted light and red by reflected light. The tungsten bronzes all show metallic luster due to selective reflection. The colors vary from red to yellow to blue. Uranium tetrachloride crystallizes in splendid dark-green octahedra having a metallic luster; the color of the luster is not given but it is probably due to selective reflection, because uranium pentachloride forms crystals which reflect light with a green metallic luster and are of a splendid ruby-red color when viewed by transmitted light. Anhydrous ferric chloride forms iron-black iridescent plates, or sometimes large hexagonal tablets, which exhibit a red color by transmitted light and a green metallic luster by reflected light. Iodine has a blue-black metallic luster and is violet-red by transmitted light. According to Abegg[2] chromic oxide may have a golden surface color. Wöhler and Martin[3] state that platinum trioxide is golden but there is nothing further to show how it is to be classified.

In the case of films thin enough to give interference colors, the thickness of the films is negligible so far as the eye is concerned and the light comes practically though not theoretically from a single surface. The contrast in color as well as in surface makes these films astonishingly metallic. We get these colors every day now in oil films on the street from motors.

We have done a few experiments on the effect of color and brightness contrast with these films. If one looks through a red filter at a thin asphaltum film on the smooth surface of water which has been colored black, the film looks metallic but not as metallic as the same film when looked at without the filter. When the filter is used, the surrounding black water plays a more important part than otherwise in determining the metallic appearance. Without the filter the color contrast in the thin film will give rise to the sensation of metallic luster irrespective of the border. Since the color contrast disappears when the red filter is used, the brightness contrast is all-important and the dark surroundings become very helpful. There may, however, be a brightness contrast in the film. If the colors happen to be red and green, the red will be bright and the green dark when seen through a red filter and this brightness contrast will be sufficient in itself to make the film look metallic.

Luckiesh[4] has discussed color contrast and the effect of environment. He gives a diagram showing that the contrast between two colors depends on their nearness. A red and a green square each about 1.4 cm on a side show strong color contrast when juxtaposed. The contrast disappears if they are separated about 1.4 cm. It is apparent with thin films that the contrast is greater the closer together the two colors are. If the separate color bands in a thin film

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[1] "Treatise on Chemistry," **2**, 1189 (1923).

[2] "Handbuch der anorg. Chemie," **4**, I (2), 120 (1901).

[3] Ber. **42**, 3327 (1909).

[4] "Color and Its Applications," 176.

are narrow, say 1-6 mm in width, the metallic appearance is stronger than if one color extends for two or three centimeters. The contrast and hence the luster is also greater if the line of demarcation is sharp and if two bands do not merge gradually one into the other.

Some experiments were made to determine the conditions necessary to enable the eye to focus on a thin film. Precautions were taken so that only the film itself was seen, floating on the water, and not the border of water nor the dish. It was found that the line of demarcation of two colors must be sharp or that some specks were visible on the surface. If the experiment was so arranged that the outline of the film could be seen, that was sufficient. This is of course about what one would have expected; but the experiments did bring out the fact that the sensation of metallic luster is well-marked only when the eye can focus easily on the surface. When the outline of the film is not seen or when the boundaries of the colors are not sharp, the film does not appear metallic.

Oil films on a wet pavement or asphaltum films on a sheet of black paper differ in one important respect from similar films on perfectly smooth water. The surfaces have small irregularities which the eye is able to resolve. This means a still greater variation in intensity. Films of this sort are therefore more metallic than smooth ones. When seen through a red filter these films may look metallic from the brightness contrasts alone, just as a sheet of glossy black paper with small irregularities may look metallic.

Mason[1] has confirmed Lord Rayleigh's view that the iridescent or metallic colors of feathers are thin-film colors due to the presence of flat plates of horn on the surface of the barbules. The brilliant colors of the peacock and the gorgeous ruby throat of the humming-bird are structural colors due to thin films, there being no bright colored pigments in any such feathers. One of the most splendid birds of this type is the Monaul or Impeyan pheasant from the Himalayas. The cock bird looks as though he were encased in plate mail with each single plate showing temper colors.

It was recognized by Sir Isaac Newton that the temper colors on steel were thin-film colors and this view has been accepted by everybody until recently, when Mallock[2] claimed that they were really pigment colors. If Mallock had been right, it might have been a difficult matter to explain why these colors should be metallic, as they unquestionably are[3]; but fortunately Mason[4] has shown the fallacy in Mallock's arguments and we can rest satisfied with the knowledge that these colors are really due to thin films.

It seems probable that the formation of thin-film colors accounts for some curious phenomena recorded by Percy.[5] When iron phosphide is made by dropping bits of phosphorus on small pieces of thin sheet-iron or iron-wire, or on iron-filings heated to redness in a crucible and the mass is left to cool in the

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[1] J. Phys. Chem. 27, 401 (1923).

[2] Proc. Roy. Soc. 94 A, 561 (1918).

[3] Cf. Beckmann: "History of Inventions", 2, 160 (1814).

[4] J. Phys. Chem. 28, 1233 (1924).

[5] "Metallurgy: Iron and Steel", 61, 169 (1864).

crucible, one such specimen had the following characters: "Its upper or flat surface was highly crystalline, presenting long, slender interlacing prisms; and similar crystals were also visible round the sides. On breaking up the button, beautiful, brilliant, iridescent, prismatic crystals were found towards the central portion, which was cavernous. These crystals as well as those round the sides, had for the most part a superficial blue colour, like that of watch springs. The fracture was very uneven, and confusedly crystalline; when freshly made, the colour was greyish white, but it soon acquires a somewhat variegated tarnish, of which the prevailing tint is reddish grey." The crystals are square prisms, in one case with a golden yellow surface while the fractured surface was more nearly tin-white. What this means is that the surface films, due to oxidation, were the right thicknesses to make the crystals blue or yellow as the case might be. The freshly fractured surface had no oxide film on it and was therefore tin-white.

In the case of an iron-lead alloy, there were obtained some "acicular plumose crystals, having the following characters:—Their colour for the most part was brass-yellow, but in certain places it was a peculiar glittering blue. They were soft, rather harder than lead, but could be easily cut, and their cut surface had a leaden lustre." This again is merely a case of thin-film colors due to oxidation.

Multiple plates on films may give the sensation of metallic luster even when they are much too thick to give interference colors. Stokes[1] has shown that the amount of light reflected at vertical incidence from a pile of perfectly transparent plates having an index of refraction of 1.52 is eight percent for one plate and seventy-four percent for thirty-two plates. If the angle of incidence is the polarizing angle the corresponding values are twenty-seven and ninety-two percent respectively. If two percent of the light is absorbed in each plate owing to imperfect transparency, the percentages reflected are eight and fifty-one for vertical incidence and twenty-six and seventy for light incident at the polarizing angle.

With multiple films we get a vastly increased reflection of light. We should expect to get the sensation of metallic luster if the reflected light appeared to come from a single surface and of vitreous luster if one were conscious of depth. This is exactly what happens.

Wundt[2] has called attention to this. "One can produce luster artifically by piling several thin plates, which are both transparent and reflect the light, upon a ground which does not permit light to pass through. The rays reflected from different depths produce a very brilliant luster which, depending on the color of the transparent plates, duplicates in an extraordinary way the luster of metals." By piling together suitably-colored films of gelatine or mica, Kirschmann[3] has prepared specimens which, by reflected light, can scarcely be distinguished from surfaces of polished gold, brass, steel, copper, silver, and platinum.

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[1] "Mathematical and Physical Papers", 4, 152 (1904).

[2] Physiologische Psychologie, 4, 625 (1902).

[3] Philosophische Studien, 11, 147 (1895).

Wundt is right in his facts but not in his implied explanation that the light reflected from different depths gives the sensation of metallic luster. It is because the eye does not get any sensation of depth and because the light appears to come practically from one surface that we get the sensation of metallic luster. We have proved this very simply. Six sheets of gelatine dyed yellow, each 60 mm square and 0.01 mm in thickness were placed together with a backing of black paper. The combination looks like a sheet of polished brass and the luster is unquestionably metallic. The total depth from which light is reflected is only a little over 0.06 mm, so that the light appears to come practically from one surface. Alongside these sheets of gelatine were placed six plates of glass each about 2 mm thick. Between each two plates of glass was placed a sheet of yellow gelatine to give the necessary color. The intensity of the reflected light was approximately the same as with the gelatine sheets alone; but the total depth from which light was reflected was over 12 mm. The eye can detect this when not too far away. At a distance of three or four feet, the pile of glass had a vitreous luster; but when the pile of glass was placed twenty feet from the eye, the luster was just as metallic as with the straight gelatine films.

Wood[1] recognizes the metallic luster due to multiple films. "A thin film of mica, when heated, becomes silvery white and almost opaque. The change appears to be due to the fact that the mica splits into a multitude of parallel laminae, in other words its opacity is due to the presence of a large number of reflecting planes."

Beckmann[2] states that in France wall-papers known as *papiers avec paillettes* were made by coating the paper with metallic dust on which thin oxide films had been produced by heating. "The luster of this paper is so durable that it continues unaltered even on the walls of sitting-apartments. The metallic dust however has a considerable weight, which may undoubtedly injure the paper. This inconvenience may have induced artists to employ, instead of metallic dust, that silver-coloured glimmer [mica], known under the name of cat-silver, which has been long used in like manner. So early as the seventeenth century, the miners at Reichinstein, in Silesia, collected and sold for that purpose various kinds of glimmer, even the black which acquires a gold colour by being exposed to a strong heat. The nuns of Reichinstein ornamented with it the images which they made, as the nuns in France and other catholic countries ornamented their *agni Dei*, by strewing over them a shining kind of talc. The silver-coloured glimmer however has not such a bright metallic lustre as metallic dust, but it nevertheless has a pleasing effect when strewed upon a white painted ground, and its light thin spangles or scales retain their brightness and adhere to the paper as long as it lasts. At present I am acquainted with no printed information on metallic dust and glimmer, nor do I know where artists procure the latter, which in many countries is indeed not scarce. I shall here observe, that I once saw at Petersburg a kind of

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[1] "Physical Optics," 599 (1911).

[2] "History of Inventions," 2, 161 (1814).

Chinese paper, which appeared all over to have a silver-coloured luster without being covered with any metallic substance, and which was exceedingly soft and pliable. It bore a great resemblance to paper which had been rubbed over with dry sedative salt or acid of borax. I conjecture that its surface was covered with a soft kind of talc, pounded extremely fine; but as I have none of it in my possession at present, I can give no further account of it."

Silliman[1] reports that the crystals of ammonium chromate "are minute prisms, which are aggregated to present brilliant thin plates, like flakes of gold, resembling the form of the index used in writing; its colour is yellow and its lustre is metallic."

Mercuric sulphate crystallizes from an excess of sulphuric acid in small stellate plates having a silvery lustre, and lead iodide crystallizes in yellow laminae resembling mosaic gold.[2] Crystals of methyl orange have a very distinct metallic luster. All these are cases of multiple films or plates. Vanadium bronze probably comes under the same head because Roscoe and Schlorlemmer say that metavanadic acid forms a fine yellow pigment, sometimes termed vanadium bronze, and is employed in place of gold bronze. It is obtained in the form of brilliant scales of a golden or orange colour.

One can get a silvery effect with small crystals in the air just as well as with crystals in a watch-glass. In a paper on the remarkable sunsets following the Krakatoa explosion, Aitken[3] says: "On all the evenings on which the first glow was distinct, I observed a thin film of silvery cloud, if cloud it could be called, form or become visible over the western sky, just after the sun had disappeared. It was rather curious that this filmy cloud seemed to have a definite boundary underneath, its wavings or undulations being quite distinct. The peculiar silvery appearance of this filmy cloud struck me at the time, as it had a strange lustre about it; but it was not till I considered the necessity for crystalline reflectors fully to explain the peculiarities in the visibility of the first glow, that it struck me that these crystals would also explain the peculiar silvery lustre of this haze or cloud."

In the case of total reflection the light comes from a single surface and the luster should therefore be metallic, as it is. It seems probable that we recognize the existence of the surface by the curvature, in which case the interesting question suggests itself as to the degree of curvature which is necessary.

When bubbles of air are blown, they will appear like globules of mercury if the conditions are right. We have found that one good way to obtain the effect is to blow the bubbles of air from the end of a tube which is at the bottom of a tall, square, glass box. The box is covered on all sides with black paint or black paper except for a narrow slit on one side for observation, and the light comes from the top. If glycerol is used instead of water, the effect is better because the bubbles rise more slowly. The bubbles appear to be solid and the light which they reflect apparently comes only from the surface. If

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[1] "Elements of Chemistry," 2, 150 (1831).

[2] Roscoe and Schorlemmer: "Treatise on Chemistry," 2, 717, 925 (1923).

[3] Proc. Roy. Soc. Edin. 12, 657 (1884); "Selected Scientific Papers," 128 (1923).

the conditions are not good, it can be seen that the bubbles are transparent and not solid, in which case the luster remains but is no longer metallic. Of course the light which seems to come from the surface does not actually come from there by total reflection; but to be certain that the appearance will be metallic, it is essential to keep all other light from reaching the eye.

Ordinarily a piece of silk is described as having a "silky" luster, which is one modification of vitreous luster. Under the right conditions, however, silk will look metallic. Stage settings sometimes have only a silk curtain for a background and this may be made to look like gold or silver. A piece of lustrous silk will look metallic when no light comes through it because then one sees only the light coming from the surface. A very small amount of transmitted light or the faintest outline of an object seen through the cloth will change the luster to vitreous. The silken curtains on the stage are usually lighted from the side or from the front, and care is taken that no light appears behind them, though this precaution is not for the sake of making them appear metallic. Since the curtain hangs in waves and folds, with deep shadows, the variation in intensity is great. The illumination is strong so the high lights are intense and the shadows are dark. Of course the spectator must not be conscious of the depth in the cloth itself; but that is assured if one sits sufficiently far back.

Alexander[1] mentions an interesting case of metallic luster in which sufficient details are not given. "When dry, the gelatin-tannin compound forms a yellowish-brown brittle mass which melts in boiling water to a tenacious, sticky mass like bird-lime. In this state it may be drawn out or spun into fibers fine as a spider's web, which have a metallic luster like silver slightly tinged with gold. When soaked in alum solution they acquire a blue tinge like polished steel." These effects can only occur under suitable lighting, so that there is no effect of transmitted light.

With the silk and the gelatine-tannin complex a normally transparent fiber looks like metal. The converse may also be true. In the main hall of the new building of the National Academy of Sciences in Washington, there is a Foucault pendulum. When sitting in a particular place, the lower portion of the steel wire to which the bob is suspended looked like a quartz fiber, being apparently transparent. It was not possible to study the phenomenon carefully at the time; but light fell on the wire from the front and side, and it was probably the double reflections, varying as the wire swung, which made the wire look like a transparent quartz fiber.

An ordinary electric fan with brass blades will look metallic under some conditions when revolving and vitreous under other conditions. The same differences can be observed when the blades are painted white. With a black background the fan will look metallic; but as soon as any objects can be seen through the revolving blades, the fan tends to look vitreous. The vitreous effect is evidently due to the combination of the reflection from the surface of the blades and the transmitted light, which is exactly what one would get with

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[1] "Glue and Gelatin", 122 (1923).

glass. On a summer evening it is possible to sit in a New York subway car in such a position that the white blades of the horizontal fan look like a revolving disc of plate glass.

If one stands close enough to a revolving fan, one can get some effect of vitreous luster even with a black background and no light coming through the fan. Owing to the curvature of the blades, there is a certain depth from which the reflection comes and this can be detected under favorable conditions, say if one is only a yard from the fan and if the blades are somewhat corroded. At a distance of ten or twelve feet, the effect becomes negligible and the fan is absolutely metallic.

A similar change from metallic to vitreous luster can be obtained with a bright gear wheel. When this is at rest, it appears metallic because the eye can follow the contours of the teeth and can see that the light from any point comes practically from one plane. When the gear is revolving, however, at a proper speed and one observes it at right angles to the axis of revolution, one gets reflections from the tops and the bottoms of the teeth. Being unable to distinguish the causes producing the two reflections from different planes, one gets the sensation of vitreous luster and the wheel looks glassy.

Somewhat analogous to these cases are those of moonlight on the water and sunlight on glass panes. Kirschmann[1] states that "it would never occur to anybody to ascribe metallic luster to a reflecting water surface." This may be true if the surface of the water is absolutely smooth; but it is not true if the surface is roughened even slightly by a breeze. Then almost everybody sees metallic luster. Brücke[2] says that "it can be shown that we get the impression of a metallic surface even with substances which have in themselves no metallic luster, provided we have simultaneously a roughened surface and a high reflection of light. The most familiar instance of this is the silvery streak which marks the reflection of the moon upon a water surface rippled by the evening breeze. The wavelets make the surface of the water seem rough and the accompanying high reflection of light makes the water look metallic, more metallic than the disc of the moon itself."

In a paper on the color of water Aitken[3] insists that smooth water may be metallic. "The effect of the light reflected from the surface of the water is also of importance. Thus, when the sky is covered with white clouds, the surface reflection is so strong as to mask the colour of the water, and when the sky is deep blue the sky-reflected light intensifies and deepens the apparent colour of the water. The effect of the surface-reflected light is best seen when the sky is covered with clouds, and glowing with a colour different from that of the water, as at sunset when the clouds are rightly coloured all over the sky and deeply down towards the horizon. The water will then, especially if calm, appear like a sea of molten metal glowing with sky-reflected light, so powerful and so brilliant as entirely to overpower the light internally reflected from the water."

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[1] J. Phys. Chem. 28, 599 (1924).

[2] Sitzungsber. Akad. Wiss. Wien, 43 II, 177 (1861).

[3] Proc. Roy. Soc. Edin. 11, 482 (1881); "Selected Scientific Papers," 73 (1923).

Over forty years ago Aitken was perfectly clear that the essential thing to make water look like metal was to have the light reflected from the surface overpower the light reflected from beneath the surface, in other words to have all the light that counted reflected practically from one surface.

In the summer of 1924 one of us was on the Baltic near the coast of Sweden. The water was fairly smooth but not absolutely and one could see the clouds and the hills reflected in the water with only a slight blur. In other words one could see either the surface of the water or the reflected images, as one preferred. If the eyes were focused on the images of the clouds or the hills, one got a sensation of depth and the luster was vitreous. With increasing roughness of the water surface, it soon becomes impossible to focus on the reflected images because they are no longer there, and one focuses necessarily on the surface of the water, which consequently looks metallic just as everybody says. Whether the water will look leaden or silvery or like copper depends upon the quality of the light. The question of eye adaptation is a factor in these observations. The moonlight on rippled water looks practically as silvery as sunlight on the same water and yet the differences in intensity may be of the general order of 1 : 500000. To an eye which was not light-adapted, the moonlit water would look like dull lead and not like silver.

This can be shown in another way. The apparent luster of silver will vary with the light reflected from the surroundings. A powerful light from a stereopticon light was turned from behind on a sheet of flashed opal glass which then gave a well-diffused light. Immediately in front of the glass, in the center, was placed a sheet of bright, slightly roughened, silver. The silver was 6 cm square and the border of illuminated opal glass was about 6 cm wide. A 75 watt Mazda C lamp was placed about one meter in front of the silver so that a bright reflection from the latter entered the eye. When the brilliant silver is surrounded by the intense light coming from the opal glass, the silver appears like a sheet of dull lead to an observer ten feet away. When the stereopticon light was turned out, however, the silver showed up in its full brilliancy and could not be mistaken for one of the darker, less metallic, metals.

This effect is, of course, well known and is tied up with irradiation and with the phenomenon called by some writers "brightness-contrast." We are using it to show the effect of a difference in intensity of the surroundings on the degree of luster of a metal.

A similar change in luster can be obtained by varying the time instead of the intensity. The observer was placed directly in front of a camera which was fitted with a focal plane shutter; but from which the lens had been removed. The object to be observed was placed about eighteen inches from the eye of the observer on the other side of the camera. The observer had his head covered with a black cloth so that he could see nothing but the object (with both eyes) and that only when the shutter was open. In order to let the observer see the object the shutter was opened for 0.1 seconds and then the observer was asked to describe the object. No limit was placed on the number of times that the observer could look at the object, always for 0.1 seconds. He was given as many glimpses as were necessary to enable him to describe his impressions. These experiments were repeated with exposures of 0.2 seconds.

The first object was a sheet of tin large enough so that the edges could not be seen. The tin was placed at such an angle that it reflected light from a window; but the light was not very intense because the window faced north on a narrow alley with a brick wall on the other side. The second object was a sheet of brass plate, about 6 cm square, etched with nitric acid to remove the tarnish. This made it so rough that it showed specular reflection only in small spots when seen from one angle. It was placed on a wooden block and set at an angle at which it reflected all the light possible from the window. The third object was a piece of matte silver placed similarly.

Seven out of nine observers did not see the tin as metallic at 0.1 seconds while five out of nine saw it metallic at 0.2 seconds. Four out of eight observers saw the brass as metallic at 0.1 seconds and seven out of eight at 0.2 seconds. Four out of nine observers saw the silver as metallic at 0.1 seconds and all nine saw it as metallic at 0.2 seconds. As was to be expected, there were differences among the observers; but, in all cases, shortening the time of exposure made it more difficult to recognize metallic luster. As might also have been expected, increasing the intensity of the light made it more easy to recognize metallic luster with an exposure of 0.1 seconds.

In order to show that the sensation of metallic luster depended in part on the recognition of differences of intensity, aluminum powder was rubbed over portions of a sheet of white cardboard. When this is viewed from a distance of ten or twelve feet, the aluminum powder looks like gray paint and no metallic luster can be detected. When examined at short range, the separate, tiny, bright points in the aluminum powder can be seen and the cardboard then appears to be covered with a metallic powder, as it actually is. From a distance the variation in intensity over the surface of the aluminum powder is too slight to give the sensation of metallic luster; but, close at hand, the variation in the intensity over the surface of the aluminum is considerable, because many of the particles are at the correct angle to reflect specularly into the eye. These are therefore very bright, while the neighboring ones are relatively dark.

While most people consider sunlight or moonlight on water as giving metallic luster, there is a wide difference of opinion when it comes to the reflection of the setting sun from the windows of an unlighted house. To some people the window panes look like burnished copper or burnished brass as the case may be, while others get the impression of a light or flame inside the room. A rough estimate is that people divide about fifty-fifty on this point. Of course the phenomenon can be seen either way. One of us was walking one evening to the west of some of the University buildings and saw through the trees what seemed to be the reflection of the setting sun from the window of a certain room. The metallic luster was very marked. On coming to a point where there was no trees to obstruct the view, it was seen that the apparent reflection was in reality yellow light from the yellow walls of the rather brilliantly illuminated room. Through the trees the window frame had been in focus and the trees had blurred things to such an extent that the light apparently came from the plane of the window and hence caused the sensation of metallic luster. As a matter of fact the sun had just set.

It is not necessary that the sunlight be reflected from a window pane in order to have metallic luster. One evening, while travelling on a train near sunset, one of us was watching the metallic appearance given by the sunlight to the car windows. At first the light came to the eye by reflection and the panes looked very metallic. The intensity was high, there was a variation in intensity because the windows were wavy, and the light came apparently from a single surface. As the train rounded a curve, the angle with the window shifted so that the light came through the window at a little more than a grazing angle. There was no marked change in the phenomenon. The intensity was still high and the wavy glass caused the necessary variation in intensity. Due to this waviness the light apparently still came from the surface of the glass, for no objects could be seen clearly through the uneven pane.

The question whether one does or does not get metallic luster when bright sunlight is reflected from or refracted through a suitable pane of glass is important for two reasons: because it brings up the question of metallic luster from a self-luminous body, and because it brings up the question of absolute intensities.

Kirschmann implies that a self-luminous body cannot have metallic luster though he admits that the eye cannot recognize self-luminosity as such. If red-hot copper or iron does not have metallic luster, the question at once arises at what temperature and under what conditions of lighting does the metallic luster disappear. From our point of view the metallic luster should persist so long as there are suitable variations in intensity and so long as the light appears to come from a single surface. From this point of view the difficulty with the red-hot metals would be the lack of suitable differences in intensity. This is a point which could easily be tested.

Dr. Forbes has suggested to us that perhaps one loses the sensation of metallic luster when the contrasts in intensity or when the absolute intensities are too great. It must be admitted that the white-hot filament of a tungsten lamp does not look metallic and that the head-light of a locomotive does not seem metallic on a dark night. Also, an etched metallographic sample very often does not look metallic when seen under a microscope with high illumination. Nevertheless, we believe that the chief difficulty is the lack of sufficient variation in intensity.

Our experiments indicate that the difficulty with the locomotive headlight is the too large expanse of uniform lighting. A sheet of yellow gelatine, 10 cm square, backed with translucent paper, and illuminated strongly from the rear will not look metallic at a distance of three or four feet. If the surface is changed by putting on a number of small black dots with India ink, then it begins to appear lustrous and seems like a piece of brass. The light apparently comes from one surface owing to the translucent paper, and the dark spots supply the necessary variation in intensity. A similar effect can be produced by rubbing carbon black over ground glass. The particles of carbon black fill the hollows in the ground glass and give the necessary variation in intensity. When viewed from a short distance away, glass so treated looks like silver.

It is quite possible to duplicate the effect of hammered silver by means of "white cathedral glass." This material is made by moulding the glass on a table which has been given the proper surface with a silversmith's hammer. By careful adjustment of the transmitted light, a piece of this glass can be made to look like hammered silver. If we place over a sheet of this glass a black paper from which has been cut the outline of a vase, and if we then adjust the lighting from behind so that a rounded effect is obtained, the glass can be made to look like a hammered silver vase. It looks metallic because of the high intensity of the light, because of the variation in intensity of the light due to the irregularities, and because the light seems to come from a single surface. The eye is not conscious that the light is transmitted through the glass and gets no sensation of depth. The Thermal Syndicate makes a vitreosil ash tray with a polished but undulating surface. Under suitable conditions this is very silvery, just as it should be.

To show that metallic luster does not depend necessarily on the presence of a metal or on reflection from a metal, a piece of the "white cathedral glass" was silvered on the front and arranged so that it was seen by reflected light. Another piece of the same glass was covered on the smooth side with a black paint which absorbed practically all of the light coming through the glass· This piece was so arranged that the observer saw the light reflected from the rough surface of the glass. A third piece of the same glass was seen by transmitted light. When the lights were arranged with the proper intensities, no differences could be seen between the three pieces, although light was reflected from a metal in one case, and from glass in the second case, while the light is transmitted through glass in the third case.

The next question is that of stereoscopic luster. Dove[1] combined black and white figures stereoscopically, and also colored figures, obtaining the effect of metallic luster in both cases although the single figures showed no luster. "In one of two pictures for a stereoscope the section of the foreshortened pyramid was painted a saturated blue while the other was painted yellow. When green was seen as a result of stereoscopic combination, it seemed as though the colors had become transparent and were seen one through the other. On the other hand if one combines stereoscopically the yellow and blue sections of a pyramid while holding a violet glass before one eye, the image resembles a polished metallic surface, whereas the surface is matt when seen with either eye alone. Probably the violet glass brings the two colors to the same intensity."

Rood[2] combined tinfoil stereoscopically with yellow, orange, and ultramarine paper and produced the effect of gold, copper, and graphite, respectively. A photograph of a crumpled piece of tin foil gave almost as good a sensation of gold when combined with yellow paper as did the original tinfoil. It

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[1] Pogg. Ann. 83, 169 (1851).

[2] Am. J. Sci. (2) 31 I, 339 (1861).

was not at all clear from the work on stereoscopic luster why one could not eliminate the stereoscope and get the same effect by looking at suitable portions of the landscape through spectacles having two differently colored glasses[1] and yet people said that it could not be done. We have succeeded however in doing it under certain conditions. The red bricks of the neighboring wall showed metallic luster when they were looked at through a red and a green filter and thus was especially true for the portion of the brick wall on which there was a green vine. We know now that practically any green object on a red background or vice-versa will appear lustrous when looked at with a red filter before one eye and a green filter before the other. The essential thing is to have such a combination that with one of the filters one of the objects will look light and the other dark, while the reverse is true for the other filter.

We believe that variation in intensity in time is the important factor. The luster appears as one shifts the attention from the red to the green and vice-versa. The appearance and change in appearance is the same in the stereoscopic vision except that then it is quite often possible to see objects as lustrous for appreciable intervals of time. This varies of course with the observer and with the colors.

This experiment was repeated in another form which brings out the theory more clearly. A red object surrounded by a green border was looked at with one eye and the red and green filters were moved forward back in front of that about four times per second, giving a shift from light to dark of twice that. The luster was apparently due to the fact that the light and dark images were superposed alternately on the retina, giving variations of intensity in time instead of in space. Since the light came practically from a single surface and since there were suitable variations of intensity in time, the luster should be metallic and was.

In connection with a semi-popular lecture to be given at the meeting of the National Academy of Sciences in Ithaca in the autumn of 1923, we desired to show to an audience the phenomenon of stereoscopic luster. It did not seem feasible to equip the audience with red and green spectacles and the experiment would not have been a success if we had, because there is something of a knack about getting the metallic luster satisfactorily.

To overcome this difficulty we devised the synthetic pie plate. A cardboard disc, 20 cm in diameter, had two black quadrants painted on it, radiating from the center with a white rim 2 cm wide on the outer edge. The white quadrants had a black rim 2 cm wide on their outer edges. When this disc was rotated at about 150 R. P. M. and was illuminated by intermittent light supplied through a sectored disc revolving synchronously, the black and white disc became exactly like an aluminum pie plate. The band round the edge formed the sides of the plate and one could get either illusion, of looking at the bottom or at the top of the pie plate. With 150 R. P. M. there were six hundred shifts in intensity per minute or ten per second, because the wheel was in quadrants.

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[1] Bancroft: J. Phys. Chem. 23, 329 (1919).

This experiment was extraordinarily successful. In most experiments with metallic luster, there are marked differences among the observers, some people seeing a thing metallic while others do not. With the synthetic pie plate there were no exceptions. All the people saw it as metallic. If one stopped the rotation and let people see what the thing really was, that did not weaken in any way the sensation of metallic luster when the rotation began again.

This rotating wheel with intermittent synchronous illumination seems to us to have great possibilities as an experimental device for psychologists. Experiments should be made with different colors and different sectors. The change from this to the ordinary color-mixing wheel should be studied. This sort of thing is of course quite outside our line. We have only been interested in getting a working definition of metallic luster because we had to account for the fact that the bright colors observed in the peacock, the Impeyan pheasant, the humming-bird, etc., were metallic.

While struggling with the theory of metallic luster, a number of other experiments were done, some of which seem worth recording. A small box was fitted at the open end with a sheet of red gelatine, 6 cm square. A 25 watt Mazda lamp was placed inside the box and ground glass for diffusing the light was set behind the gelatine. In front of the gelatine was placed a black wire gauze with meshes 2 mm square. If one looked at this arrangement from a distance of about five feet, it appeared very lustrous. When closer, the meshes of the screen could be seen too easily, while they were not visible enough if one stood too far away. This is of course another form of the experiment with the black dots on the gelatine. It differs in that one can vary the distance of the black gauze from the gelatine.

In the early days, while we still assumed the correctness of Wundt's view that one gets [metallic] luster when one object is seen through another with slightly blurred outlines, we devised an experiment which seemed more promising than the one actually used by Wundt. A black wire gauze with meshes about 0.5 mm was placed 10 cm in front of a sheet of white paper illuminated strongly by 100 watt Mazda C lamp. A small-scale reading telescope was placed about one meter away and was focused on a point about midway between the paper and the gauze, so that both images should be slightly out of focus. As seen through the telescope, the paper was lustrous; but the luster was slightly vitreous rather than metallic. The lustrous appearance was due to the breaking-up of the uniform white background by the gauze, thereby giving rise to the necessary variation in intensity. The vitreous appearance was due to the slight curvature of the field. The wires of the gauze, being slightly out of focus were seen as curved and not as straight. This gave the sensation of depth, the light no longer seeming to come from one surface.

Instead of using a black screen and a telescope, we next used two cheese-cloth screens placed one in front of the other and looked at from different distances with the unaided eye. The screens were each about 15 x 30 cm, of 1 mm cheese-cloth; one was black and the other yellow. The yellow was placed about 10 cm behind the black one and was illuminated strongly, practically no light falling on the black screen in front. When this arrangement was viewed from a distance of 4-6 feet it looked like a piece of brass or gold cloth depending on the color of the yellow screen, but always being distinctly metallic. When looked at from a distance of 10-15 feet the luster was vitreous. The actual distances at which these effects occur vary with the observer and with the state of his eyes; but the general relation was in every case that the cloth appeared metallic at short range, though not too close, and vitreous when seen from farther off. The luster, whether metallic or vitreous, is due to the diffraction patterns. When the line of sight is such that the illuminated yellow strands of the rear screen can be seen through the open spaces of the black screen, a light patch is formed; but when each black thread just covers a yellow thread, no light reaches the eye from that region which therefore is dark. One therefore sees alternate light and dark streaks over the entire surface of the screen. This watered-silk effect gives rise to the sensation of luster, because these alternate light and dark streaks simulate reflection from a wavy piece of metal or glass.

Whether one gets the sensation of metallic or of vitreous luster depends whether one sees the reflected light as coming apparently from a single surface or whether one gets a feeling of depth. Several experiments were made to see what the determining factors were, since we were not able to predict them.

With a dark blue screen instead of a black one about 10 cm in front the appearance was metallic at 3-6 feet and vitreous at 12 feet. When a white screen was substituted for the blue one the luster was vitreous at all distances. When the white screen was placed only one centimeter in front of the yellow screen the appearance was distinctly more metallic. The conclusion that we drew from these experiments is that there are two factors in regard to the appearance of the diffraction patterns which exert an influence on the metallic or vitreous appearance of the screen. These are the character of the edges of the light and dark streaks, and the relative intensities of the light and dark patches. Let us take first the case of the yellow screen with the black one in front of it. When the observer is at a considerable distance from the screens, the border of a light spot merges very gradually into the adjacent dark spot, while this transition is much sharper when the observer is nearer the screens. The effect is much more striking if the head is moved slightly from side to side. From the shorter distance the threads in the front screen cover the threads in the back screen more effectively, because the angle subtended by a single thread of the front screen is greater the nearer one is to the front screen. The difference between light and dark is more intense and the transition is more rapid when one is nearer the front screen and therefore the effect is more metallic. Of course one must not get too close to the front screen because then the distance between the two screens becomes too large relatively to the distance of the observer from the front screen.

The more hazy the appearance of the diffraction patterns, the more closely will the screens resemble the reflections from different depths in glass and consequently the screens will appear more vitreous, as indeed they do. When a white screen is substituted for the black screen in front, the difference between the dark and light patches becomes less because there is more light reflected from the front screen, and consequently the appearance becomes vitreous at all distances. When the white screen is put only one centimeter in front of the yellow screen, the actual depth from which light is reflected to the eye becomes less relatively and consequently the effect is somewhat more metallic. A blue screen in front will be intermediate between the black and the white screens, a dark blue behaving nearly like a black screen and a pale blue like a white one.

Since the sensation of metallic luster is essentially a psychological phenomenon, it makes no especial difference whether one sees the light coming from a single surface or whether one thinks unconsciously that one does. One interprets what one sees in terms of one's preconceived idea. In an experimental study of memory color and related phenomenon, Miss Adams[1] gives a number of cases which come under this head. "I was at dinner and on the table in front of me were two silver candlesticks. I saw the polished silver quite plainly; it was very shiny and opaque, like the silver of the candlesticks we used to have at home. I looked away from the candlesticks to speak to my neighbor at the table, and when I again looked at them I saw that they were made of colorless, semi-transparent glass."

"A little while before I had found a dime on the floor of the lecture room. When I walked into my sitting-room a little while ago I saw another dime. It lay on the floor just opposite the window. I went over to pick it up, and found that it was only a mother-of-pearl button with two holes in it. I went back to where I had first seen it, and by persuading myself that the button was a dime, could make it look like a dime again. I could see the silvery luster, and the two holes in the dime became the face of the coin." "In the shadow of a large box which stood below a window I saw a ten-cent piece on the floor. As I stopped to pick it up, I distinctly saw the metallic luster of the silver; at the same moment (as far as I can tell) I knew positively that the disc was *not* of metal but of paper. I was already moving, and went on to pick the thing up; it was a paper disc from the end of a spool of cotton, white, with a border of black; within this was a ring of print in thin capitals; across the white central disc enclosed by this ring were two lines of print in similar capitals. As it happened, I had my glasses off."

"Up in the workshop Dr. D. had been making a cast for observations to be made with the Titchener quadruple pendulum. I knew what had been going on, but had forgotten about the pendulum and the cast for the moment. I turned toward the window above the work-bench. The apparatus was on the bench directly in front of the window. As my eye passed to such a position that the plaster block fell just off the fovea, I saw the top of the block of plaster just like aluminum which is unpolished but still smooth and bright. I think the sides of the block which were under poorer illumination did not become metallic. I am sure I had the meaning of aluminum, and there was a half-formed query which completed would have been, "why how did he get the aluminum?" The perception vanished under scrutiny; but, while it persisted, it had the sheen and the fine grey flecks of metallic luster. It did not return;

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[1] Am. J. Psychology, 34, 359 (1923).

but I tried to give it a chance to return. I think the plaster stood out, after the metallic look had gone, as it should have, very white."

"I was knitting a sweater on half of a hair-pin off which some of the enamel had been rubbed, so that the glint of the metal could be seen. I dropped the hair-pin on the rug and stooped to pick it up. I saw it plainly; the glint of the metal stood out against the dark of the rug; but to my surprise what I tried to pick up was not the hair-pin but a thread in the rug itself. This thread was light in tint, but was composed of several different colors."

"I had my eyes shut while observing in an experiment on audition. When I opened them I saw a silvery luster. At first this meant nothing to me and I asked myself 'What is it?' I recognized my black tie. The silvery luster disappeared and I saw the ribbon as black with sunshine on it."

"The roof of the tower of the University Library aided in our study of the memory color of gold. This roof is made of slightly pinkish yellow tiles, of moderate chroma; but a number of the faculty and students take it to be gilt and see it with a metallic luster. E asked members of the department, and the girls in the house in which she lived, the color of the roof. Those who replied 'gold' and described the color and luster, she asked to watch for it afterward to be sure. The reports of the trained observers, while agreeing with one another, differed from those of the psychologically untrained. We quote one report from each group.

"N (trained): I was on the east side of the tower at eight o'clock this morning and the sun was shining brightly on that side. When I first looked at the roof, it blazed out as solid, brilliant yellow, gold, all in one piece. Then I looked more carefully, as you had asked me, and it was nothing more than a pinkish buff with no metallic luster. It seemed to be made of great heavy tiles which did not fall together very well and between which were big heavy seams.

"O (untrained, facing a shaded side of the roof): It isn't gold from here, but a yellowish gray; but if you come around to the other side you will see it looks just like gold. I have been watching it since you asked me to, and yesterday it was a perfect yellow gold. I showed it to the person I was with and he also saw the gold. Again (facing a side of the tower on which the sun was shining): No, it isn't gold from here either, though it is more like it than it was on the other side. I am absolutely certain that it did not look like this yesterday but was perfect gold."

The senior writer has observed one similar case. Coming up on the campus in an open street car, he noticed a fresh board about ten inches wide laid across the bottom of a colleague's front door. It immediately occurred to him that this was preposterous because people might trip over it on coming out. A second glance gave a satisfactory explanation of a brass strip about ten inches wide fastened on the lower part of the door. On getting a little nearer it turned out that the first impression was right.

From the point of view of the chemist, it is interesting to note that when a pure compound looks metallic, it is either very opaque like the heavy-metal sulphides, has selective reflection like magenta, or crystallizes in plates or small crystals which give a multiple-film effect like methyl orange.

The general results of the investigation are as follows:—

1. All classes of metallic luster can be grouped under one heading.

2. We get metallic luster when sufficient light seems to come from a single surface and there are suitable variations of intensity in space or time.

3. The metals and many of the sulphides, phosphides, silicides, selenides, tellurides and arsenides are so opaque that the reflected light comes practically from the surface of the crystals. They look more metallic when the surface is not too smooth.

4. With interference colors the thickness of the films is so slight that the eye does not detect any depth of reflection. The color contrast helps to accentuate the metallic luster.

5. With multiple films the luster is metallic only when the observer is far enough away that the thickness of the films becomes negligible.

6. With total reflection the light comes practically from a single surface and the luster is therefore metallic.

7. Substances showing selective surface reflection are so opaque for the rays thus reflected that the light comes practically from a single surface.

8. Stereoscopic luster involves primarily a variation of intensity in time though an additional variation of intensity in space is very helpful in causing the sensation of metallic luster.

9. Synchronous intermittent lighting of a rotating, particolored disc gives everybody the sensation of metallic luster. This has been shown in the case of the synthetic pie plate.

10. There seems to be no reason to suppose that self-luminous substances will not look metallic if they satisfy the regular criteria.

Cornell University

STUDIES IN EMULSIONS*

BY WILLIAM SEIFRIZ

I. TYPES OF HYDROCARBON OIL EMULSIONS

Introductory

Experimental work on the behavior of emulsions has had to do primarily with the efficacy of stabilizers, and with the influence of stabilizers and added electrolytes on emulsion type and reversibility. Relatively little attention has been given to the rôle which the oil phase plays in the behavior of liquid-liquid systems. The experimental work presented in this the first part of these studies (as also that in Part VIII) is concerned with the rôle played by the oil phase in the determination of type and reversibility of emulsions.

Experimental

Preliminary experiments.—Preliminary work with various oils revealed that an emulsion of a light petroleum oil (kerosene) and water, with casein as the stabilizing agent, is of the oil-in-water type, while an emulsion of a heavy (lubricating) oil, with casein as the stabilizer, is of the reverse, water-in-oil, type. From this it is to be expected that somewhere in the hydrocarbon series there exists a point at which reversal in type of emulsion takes place. With the purpose of ascertaining this point, at first crudely, nine high-grade hydrocarbon oils, ranging in specific gravity from 0.669 to 0.918, were emulsified with aqueous dispersions of casein. The results are set forth in Table I, where are given the designations of the oils, their specific gravity, and the type of emulsion formed.

TABLE I

Commerical designation.	Specific gravity.	Boiling range.	Type of emulsion.
Petroleum ether	0.669	38 - 80°C.	OW[3]
Oleum spirits	0.788	144 - 211°C.	OW
Perfection Water White kerosene	0.822	177 - 275°C.	OW
Mineral seal oil	0.848	254 - 350°C.	OW
Miner's oil	0.874	267 - 388°C.	OW - WO[4]
Straw oil	0.882	283 - 400°C.	——————[5]
Diamond Paraffin oil	0.886	305 - 400°C.	WO - OW
2900 Red oil	0.896	315 - 400°C.	WO - OW
FFF Steam Refined Cylinder oil	0.918	——————	WO

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* Papers from the Department of Botany of the University of Michigan, No. 223.

[1] The oils are highly refined Standard Oil Co.[6] products from mid-continental (American) crude petroleum.

[2] The casein used is "Casein Pfanstiel, highest purity" (Special Chemicals Co.).

[3] OW = oil-in-water, WO = water-in-oil.

[4] When both types of emulsions occur at the same time, that type which predominates is mentioned first.

[5] No stable emulsion is formed in the case of Straw oil.

[6] These high grade petroleum oils were kindly supplied to the writer by the research laboratories of the Standard Oil Co. of Indiana. The writer wishes to express his gratitude to those in charge of these laboratories for their courteous cooperation.

From the preceding table it will be seen that all the lighter petroleum oils form, with water and casein, emulsions of the OW (oil-in-water) type, while the heavier oils form WO (water-in-oil) emulsions. The oils of intermediate weight form dual emulsions, *i. e.*, both type of systems, and in one instance, no emulsion at all is produced. The OW emulsion in the dual systems, predominates if the specific gravity of the oil (*e.g.* Miner's oil) is below that of the critical value, *i. e.* that value at which reversal in type takes place. If the specific gravity of the oil (*e.g.* Diamond Paraffin oil) is slightly greater than the critical value, the WO type of emulsion predominates in the dual system. Precisely at the critical point—which, as will be more evident later, is better described as a zone of instability—no emulsion can be formed. This is true of Straw Oil which is emulsified with water and casein with difficulty. Usually the two phases separate immediately after shaking. If a temporary emulsion is produced, it is coarse and unstable, and may be of either type, or a combination of the two.

Whatever our conception of the mechanism of emulsification is, the behavior of straw oil is just what one would expect of an oil which stands precisely at the critical point (midway in the zone of instability).

Without further discussion of these results we shall consider similar data pertaining to a much longer series of purer hydrocarbon oils obtained by fractional distillation of the above stock.

Principal Experiments.—Distillation. Five of the petroleum oils (Kerosene to Diamond Paraffine oil) yielded, through fractional distillation, 37 oils of different specific gravity.* The distillation of the petroleum oils was carried out in a glass still in which the fractionating column was packed with thin sheet metal cylinders, and surrounded by an outer, glass, vacuum jacket.[1]

The distillations were made under relatively high vacuum, averaging 67 cm. of mercury, which is a necessary condition for the fractionating of the heavier oils if decomposition is to be avoided. As far as was experimentally possible the boiling range of each distillate was held within 20°C. To keep, however, the heavier distillates within this limit is difficult with even the better laboratory fractional stills. The fractionating column readily floods with a maximum temperature of 270°C.

The oils used as crude stock for distillation were five of those listed in Table I which are all from mid-continental petroleum. In order to ascertain whether or not the large percent of naphthenes present in mid-continental oil is in any way responsible for the behavior of the emulsions, a supply of pure paraffin base oil (one of the heavier of the kerosene series) was obtained from east-continental (West Virginia) fields.† The behavior of emulsions from these distillates was precisely the same as that of the naphthene containing oils.

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* The writer wishes to express his appreciation of the loan of apparatus and of the kind assistance given him in the distillation of these oils, by Professor E. H. Leslie and Dr. J. G. Geniesse of the department of Chemical Engineering of the University of Michigan.

[1] E. H. Leslie: "Motor Fuels," New York, 1923.

† The writer is indebted to the Elk Refining Co. of West Virginia for oil from a pure paraffin base crude stock.

Technique of emulsification.—The technique of making the emulsions is as follows.

The emulsions are prepared by shaking 50 c.c. of oil with 50 c.c. of a 0.2% concentration of an aqueous dispersion of casein in a 150 c.c. Erlenmeyer flask after the manner of Briggs.[1] Briggs' method consists in intermittent shaking by hand. The emulsion is given five violent shakes and then allowed to rest one minute. This procedure is repeated nine times. The method is more efficacious than an hour or more of continuous shaking in a mechanical shaker.

The oil phase may be stained with Sudan III to aid in determining the emulsion type. A microscopic examination was made of every emulsion at each new point in the process of handling.

In previous work[2] the electrical conductivity method[3] of ascertaining the type of system was primarily used. Not only does this method involve the use of considerable apparatus but it cannot be relied upon always to reveal the true condition of an emulsion; nor is the color of the emulsion, when microscopically viewed in a flask, a certain indicator of the emulsion type. If both types of systems, OW and WO, coexist in an emulsion, the color may be red, indicating a WO emulsion, and the conductivity high, pointing to an OW emulsion, neither criterion necessarily giving any indication of the presence of the other type of system. Only a microscopic examination reveals the true state of affairs.

The casein used was of four kinds: (1) "Casein Pfanstiel, highest purity" (Special Chemicals Co.); (2) "Casein after Hammersten" (Merck Darmstadt); (3) a very pure laboratory preparation kindly supplied to the writer by Professor Thomas B. Osborne (a fat- and carbohydrate-free casein with 0.021% of ether soluble matter), and (4) a dialzyed casein prepared by the writer in the following manner. Ten grams of casein (Pfanstiel) were dissolved in 500 c.c. of N/10 KOH and brought to the neutral point with acetic acid. The fine colloidal suspension of casein thus obtained was dialyzed for several days in a colloidion bag until the conductivity of the water in which the dialyzer was suspended was reduced to that of distilled water. The electrolyte-free colloidal suspension of casein thus obtained was used as the aqueous phase of the emulsion.

The first three caseins were prepared for use as stabilizers by dispersing 0.2 gr. in 100 c.c. of water. Grinding of the commercial caseins in a mortar makes a finer dispersion and therefore a more efficient emulsifier. Allowing the casein to remain for some time in the water likewise increases the efficacy of the casein as a stabilizer. Of the four caseins, the laboratory preparations of Profesor Osborne, because of its purity and especially its fineness of texture, made the best emulsifier. As regards type, reversibility, and reaction to electrolytes, emulsions made from all four preparations of casein gave corroborative results.

While the concentration for aqueous casein used was, in all final experiments, 0.2%, yet various other more concentrated dispersions of casein were

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[1] J. Phys. Chem. 24, 120 (1920).

[2] W. Seifriz: Am. J. Physiol. 66, 124 (1923).

[3] W. Clayton: Brit. Assn. Colloid Reports, 2, 96 (1921) Second Edition.

tried. So far as these experiments indicate, the concentration of casein used as stabilizer in no way affects emulsion type.

Characterization of the emulsions.—Of some 40 fractional distillates obtained from the petroleum stock, 31 differed by at least 0.001 in specific gravity. To this list of 31 distillates were added two heavy oils left as residues in the retort, and two pure light hydrocarbons, a hexane and an octane. There was thus obtained a series of 35 petroleum distillates differing by at least 0.001 in specific gravity from 0.664 to 0.895. (Specific gravity measurements are for 22°C.). From each of these 35 oils several emulsions were made with a fine aqueous dispersion of casein. To list the data obtained from all of the 35 oils would tell no more than a selected list, and such a selected list will present the data in a more condensed and intelligible form. Accordingly, 14 oils from the lightest to the heaviest are given in Table II, together with the type, texture, and stability of the emulsions made from them.

TABLE II

Specific gravity	Type of emulsion	Texture	Stability
0.664[1]	OW[6]	fine[8]	stable[9]
0.726[2]	OW	"	"
0.803	OW	"	"
0.818	OW	"	"
0.820[3]	OW	medium	moderately stable
0.828	OW	coarse	unstable
0.839	—	—	separates immediately
0.849	—	—	"
0.856	—	—	" "
0.857	1 {OW	coarse	unstable
	or {WO[7]	fine	stable
	2 WO	medium	moderately stable
0.869[4]	WO	medium	stable
0.874	WO	fine	"
0.884	WO	"	"
0.895[5]	WO	"	"

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[1] Isohexane (boiling point = 77°C).

[2] Iso-octane (" " = 118°C).

[3] Boiling range = 130-150°C. at 67 mm. Hg. of vacuum.

[4] " " = 210-230°C. " 67 " " " "

[5] " " = over 270°C." 67 " " " "

[6] OW = oil-in-water, WO = water-in-oil.

[7] Both types coexist in the same emulsion.

[8] A fine texture is one in which the oil or water droplets average 0.02 mm. or less: in an emulsion of medium texture the globules vary from 0.02 to 0.5 mm.: and a coarse emulsion is one in which the dispersed oil or water drops are over 0.5 mm. in diameter.

[9] Stability is purely a relative term here. Since most emulsions were treated with electrolytes, they were not allowed to stand, except in a few instances, for more than 15 minutes. An emulsion which showed little or no sign of separating during that time was recorded as "stable." A "moderately stable" emulsion was stable for several minutes only. An "unstable" emulsion separated in less than a minute.

From the foregoing table it is evident that all hydrocarbon oils of 0.818 or less specific gravity form fine, stable, oil-in-water emulsions when emulsified with an equal volume of aqueous casein, while those oils of 0.874 or higher specific gravity form fine, stable, water-in-oil emulsions. Those petroleum distillates of between 0.818 and 0.874 specific gravity form emulsions which are less fine in texture and less stable, or do not emulsify at all. Of this last group of distillates, between 0.818 and 0.874 specific gravity, those oils which are just within these border values, form emulsions of medium texture and moderate stability. Those still nearer the middle specific gravity value of 0.849 form coarse, unstable systems, while the three oils of 0.839, 0.849 and 0.856 specific gravity cannot be emulsified at all with a casein stabilizer. The region from specific gravity 0.828 to 0.857 constitutes a zone of instability.

Irregularities in the above behavior occur but are not frequent and are usually ascribable to a less perfect fractionation of the distillates. Thus, the specific gravity of an oil may place it in a certain position in the series while the boiling range will clearly indicate the presence of some hydrocarbons of higher or lower specific gravity.

All of the oils between 0.828 and 0.857 specific gravity are emulsified with difficulty, if at all, and when an emulsion is formed it is poorly stable and may be either of one type or of both types, the two systems existing side by side, or one within the other.

Conclusion

From these data we may conclude that when petroleum distillates are emulsified with water and casein and are: (1) of less than 0.820 specific gravity they form fine, stable oil-in-water emulsions; (2) when of 0.820 to 0.828 specific gravity, they form coarse and poorly stable oil-in-water emulsions; (3) when of 0.828 to 0.857 specific gravity, which constitutes a zone of instability, no emulsion at all is formed; (4) when of 0.857 to 0.869 specific gravity, the oils form coarse to medium, poorly to moderately stable water-in-oil emulsions; and (5) when of 0.869 to 0.895 specific gravity and above, fine and stable water-in-oil emulsions are produced.

Theory

The two hypotheses on the mechanism of emulsion stability which give most promise of explaining the behavior of liquid-liquid systems, are the surface tension hypothesis of Bancroft[1] and the oriented molecular wedge hypothesis of Langmuir[2], Hildebrand[3], Harkins[4], et al (including the hypothesis of contact angles advanced by Hildebrand where the stabilizer is a powdered solid).

The surface tension hypothesis.—The surface tension hypothesis of Bancroft explains the behavior of certain emulsions with soap stabilizers. How

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[1] J. Phys. Chem., **17**, 501 (1913).

[2] Chem. and Met. Eng., **15**, 468 (1916).

[3] J. Am. Chem. Soc., **45**, 2780 (1923).

[4] Science, **59**, 463 (1924).

far the theory is applicable future work will show. The writer has made the following series of observations bearing on the relation of this theory to reversal in type of the hydrocarbon oil emulsions.

It was thought possible that the surface tension value of the oils themselves might be a factor in determining emulsion type. With this in view a series of surface tension readings were made of eight oils enumerated in Table II, together with the readings of water and of an aqueous casein dispersion. These values are given in Table III.

TABLE III

Specific gravity[1]	Surface tension[2]	Specific gravity	Surface tension
0.664	22.5	0.874	33.7
0.800	29.6	0.884	34.4
0.818	30.2	0.895	35.0
0.834	31.7	Casein[3]	54.8
0.852	32.8	Water	74.2

The above data reveal no apparent relation between surface tension value of oil and type of emulsion. Of the eight oils selected, there is a continuous and uniform increase in surface tension values at the rate of about 1 dyne for every 0.02 increase in specific gravity, yet the surface tension values of all the oils are far below that of aqueous casein.

Further data bearing on the surface tension hypothesis of emulsion behavior is given in Part II of these studies in connection with the effect of electrolytes.

The oriented molecular wedge hypothesis.—The oriented molecule hypothesis, which has been advanced by several investigators as an explanation of the behavior of emulsions, offers means for some interesting speculation in connection with the change in type of petroleum emulsions.

The molecular wedge hypothesis is based on the curvature a membrane will assume if built up of wedges with the same (thick or thin) ends all in line. The wedge shape of the molecules is due to their polarity. The large or polar end of the molecular wedge would, in the case of an oil-in-water emulsion stabilized with casein, be the casein end of the associated molecule of casein and hydrocarbon, and the membrane consequently would bend so that the oil ends of the interfacial molecules are toward the inside. In the reverse, water-in-oil, type of emulsion, the hydrocarbon chains become the polar ends of the associated interfacial molecules, and therefore are the outer surface of the stabilization membrane.

At first thought the oriented molecular wedge hypothesis is nicely supported by the change in type of petroleum emulsions with change in size of the hydrocarbon molecule. If we regard the casein molecule as of X diameter, and the thickness of the hydrocarbon molecule as less than X if of light weight

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[1] The specific gravity determinations were made with a du Noüy ring tensiometer.

[2] Surface tension values are in dynes per centimeter.

[3] The casein is an aqueous solution of 0.02% concentration.

(specific gravity up to 0.828), as X if the oil is of medium weight (specific gravity 0.849), and as more than X if the oil is of heavy weight (specific gravity above 0.857), then the interfacial stabilization film will assume the curvatures pictured in Fig. 1.

The fact that the casein molecule is probably of sufficient size to accommodate some dozens or hundreds of hydrocarbon molecules need not disturb our speculations since it is merely necessary to assume that the valency of casein for the petroleum oils is high, and that instead of X being the diameter of one hydrocarbon chain, it is the diameter of one hundred of them.

A more serious difficulty is that pertaining to the assumption that there is an increase in *diameter* of the hydrocarbon molecule with increase in specific gravity of the oil. The hydrocarbon chain is ordinarily regarded as increasing in *length only* as more C atoms are added with increase in weight. There are, however, many reasons to believe that with increase in specific gravity the hydrocarbon molecule increases in diameter as well as in length.

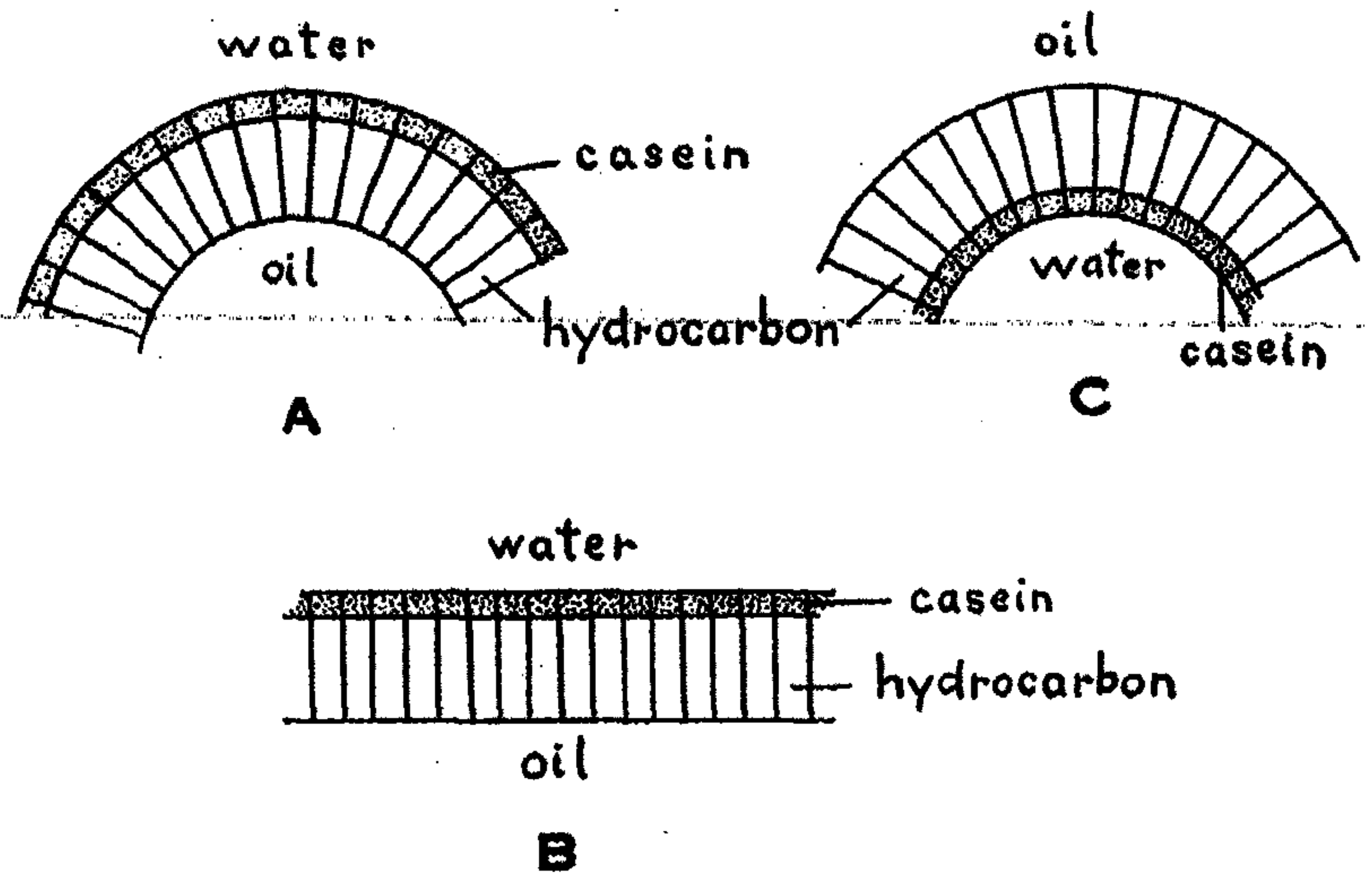

FIG. 1

A. The petroleum oil is of light weight (specific gravity below 0.828) and the emulsion is an oil-in-water one.

B. The petroleum oil is of medium weight (specific gravity 0.828 to 0.857) and cannot be emulsified.

C. The petroleum oil is of heavy weight (specific gravity above 0.857) and forms a water-in-oil emulsion.

Without attempting a detailed discussion the writer wishes merely briefly to refer to several facts which indicate that there is an increase in diameter of the hydrocarbon molecule with increase in specific gravity. There is, first, the general idea that the normal configuration of the C chain is distorted by peculiarities in the molecular "field of force" which give rise to such properties as double and triple bonds, to latent valence, and to adsorption. Such forces are very likely to shorten the hydrocarbon chain. It is also possible that the chain is not a straight one but spiral, and that this spiral is more or less steep depending upon the number of C atoms, the flatter the greater the number of C's. The existence of isomers and branched C chains, are further facts pointing toward a configuration other than a purely linear one of the hydrocarbon molecule. That there is actually an increase in diameter of the chain with increase in number of C atoms has been demonstrated experimentally by Langmuir in the case of certain fatty acids.

Langmuir[1] gives the area of cross-section and increase in length per C atom of the molecules of palmitic, stearic, and cerotic acids as follows.

Acid	Formula	Length of molecule	Area of cross section of molecule	Increase in length of chain per C atom
Palmitic	$C_{15}H_{31}COOH$	24×10^{-8}cm.	21×10^{-16}sq.cm.	1.50×10^{-8}cm.
Stearic	$C_{17}H_{35}COOH$	25×10^{-8}cm.	22×10^{-16}sq.cm.	1.39×10^{-8}cm.
Cerotic	$C_{25}H_{51}COOH$	31×10^{-9}cm.	25×10^{-16}sq.cm.	1.20×10^{-8}cm.

From the data in the fourth column of the table it is clear that the diameter of the molecular chain increases with increase in length. This is also suggested by the figures in the last column which show that the rate of increase in length of the molecule decreases with each additional C atom.

The increase in thickness of the C chain as given above is not sufficient to account for reversal in emulsion type on the basis of the oriented molecular wedge hypothesis if we are dealing with one hydrocarbon chain associated with so large a molecule as is that of casein. The increase in thickness given by Langmuir for the molecules of these fatty acids would, however, suffice if multiplied some hundred-fold as would be the case if the colossal casein molecule has a high valency for hydrocarbon oils.

It is, of course, conceivable that the valency of casein for petroleum oils may increase with increase in specific gravity of the oil, which would account for the change in type of the hydrocarbon oil emulsions on the basis of the oriented molecular wedge hypothesis.

If the valency of casein for the light hydrocarbon oils is V, for the medium oils (in the zone of instability) 2V, and for the heavy oils 3V, then we can assume that V hydrocarbon chains are of less diameter than the casein molecule so that the oil end of the associated molecule is non-polar and the molecule membrane curves toward the oil, the resulting emulsion being an oil-in-water one. 2V hydrocarbon chains should be of the same diameter as the casein molecule so that no wedge and therefore no emulsion is formed. 3V hydrocarbon chains would exceed the diameter of the casein molecule and the membrane would curve toward the water, the emulsion consequently being a water-in-oil one.

Until more is known of the chemical affinities between casein and hydrocarbons the above suggestion must be regarded as highly speculative.

The chief difficulty which the writer has in accepting an oriented molecular wedge hypothesis in explanation of the type and stability of emulsions, is that such a hypothesis demands a monomolecular film, or at least a membrane of

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[1] J. Am. Chem. Soc. 39, 1848 (1917).

the order of molecular dimensions; while, as a matter of fact, the membranes surrounding the dispersed globules of many of the emulsions here considered are at times optically visible, and often, when stiffening sets in, separate off as persistent structures. This phenomenon will be considered in detail later.

II. THE EFFECT OF ELECTROLYTES ON PETROLEUM OIL EMULSIONS

Introductory

Emulsions made from 35 distillation fractions of petroleum oils proved to be, as set forth in the first part of these studies, of two types, oil-in-water and water-in-oil, with an intermediate zone of instability. Emulsions made from hydrocarbon distillates of 0.664 to 0.828 specific gravity, and stabilized with an aqueous dispersion of casein, are of the oil-in-water type. Oils of from 0.828 to 0.857 specific gravity form coarse and poorly stable emulsions if near these limiting values, and cannot be emulsified at all with casein as stabilizer if midway in value, i. e., near 0.850 specific gravity. Petroleum distillates above 0.857 specific gravity form fine stable water-in-oil emulsions when stabilized with casein.

Experimental

Numerous casein-stabilized emulsions were made from each of the 35 petroleum distillates, the latter differing by at least 0.001 in specific gravity, ranging from 0.664 (hexane) to 0.895 (a heavy lubricating oil). To all of these emulsions NaOH and $Ba(OH)_2$ were added, and to enough scattered samples of them NaCl, $BaCl_2$, $Al_2(SO_4)_3$, and $Th(NO_3)_4$ were added to warrant drawing general conclusions on the effect of all six of these electrolytes on casein stabilized petroleum emulsions.

The technique of preparing the emulsions is described in Part I of these studies.

The electrolytes of M/5 concentration were added to 50 c.c. of emulsion in the following proportions: 0.033 c.c., 0.066 c.c., 0.1, 0.2, 0.3, 0.5, 1.0, 2.0, 3.0, 5.0, 10, 15, 25, 35, and 50 c.c. If no change was noticed on the addition of 50 c.c. of electrolyte the emulsion was regarded as irreversible and otherwise uninfluenced by the electrolyte.

The *oil-in-water* emulsions made from petroleum distillates of *light weight* and stabilized with casein are unaffected as to *type* by *any* of the six electrolytes used, which represent salts of mono-, di-, tri-, and quadrivalent cations, and hydroxides of a mono- and a divalent cation. The emulsions are irreversible with these electrolytes.

There is a tendency with all six electrolytes to stabilize the oil-in-water emulsions and increase the dispersity of the oil. In their capacity to stabilize, the electrolytes fall into the following order: $NaOH > Ba(OH)_2 > Th(NO_3)_4 > Al_2(SO_4)_3 > BaCl_2 > NaCl$. The powers of the first three electrolytes to stabilize are pronounced and very nearly equal, while the ability of the two chlorides is almost negligible.

Emulsions made from heavy petroleum distillates and stabilized with casein, are always of the water-in-oil type if the specific gravity of the oil is above 0.857. This is the reverse type of that of the light distillates. These water-in-oil emulsions of the *heavier* petroleum oils, stabilized with casein, are all readily reversible into the opposite type of system by NaOH, $Ba(OH)_2$, and $Th(NO_3)_4$, and less readily by $Al_2(SO_4)_3$; while NaCl and $BaCl_2$ have no noticeable effect. The higher the specific gravity of the oil the more stable is the emulsion and the less readily is it reversed. In their ability to reverse these stable water-in-oil emulsions of heavy hydrocarbon distillates, the electrolytes are effective in the following order:—$NaOH > Ba(OH)_2 > Th(NO_3)_4 > Al_2(SO_4)_3$, with the first three of practically equal efficacy, and the last, Al, much less effective. NaCl and $BaCl_2$ are omitted from the series since no water-in-oil casein stabilized petroleum emulsion studied by the writer can be reversed by them. It will be noticed that the order of the electrolytes just given based on their capacity to reverse water-in-oil emulsions, is the same as that given for their ability to stabilize oil-in-water emulsions.

While a low concentration of NaOH and $Ba(OH)_2$ will ordinarily reverse a water-in-oil petroleum emulsion, yet if the oil is a very heavy one it reverses only after the addition of a high concentration of hydroxide, and sometimes not at all. A casein-stabilized emulsion of FFF Cylinder oil (Standard Oil Co. product) of 0.918 specific gravity, cannot be reversed by ever so high a concentration of NaOH.

The obstinacy of some of the water-in-oil emulsions is unintelligible at times in the light of their customary behavior. An emulsion of Straw-oil, a commercial product of 0.882 specific gravity, which emulsifies with difficulty and usually not at all, sometimes forms a bimultiple system consisting of a coarse oil-in-water emulsion, the 1 mm. oil globules of which being themselves a fine water-in-oil emulsion. These double emulsions are to be regarded as near the reversal point and therefore in the zone of instability. They are, consequently, very sensitive to electrolytes.

The occasional double nature of the Straw-oil emulsion is undoubtedly due to the fact that the oil, being of wide boiling range—from 283 to 400°C—is a complex of hydrocarbons which individually as well as collectively determine the behavior of the emulsion.

Part of an original sample of such a double emulsion of Straw-oil is readily reversed with 1 cc M/5 NaOH, the water-in-oil part of the bimultiple system being reversed, and the rest of the system stabilized into a fine oil-in-water emulsion. If, in the meantime, the other half of an original sample is standing awaiting treatment, it may, on re-shaking, yield a fine water-in-oil emulsion which is so stable as to require 70 cc of M/5 $Ba(OH)_2$ to reverse it. The excess of water undoubtedly plays a part in causing reversal as well as the high concentration of hydroxide.

The behavior of emulsions from petroleum oils which are of *intermediate* specific gravity, and which, therefore, are in or near the zone of instability, is extraordinary in that reversal can be obtained in both directions by the *same* electrolyte. This behavior phenomenon will be taken up separately in the next part of these studies.

Theory

The Relative Potency of Ions.—NaOH, Ba(OH)$_2$ and Th(NO$_3$)$_4$ are of nearly equal potency in their ability to increase the dispersity of oil-in-water, and and to reverse water-in-oil hydrocarbon emulsions stabilized with casein. Since Al$_2$(SO$_4$)$_3$ also has this ability, although to a less degree, we have the interesting fact that a mono-, di-, tri-, and a quadrivalent cation, if the cation is the effective ion, all produce the same end result. If the anion is the effective ion, then a hydroxide, a nitrate, and a sulphate radicle all have a similar effect on petroleum emulsions. That the hydroxyl anion is primarily if not solely the effective ion in the case of the hydroxides of Na and Ba, is suggested by the fact that NaCl and BaCl$_2$ have little or no influence on the behavior of the petroleum emulsions. In this connection the effect of these salts on other emulsions should be noted.

Olive oil emulsions stabilized with casein, soap, gliadin, or cholesterin are not noticeably influenced by NaCl but are readily reversed into water-in-oil emulsions by BaCl$_2$ or Ba(OH)$_2$[1]. BaCl$_2$ is practically ineffective in the case of petroleum emulsions, and Ba(OH)$_2$ reverses the petroleum emulsions into *oil-in-water* systems, not *water-in-oil* as in the case of a soap or casein stabilized *olive oil* emulsion. In olive oil emulsions, then, the cation Ba is apparently the effective ion, while in petroleum emulsions Ba cannot be alone the effective ion.

Of six reversible olive oil emulsions out of eleven studied[3] (each with a different stabilizer) all but one are reversible with BaCl$_2$. BaCl$_2$ has no effect on an olive oil emulsion stabilized with gelatose, while Ba(OH)$_2$ has. The emulsion is irreversible with BaCl$_2$ but reversible with Ba(OH)$_2$, thus behaving like the hydrocarbon emulsions.

A recapitulation in tabular form of those facts bearing on the reaction of emulsions to Ba compounds will show the situation more clearly.

Oil	Stabilizer	Effect of	
		BaCl$_2$	Ba(OH)$_2$
Olive	casein	reverses OW to WO[2]	reverses OW to WO
Olive	gelatose	no effect	reverses OW to WO then back to OW[3]
Hydrocarbon	casein	no effect	reverses WO to OW[4]

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[1] W. Seifriz: Am. J. Physiol. 66, 124 (1923).

[2] OW = oil-in-water, WO = water-in-oil.

[3] This extraordinary case is to be discussed in detail later.

[4] The ultimate result.

The facts set forth in the above table, together with those having to do with the like effect of mono-, di-, tri-, and quadrivalent cations on petroleum emulsions, all go to indicate that a valency hypothesis of the effect of electrolytes on emulsions, so far as it is to be regarded as a general rule, is untenable. The chemical interaction of oil, stabilizer, and electrolyte determines the behavior of emulsions, and, as it is reasonable to expect, this interaction is likely to differ if one of the three factors determining it is changed.

Surface Tension as a Possible Factor in the Effect of Electrolytes on Emulsions.—It is natural to assume that the liquid with the greater surface tension should take the convex form in an emulsion, and therefore, that surface tension should play a part in determining the type and behavior of emulsions (even though the assumption is in some systems completely broken down, where, for example, we have both foams and mists with liquids of high tension and gases where the tension is negative).

With the surface tension hypothesis in mind the writer determined the effect of the six electrolytes on the interfacial tension existing at the surface of the aqueous casein phase and the oil phase of an emulsion. The method employed consists in allowing drops of the aqueous phase to fall through the oil phase from a Traube stalagmometer the aperture of which is submerged in the oil. In the present experiments 9 c.c. of solution were permitted to fall through kerosene, the number of drops being counted in each case. This number may vary considerably, especially in the case of casein with $Ba(OH)_2$, but the majority of the readings are close to the averages given in Table IV.

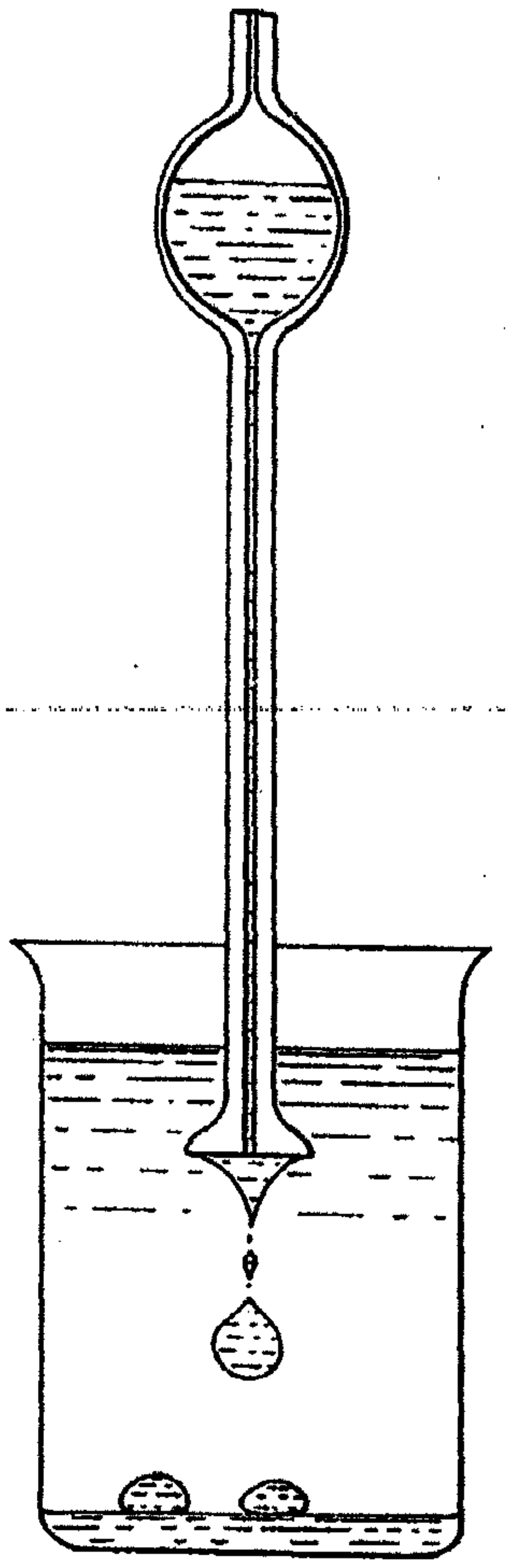

FIG. 2

A Traube stalagmometer with the aperture submerged in olive oil into which droplets of an aqueous solution of casein and $Ba(OH)_2$ are falling. The droplets assume top-shaped form owing to the formation of a tough plastic membrane.

One series of readings was made of the number of drops formed by 9 c.c. of a pure casein solution (0.2 gr. dispersed in 100 c.c. of water) falling from a Traube stalagmometer with its aperture in kerosene. The average number of drops was 42, with occasional readings as low as 35 and, in one or two cases out of some 40 tests, as high as 50. In six other series of readings 1 c.c. of M/5 concentration of one of the six electrolytes was added to 20 c.c. of the aqueous casein dispersion. The whole procedure was duplicated using olive oil and casein and four of the electrolytes. The average results, in number of drops, are given in the following table.

TABLE IV

Number of drops of 9 c.c. of solution falling from a Traube stalagmometer.

In Kerosene

Pure casein	Casein + NaOH	Casein + NaCl	Casein + $Ba(OH)_2$	Casein + $BaCl_2$	Casein + $Al(SO_4)_3$	Casein + $Th(NO_3)_4$
42	25	58	52	59	43	26
In Olive Oil						
30	stream[1]	31	36[2]	30	—	—

Considering the hydrocarbon oil experiments first, it is quite evident from the above table that changes in surface tension occasioned by the addition of an electrolyte to casein, even though pronounced in most instances, bear no relation to the changes in emulsion behavior which these electrolytes bring about. NaOH, $Ba(OH)_2$, and $Th(NO_3)_4$ all have the same effect on type and stability of petroleum oil—casein emulsions, and to practically the same degree, yet 2 of them, NaOH and $Th(NO_3)_4$, nearly double the surface tension between aqueous casein and kerosene (have the number of drops), while $Ba(HO)_2$ markedly lowers the surface tension (increases the number of drops). $Al_2(SO_4)_3$, on the other hand, which has a very definite effect on the emulsions, in the same direction as the above group of three electrolytes though to a less degree, has no influence whatever on the surface tension, while NaCl and $BaCl_2$ which have but a very slight and often no discernable effect on the emulsions, lower the surface tension to about the same extent as does $Ba(OH)_2$.

The above facts seem to preclude changes in surface tension as a factor in determining the effect of electrolytes on petroleum emulsions.

It is remarkable, though at present of purely theoretical interest, that NaOH, $Ba(OH)_2$, and $Th(NO_3)_4$ should have an effect on the surface tension between aqueous casein and kerosene which is quite out of harmony with the chemical reaction between these electrolytes and casein. Casein is soluble in NaOH and $Ba(OH)_2$. The cloudy aqueous casein dispersion used as stabilizer becomes clear immediately on the addition of very little of the hydroxides, while no such effect or any other is to be noticed when $TH(NO_3)_4$ is added. So far as the writer is aware no reaction takes place between Th and aqueous casein. Yet, the casein dissolved in a NaOH solution markedly *increases* the surface tension over that between pure insoluble aqueous casein and petroleum oil, while $Ba(OH)_2$ *lowers* the surface tension value below that of a pure casein dispersion in contact with kerosene. $Th(NO_3)_4$, on the other hand, which apparently has no chemical effect on aqueous casein, increases the surface tension between the casein and the hydrocarbon oil to the same degree as does NaOH in which casein is soluble.

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[1] The drops fall so rapidly as to form a continuous stream.

[2] At first the drops fall at the rate of about 309, then suddenly a substantial membrane is developed around the enlarging drop permitting it to assume great size, after which the number of drops formed is at the rate of 36 for 9 c.c. of solution. When the large drops fall the semi-plastic morphological membrane is torn and the just severed drop is the shape of an inverted top. (see text fig. 2).

The influence of the electrolytes on the surface tension between *olive oil* and aqueous casein is in equally poor agreement with the influence of these electrolytes on emulsions of olive-oil stabilized with casein.

A casein-stabilized emulsion of *olive oil* and water is of the water-in-oil type. It is readily reversed into an oil-in-water emulsion by NaOH and reversed back again by *$BaCl_2$* or $Ba(OH)_2$. NaCl has no noticeable influence on the emulsion. On the surface tension between olive oil and aqueous casein these four electrolytes have the following effects: NaOH, which will reverse the oil-in-water olive oil emulsion, greatly lowers the surface tension between the oil and the aqueous casein, while $Ba(OH)_2$, which reverses the water-in-oil emulsions also lowers the surface tension between olive oil and aqueous casein until there is time to establish a tough plastic membrane, when surface tension between the pure oil and the aqueous casein ceases to exist as such. The presence of such optically visible membranes proves, in the first place, that one is not always dealing with monomolecular surface tension films in stabilized emulsions, and, secondly, how inaccurate the drop method of determining surface tension values can be. This has been emphasized by Clayton[1].

NaCl, which has no noticeable effect on the olive oil emulsions, and $BaCl_2$, which reverses the oil-in-water emulsions as readily as does $Ba(OH)_2$, have no effect whatever on the surface tension between olive oil and casein.

Conclusion

The behavior of certain petroleum oil emulsions, stabilized with casein, in the presence of electrolytes, bears no apparent relation to the valency of the ions, nor to the surface tension changes between the oil and the aqueous casein occasioned by the electrolytes.

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[1] "The Theory of Emulsions and Emulsification," Philadelphia, 1923.

THE ADSORPTION OF VAPORS BY SILICA GEL BY A DYNAMIC METHOD[1]

BY W. A. PATRICK AND L. H. OPDYCKE

Up to the present time all of the published work dealing with the adsorption of vapors by silica gel has been based on measurements made by the static method,—i.e. the gel has been placed in contact with the vapor, the system allowed to come to equilibrium, and the amount of vapor adsorbed and the equilibrium pressure noted. This method permits of very accurate measurements; but unless extraordinary precautions are taken to exclude permanent gases, the time necessary to reach equilibrium is exceedingly long. This has been discussed at length in the case of the adsorption of sulfur dioxide by Patrick and McGavack.[2]

On the other hand, we have found that the results of the above careful static measurements made with the absolute exclusion of all air were very accurately duplicated by passing mixtures of sulfur dioxide and air over the gel until saturation was reached. In other words, the dynamic method, involving a mixture of vapor and air, gives the same results as the static method, which is carried out with the exclusion of air.

Inasmuch as the dynamic or air bubbling method is much simpler from an experimental standpoint, it was planned to measure the adsorption of a few vapors by this method in order, mainly, to throw more light upon the hysteresis effects noted by earlier investigators. Van Bemmelen,[3] using a static method, first noted hysteresis phenomena in the case of adsorption and desorption by silica gel; but it is to be noted that he performed his experiments in the presence of air. Later, Anderson[4] studied the adsorption of water, alcohol and benzene also by a static method. However, although he first evacuated the system, it is obvious that not sufficient precautions were taken to remove the last traces of air which interfere with the attainment of true equilibrium. Patrick and McGavack,[5] in their study of the adsorption of sulfur dioxide, found no hysteresis when precautions were taken to exclude all air from the system.

Besides investigating hysteresis effects, it was desired to test out, in the case of vapors here used, adsorption formulae which have accounted for the adsorption of a large number of substances by silica gel.[6]

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

[2] J. Am. Chem. Soc. 42, 946 (1920).

[3] Z. anorg. Chem. 13, 233 (1896); "Die Absorption", p. 196 (1910).

[4] Inaugural Dissertation, Göttingen (1914).

[5] Loc. cit.

[6] Patrick and McGavack: loc. cit.; Patrick and Davidheiser: J. Am. Chem. Soc. 44, 1 (1922); Patrick and Long: J. Phys. Chem. 29.

Apparatus

The apparatus used was a slight modification of that devised for the present experiments by W. A. Patrick and F. K. Bell of this laboratory. Briefly, the arrangement allowed air, saturated with the vapor to be adsorbed, to be mixed with dry air free from the vapor. The resulting mixture had a partial vapor pressure dependent on the relative speeds of delivery of the two streams. This resultant mixture could be varied at will by devices to be explained later, and could be tapped off for analysis of vapor content. From the vapor content of the equilibrium gas mixture, the partial pressure of the vapor could readily be calculated from vapor density data.

Fig. 1 shows a general arrangement of the apparatus in the water thermostat. An automatic electric regulator and cooling coils maintained the temperature at 30°C. within 0.01 degree. A, A represent gas bubbling devices which gave a regular flow. With a maximum delivery rate of 700 cc. per minute, the saturation obtained was constant and found to be over 98%. B, B are coils through which the gas mixtures (on the left) or pure air (on the right) were passed in order to insure constant temperature. C, C are flowmeters, in the manometers of which nitrobenzol was used on account of its low vapor pressure and low density. D is a mixing bulb; F is a fitting for the adsorption bulb (Fig. 2) provided with ground glass joints. E is a side tube through which samples of the gas were aspirated, measured and analyzed for vapor content.

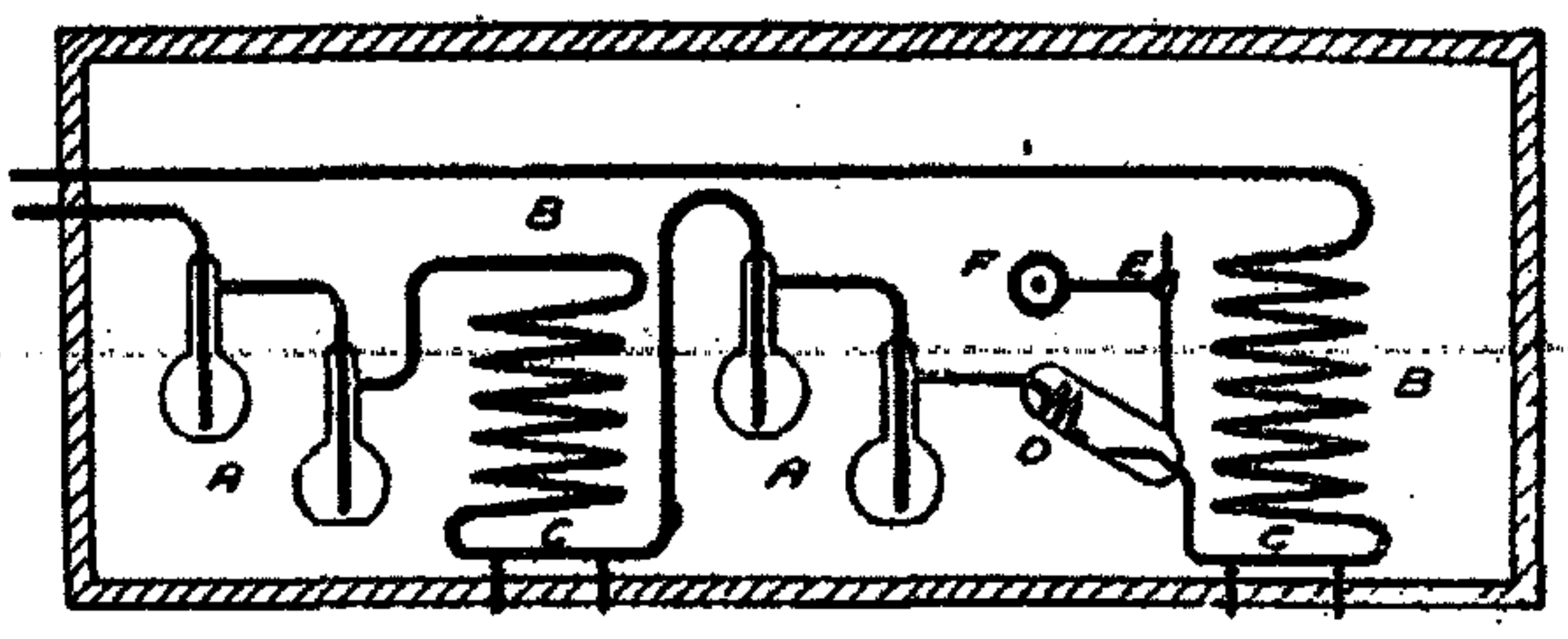

Fig. 1

Both streams of air were derived from a common reservoir. Before division the initial stream was purified and dried by passing it through four gas wash bottles containing concentrated H_2SO_4. This was sufficient to completely dry the air, since a P_2O_5 tower at the end of the train showed no trace of gelatinous metaphosphoric acid after more than a month of almost continuous streaming during atmospheric conditions of high humidity.

The flowmeter manometers (C, C) attached to the bath registered the streaming velocities by differences in pressure (measured by the nitrobenzol levels) between the source pressure on one side of a capillary tube in the course, and the atmospheric pressure on the further side. To sensitize this arrangement to dependence only upon fluctuations in the atmospheric pressure, large air reservoirs (R, R, Fig. 3) were interposed between the original current source and its inlet to the system. These reservoirs were separated by automatic devices whereby excessive source pressure was relieved by an outlet valve (gas thermoregulator relay) which was automatically closed when the pressure was sufficiently relieved. At optimum conditions this opening and closing approximated a vibration.

Having once fixed upon a certain difference in manometer levels as determined for a "run", this could be established by adjustment of the contacts in the regulator-flowmeter between the air reservoirs R, R. If, during a run, the atmospheric pressure changed, the contact points needed but a slight adjustment to compensate. Sparking at the contacts was reduced by a static condenser in parallel, and the fouling of the mercury surfaces was reduced by a superficial layer of high grade machine oil.

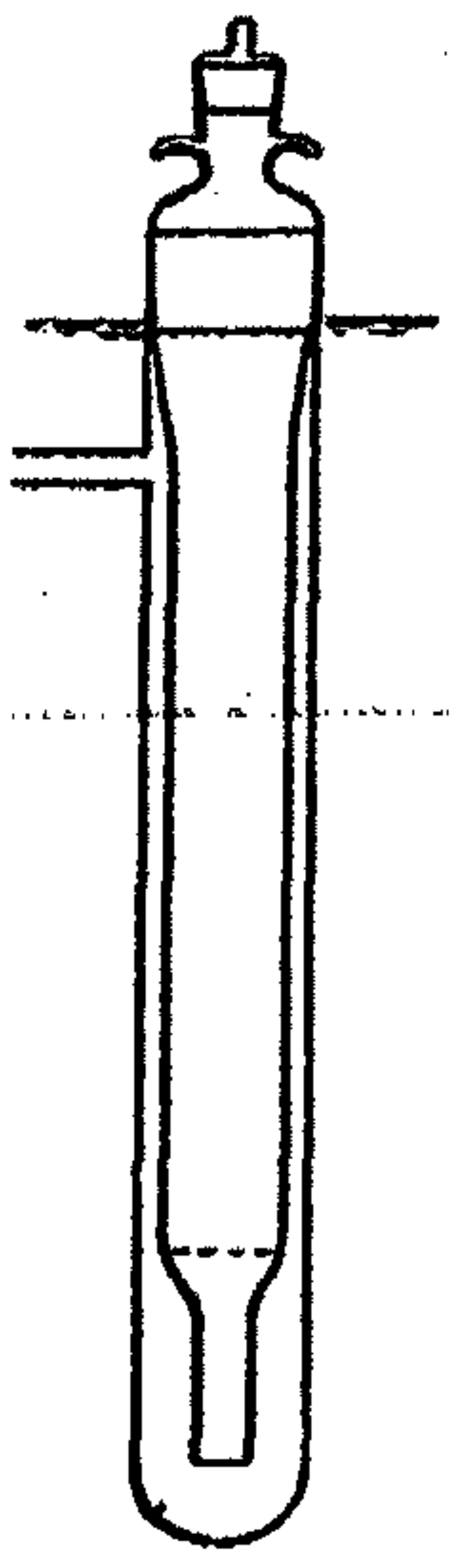

Fig. 2

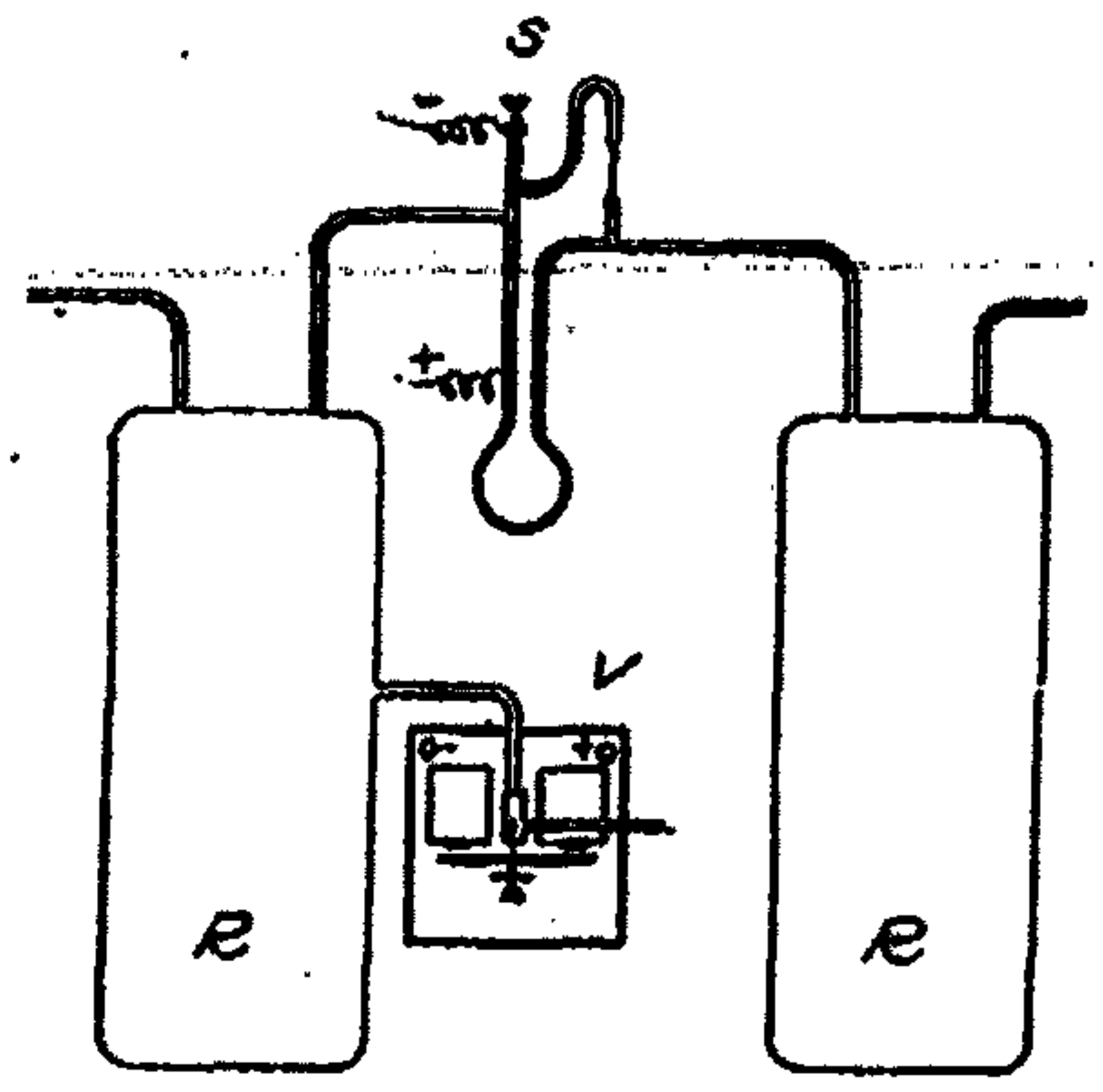

Fig. 3

Stopcocks were introduced in places in the outer parts to secure further control. All connections were of glass and rubber, and those under water were covered with an elastic wax impermeable to water or the vapors used. The runs with carbon tetrachloride required a change of connections every three days owing to the swelling of the rubber,—but no leaks were observed at any time.

The experiments were all made at 30°C. If the room temperature fell far below this, the mixtures of high saturation would cause condensation on that part of the adsorption bulb protruding above the water level of the thermostat. To overcome this, a stream of dry air at about 40°C. was directed at the necessary point.

The mechanism of the streaming and mixing control was not used to measure the partial vapor pressure. In order to do this, samples of the vapor-air mixture, after an initial preliminary running, were drawn by a water aspirator through the side tube E, measured for one litre by a measuring flask, and corrected for volume at room temperature to 30°C. The samples were run through analysing tubes and the vapor contents by weight determined according to the methods outlined later.

Materials

The gel used for all the experiments was from one sample of that used by Patrick and McGavack[1] in their work with sulfur dioxide. It was analyzed for water content and found to have 3.57% H_2O,—having remained practically constant in a stoppered bottle for two years. A gel of this water content has negligible water vapor tension at ordinary temperatures,—the water being held other than mechanically; and for this reason would not lose weight by contact with air of no water content. Samples of from 3 to 5 grams of uniform particle size were chosen.

The water used was distilled water.

The ethyl alcohol was from a highest grade special sample obtained from the Industrial Alcohol Co., and was free from all impurities except H_2O, which was present to the extent of 0.05%.

The carbon tetrachloride was a C. P. sample fractionated six times, and having a constant boiling point of 77°C.

The benzol was a high grade C. P. sample redistilled.

Procedure

A sample of gel was weighed in the adsorption bulb which was then unstoppered and placed in its container in the bath. The vapor currents both dry and saturated had already been regulated to relative speeds for a desired mixture. At constant temperature and pressure the gel in the bulb reached a constant weight in adsorbed vapor in a few hours. The weight, at equilibrium, varied ± 1 milligram from the mean value due to unavoidable uncorrected fluctuations in the atmospheric pressure. Between weighings, the nitrobenzol levels were carefully maintained constant, and samples of the vapor withdrawn at such rates that the end of the withdrawal coincided with the time set for the adsorption-bulb weighings. After each equilibrium point was reached, the mixture was made richer in vapor until finally the stream of dry gas was entirely omitted. The gel sample remained the same, of course, throughout the experiments with any one vapor. From the saturation point the sample was subjected to successive decrements of the partial vapor pressure in order to test reversibility.

Analysis of Vapor Mixtures

For water, two glass-stoppered U-tubes containing P_2O_5 were used. For ethyl alcohol, two Geissler bulbs containing concentrated H_2SO_4 were used, the second of which remained constant in weight throughout forty

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[1] Loc. cit.

determinations. For benzol and carbon tetrachloride, two U-tubes containing freshly activated silica gel were used. In this case it was necessary afterward to pass dry air through these analyzing tubes, or else subsequent passage of vapor with relatively large amounts of air would simply bring the analyser gel to equilibrium values instead of giving the total content for the amount aspirated. By attention to this after each run, it was possible to make ten to twenty determinations with but slight increase in the weight of the second tube.

Excepting the case of water (which see later) all the experiments showed that a true equilibrium was obtained. In all experiments, the flow was continued one hour after the attainment of equilibrium, and weighings were made to prove conclusively that the true equilibrium point had been reached. With water, equilibrium was very slowly attained. The reversed process showed some hysteresis from which the system apparently recovered on later dilution of the vapor. When the hysteresis was overcome in this manner, equilibrium was not reached until after forty hours continuous run.

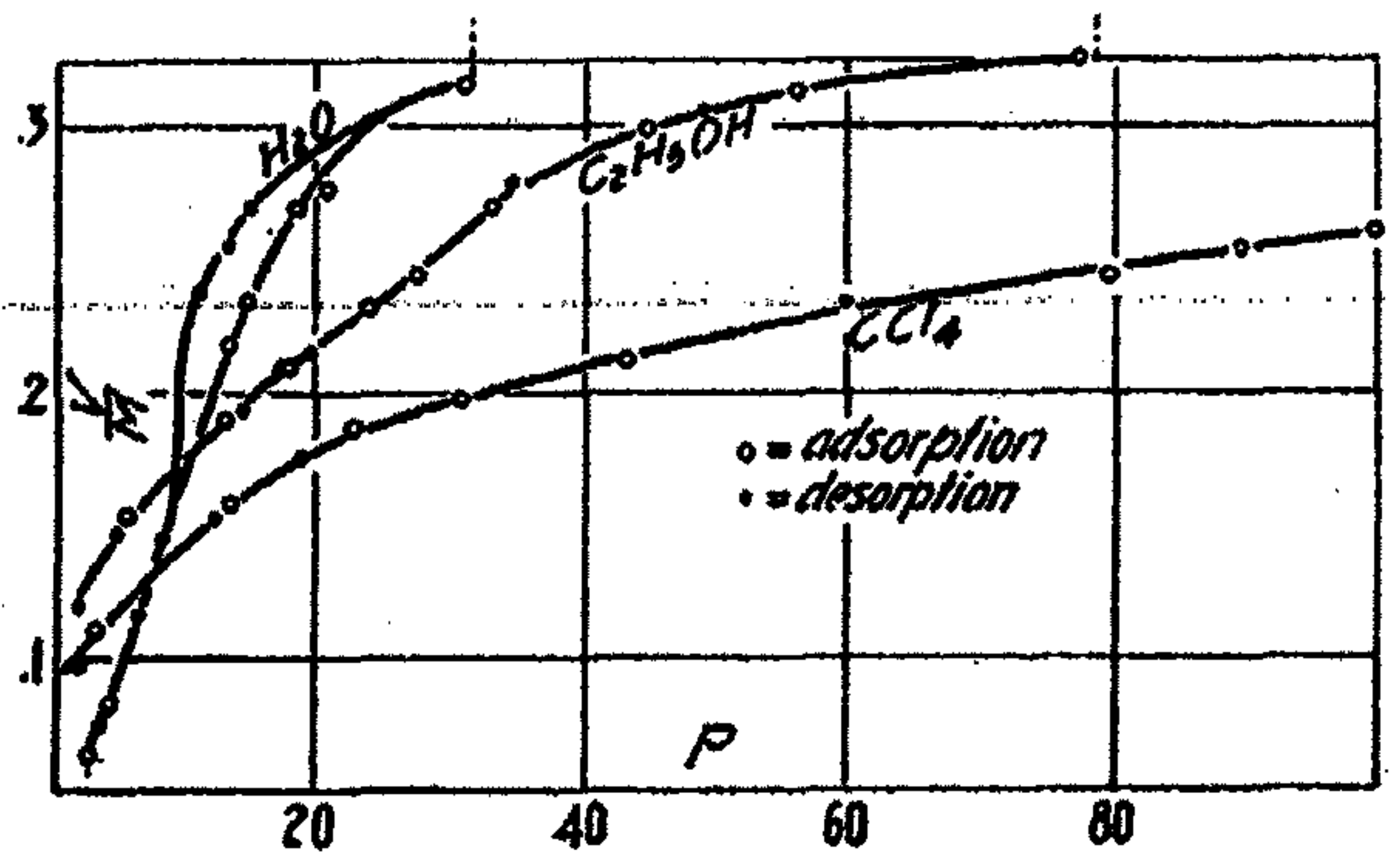

FIG. 4

Tabulation of Results

In the following tables P is the partial pressure at equilibrium of the vapor adsorbed, P_o is the saturation pressure at the temperature, σ the surface tension, and $\frac{V}{M}$ the cc. of vapor adsorbed per gram gel. The tables give values for the adsorption and desorption of the gel. The analysis of the vapors were all checked a number of times at each equilibrium point to within 1%, and from each average value, P was then calculated with the aid of vapor density data of Regnault, Ramsay, and Young.[1]

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[1] Castell-Evans: "Physical Chemical Tables".

Water Vapor

Sample gel 4.1701 gm.; T = 30°;
P_o = 31.51 mm.; σ = 70

Ethyl Alcohol Vapor

Sample gel 4.0268 gm.; T = 30°;
P_o = 78.4 mm.; σ = 21.8

	Water Vapor			Ethyl Alcohol Vapor		
Exp.	P(mm)	$P\sigma/P_o$	V/M	P(mm)	$P\sigma/P_o$	V/M
1	2.91	6.46	.064	5.57	1.55	.153
2	4.42	9.82	.082	8.75	2.43	.170
3	13.60	30.21	.218	13.04	3.62	.189
4	14.88	33.06	.234	18.18	5.05	.208
5	18.55	41.21	.269	20.97	5.83	.220
6	20.85	46.32	.279	24.02	6.73	.232
7	31.00	68.87	.315	27.66	7.69	.244
8	15.35	34.10	.267	33.11	9.20	.270
9	13.68	30.39	.254	44.37	12.33	.300
10	11.66	25.91	.236	56.01	15.58	.312
11	8.13	18.06	.145	77.00	21.39	.326
12	6.48	14.40	.116	48.50	13.48	.305
13	3.55	7.88	.075	33.98	9.44	.278
14				19.70	5.47	.214
15				14.38	4.00	.192
16				9.35	2.60	.170
17				4.80	1.33	.146
18				1.77	0.49	.119
19				1.26	0.35	.105

Carbon Tetrachloride

Sample gel 3.8216; T = 30°;
P_o = 142.3 mm.; σ = 24.6

Exp.	P(mm)	$P\sigma/P^{\circ}$	V/M
1	3.0	0.52	.112
2	5.37	0.93	.127
3	13.7	2.37	.159
4	22.8	3.93	.188
5	30.7	5.29	.197
6	42.8	7.37	.212
7	79.7	13.73	.244
8	89.1	15.34	.255
9	100.1	17.37	.260
10	141.0	24.28	.283
11	60.0	10.33	.234
12	18.7	3.22	.176
13	12.2	2.11	.153
14	9.5	1.64	.145
15	4.1	0.71	.119
16	1.7	0.30	.096

Benzol

Sample gel 4.923 gm.; T = 30°;
P_o = 120.2 mm.; σ = 29.0

Exp.	P(mm)	$P\sigma/P^{\circ}$	V/M
1	117.8	28.42	.280

Discussion of Results

Fig. 4 shows the V/M — P curves for the water vapor, alcohol and carbon tetrachloride. The shape of these curves, especially those of alcohol and carbon tetrachloride, shows that the empiric adsorption equation of Freundlich, $a = K P^{1/n}$ applies. It will also be noted that, contrary to the results of Anderson[1] and earlier workers, there is practically no hysteresis in the case of the organic liquids. The case of water will be referred to later.

In order to apply our own ideas of capillary condensation, it will be necessary to test out the above results by the formula

$$V = K\left(\frac{P\sigma}{P_o}\right)^{1/n}$$

which has accounted for the adsorption of a large number of substances by silica gel.[2] In this formula V corresponds to V/M in the tables, K and 1/n are constants dependent only upon the structure of the gel and P, P_o and σ are defined above. Unlike the Freundlich formula, the above relationship enables one to calculate adsorption at any temperature from measurements at any other temperature. When log V is plotted against log $P\sigma/P_o$, straight lines, coincident for all temperatures and all substances adsorbed by the same sample of gel, should be obtained. This is done in Fig. 5 which shows that the organic liquids are adsorbed according to the above tenets (the slight noncoincidence being due to different gel samples), while water vapor behaves in an anomalous manner. That is to say, for the same "corresponding pressures" ($P\sigma/P_o$) the volumes of alcohol and carbon tetrachloride adsorbed are practically the same, while the volume of water adsorbed is much less. This effect is more marked at the lower corresponding pressures, while at the higher pressures, water behaves like the other liquids. In other words, the deviation is greater where the capillary forces are stronger. That the capillary forces are stronger at low corresponding pressures is readily understood when one remembers that the pores of silica gel are conical in shape,[3] and that therefore the first quantity of liquid adsorbed occupies the "bottom" of the V-shaped capillaries and presents a highly concave surface.

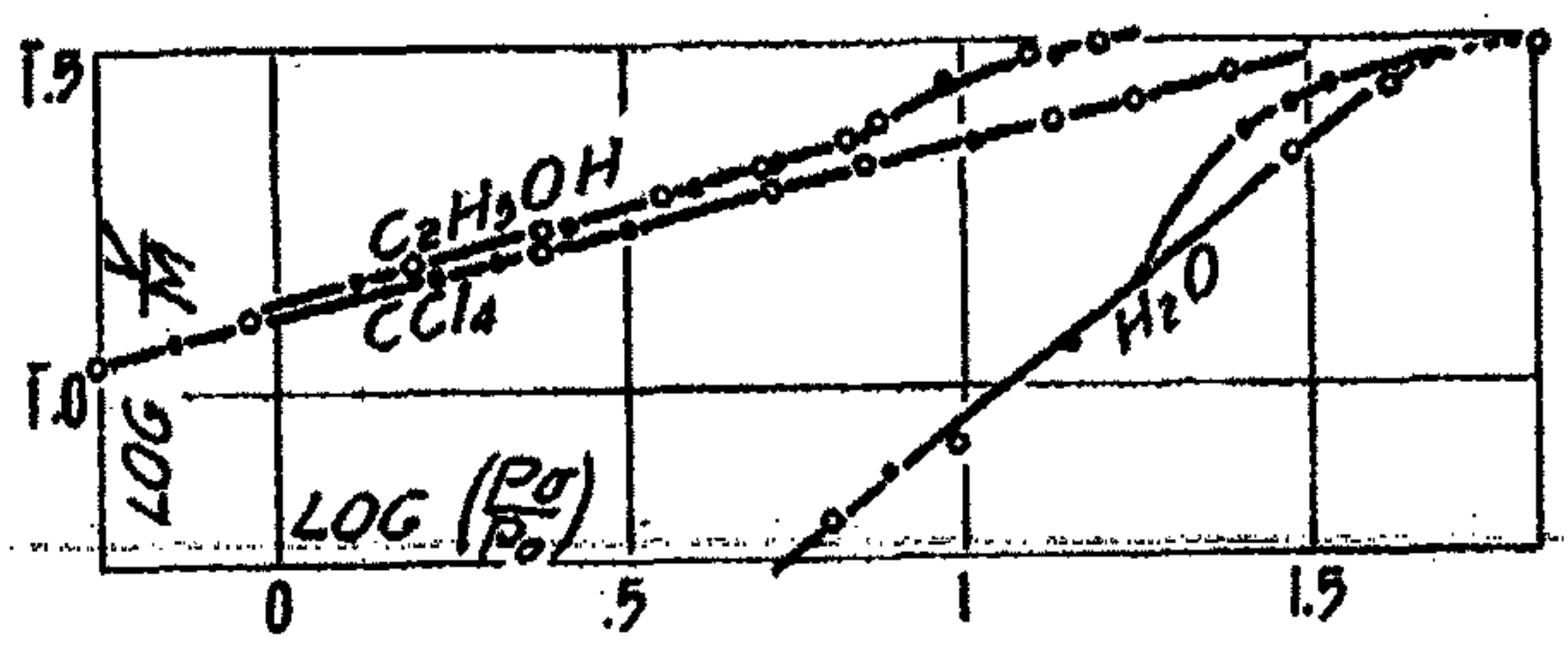

FIG. 5

Upon closer examination of all the factors involved, it will readily be seen that the anomalous behavior of water supports rather than weakens the capillary adsorption theory. It can readily be shown from the laws of capil-

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[1] Loc. cit.

[2] Patrick and McGavack: loc. cit.; Patrick and Davidheiser: loc. cit.; Patrick, Preston and Owens: J. Phys. Chem. 29, 421 (1921).

[3] Patrick and McGavack: loc. cit.; Patrick, Preston and Owens: loc. cit.

larity that, other things being equal, that liquid which possesses the greatest surface tension will be adsorbed or condensed in a capillary system more strongly. This, in fact, accounts for the presence of σ in the above formula. It must be remembered that the above formula also applies to the adsorption of gases such as sulfur dioxide and ammonia, in which case V is the volume of *liquefied gas* and σ the surface tension of the same. Once the gas or vapor is condensed in the capillary system of silica gel, the surface tension forces cause a "dilation" or pull "upwards" of the adsorbed liquid in the attempt to make the liquid surface as small as possible.[1] In other words, the liquid in the capillary undergoes a decrease in internal pressure, due solely to the capillary forces. This decrease in internal pressure is obviously greater the smaller the capillary, i. e. the smaller the corresponding pressure $P\sigma/P_o$. Now it is known that most liquids exhibit a decrease of viscosity with decreased pressure. Water, however, is an outstanding exemption to this general rule; for it has been shown by E. Cohen[2] and others that under 33°C. water undergoes an increase in viscosity with decreased pressure. Upon this basis, it is evident that in the case of the first amounts of water adsorbed ($P\sigma/P_o$ small) the capillary influence is at a maximum, i. e., the water is under a high reduction of internal pressure, and therefore must be very viscous. This increase of viscosity prevents true equilibrium from being reached, and thus explains the low values for the amount of water adsorbed at low corresponding pressures ($P\sigma/P_o$). On the other hand the effect becomes less marked with higher pressure until at the saturation pressure we find water behaving in a normal manner. It is obvious that near the saturation pressure the viscosity of all liquids must be normal inasmuch as the capillary influence is then negligible.

This view is greatly strengthened by a study of the time necessary to reach apparent equilibrium in the case of the different liquids. In the case of benzene, carbon tetrachloride and alcohol, equilibrium was reached very quickly, always within a few hours. With water, however, it was sometimes necessary to continue the flow of vapor for as long as three days. Furthermore, water was the only liquid showing a marked hysteresis in the adsorption and desorption processes.

Summary

1. The adsorption of vapors of alcohol, carbon tetrachloride, benzene and water by silica gel have been investigated by a dynamic method. (It was found that in the case of sulfur dioxide adsorption the same equilibrium points were obtained by the dynamic method as in the case of the static method which requires the removal of all air).

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[1] Patrick and McGavack: loc. cit.; Fisher: J. Phys. Chem. 28, 360 (1924).

[2] "Piezochemie", Chap. 9

2. It was found that the adsorption of all liquids except water was in complete accord with the capillary theory of adsorption expressed by the equation

$$V = K\left(\frac{P\sigma}{P_0}\right)^{1/n}$$

3. Contrary to earlier work by static methods, no hysteresis was observed except in the case of water. This indicates that, if sorption hysteresis is to be studied, either dynamic methods or static methods with the absolute exclusion of air must be used.

4. The anomalous behavior of water as regards hysteresis, time required for equilibrium, and disagreement with the capillary theory has been accounted for by the increase in viscosity of the adsorbed water due to the decrease in internal pressure brought about by capillary and surface tension forces.

THE EVAPORATION OF WATER FROM CLEAN AND CONTAMINATED SURFACES

BY N. K. ADAM

Some time ago I made a few experiments on the rate of evaporation of water from surfaces known to be clean, and from surfaces covered by a monomolecular film of contamination, in order to discover whether such experiments could give information as to the resistance, if any, which a film offers to the passage of the evaporating molecules through the surface. These were not published, as it was clear that the rates which were observed were so much smaller than the rate at which the vapour must escape from the surface, in order to be in equilibrium according to kinetic theory with the rate at which molecules of the saturated vapour strike the surface, at the pressure of the saturated vapour, that all that was being measured was the rate of diffusion of the evaporated molecules away from the surface, and not the rate of evaporation itself. Though Hedestrand[1] obtained considerably higher rates of evaporation, it is clear from the following calculation that the same criticism applies to his experiments as to mine, and that his experiments in which the same rates of "evaporation" were obtained on clean and film-covered surfaces give no information of the real rate of escape of molecules from the surface, except that the film allows the water to escape from the surface at a rate which need not, but may, be more than 1/500 of that at which water escapes from a free surface.

The formula for the rate of striking the surface, by the molecules of a vapour obeying the gas laws, becomes $r = .0583\ p\sqrt{M/T}$, r being the rate of striking in grams per sq. cm. per second, p the pressure in mm. of mercury, and M the molecular weight. This is approximately also the true rate of evaporation, p being the pressure of the saturated vapour.

At 20° C, therefore, water should evaporate at a rate of 0.253 grams per second per sq. cm. The maximum rate observed by Hedestrand was 0.3315 grams from 18.2 sq. cm. in one hour, or 5.05×10^{-6} grams per sq. cm. per second, about one fifty-thousandth of the true rate of evaporation. The fact that the water accumulated in the absorption vessels at the same rate, within one per cent, whether a film was present or absent, shows only that the film did not diminish the rate of evaporation to *less than one five-hundreth* of its normal amount.

My experiments were made by allowing the water to evaporate into a rectangular enclosure over part of the trough in which experiments on the compression of films had been done;[2] this was provided with tubes so that a current of air to collect the evaporated water could be passed. After the ex-

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[1] Proc. Roy. Soc. 101 A, 452 (1922).

[2] J. Phys. Chem. 28, 1245 (1924).

periment on the clean water, the enclosure could be removed in order to test the cleanliness of the surface, as otherwise it would be difficult to be certain that the experiments supposed to be done on clean water were not really done on a contaminated surface. The rate of evaporation at 18° was, from both a clean and film covered surface, 1×10^{-7} grams per sq. cm. per second, the theoretical rate at this temperature being 0.224. Approximately three litres of dry air were passed over the surface in half an hour, and it was observed that the rate of collection of water vapour was very nearly the rate at which it would have been collected if the issuing air was completely saturated with water vapour. Hence in these experiments the limiting factor in the observed "rate of evaporation" was the capacity of the air current to remove the water vapour. In Hedestrand's work it is probable, from the fact that the relative heights of the water surface and the rim of the containing vessel greatly affected the rates observed, that the main resistance to "evaporation" was in the more or less stagnant air layer close to the water surface.

Unfortunately, owing to the high real rate of evaporation of water, it seems unlikely that experiments on these lines can be successful in determining the real rate of evaporation from water covered with a film. The rate of removal of the evaporated water molecules would need to be about fifty thousand times as rapid as in Hedestrand's experiments, and any air current strong enough to effect this would probably be so violent as to destroy completely a monomolecular film on the surface. Evaporation into a vacuum would be explosive and would of course destroy a film. It would seem probable, on general grounds, that the film would considerably slow the real rate of evaporation, as in condensed films the film molecules are closely packed and are strongly attracted to the surface water molecules; the non-volatility of the film molecules would therefore hinder evaporation. Hedestrand's argument (p. 1245) that the decrease in surface tension caused by the film might actually accelerate evaporation, appears quite unsound; for with these films, "decrease in surface tension" simply means increase in compression in the films, and there is no evidence that the "surface tension" of water means that it is covered with some kind of skin which prevents evaporation.

The Sorby Research Laboratory
University of Sheffield
Jan. 12, 1925.

NEW BOOKS

The Micro-organisms of the Soil. *By Sir E. John Russell. 22×14 cm; pp. vii+178. New York and London: Longmans, Green and Co., 1923. Price: $2.50.* "The purpose of this volume is to give the broad outlines of our present knowledge of the relationships of the population of living organisms in the soil to one another and to the surface vegetation. It is shown that there is a close relationship with vegetation, the soil population being dependent almost entirely on the growing plant for energy material, while the plant is equally dependent on the activities of the soil population for removing the residues of previous generations of plants and for the continued production in the soil of simple materials, such as nitrates, which are necessary to its growth. It is also shown, however, that the soil population takes toll of the plant nutrients and that some of its members may directly injure the growing plant."

This is another of the admirable co-operative books which are so justly popular. The subject is presented under the following heads by different members of the staff at Rothamsted: development of the idea of a soil population, by Sir E. John Russell; occurrence of bacteria in soils, by H. G. Thornton; conditions affecting bacterial activities in the soil, by H. G. Thornton; protozoa of the soil, by D. W. Cutler; soil algae, by B. Muriel Bristol; the occurrence of fungi in the soil, by W. B. Brierley; the life of fungi in the soil, by W. B. Brierley; the invertebrate fauna of the soil other than protozoa, by A. D. Imms; the chemical activities of the soil population and their relation to the growing plant, by Sir E. John Russell.

While complete sterilisation of the soil prevents oxidation of ammonia to nitrates practically completely, partial sterilisation increases the rate of oxidation and therefore presumably of bacterial activity, p. 8. "From the outset the phenomena were recognised as dynamic and not static, and the rates of change were always determined: thus the bacterial numbers, the nitrate and ammonia present were estimated after the several periods. Close study of the curves showed that the chemical and bacterial changes were sufficiently alike to justify the view that bacteria were in the main the causes of the production of ammonia and of nitrate; although non-biological chemical action was not excluded, there was no evidence that it played any great part. Thus the importance of micro-organisms in the soil was demonstrated."

"Finally, it is necessary to refer to the physical conditions obtaining in the soil. These make it a much better habitat for organisms than one might expect. At first sight one thinks of the soil as a purely mineral mass. This view is entirely incorrect. Soil contains a considerable amount of plant residues, rich in energy, and of air and water. The usual method of stating the composition of the soil is by weight, but this is misleading to the biologist because the mineral matter has a density some two and a half times that of water and three times that of the organic matter. For biological purposes composition by volume is much more useful, and when stated in this way the figures are very different from those ordinarily given.

"The first requirement of the soil population is a supply of energy, without which it cannot live at all. All our evidence shows that the magnitude of the population is limited by the quantity of energy available. The percentage by weight of the organic matter is about two to four or five, and the percentage by volume runs about four to twelve. Not all of this, however, is of equal value as source of energy. About one-half is fairly easily soluble in alkalis, and may or may not be of special value, but about one-quarter is probably too stable to be of use to soil organisms," p. 16.

"When plant remains decompose in the soil there are ultimately produced brown colloidal bodies collectively known as humus. The processes by which this humus is produced are not yet properly understood. Humus is of great importance in the soil in rendering the soil suitable for the growth of crops. It affects the physical properties of the soil to a great extent. In the first place, it improves the texture of the soil, making heavy clay soils more friable, and loose sandy soils more coherent. Secondly, it has great water-retaining powers, so that soils rich in organic matter suffer comparatively little during periods of drought. And lastly, it exerts a strong buffering effect against soil acids. Now, it is one of the problems of present-day farming that soil is becoming depleted of its humus. This is due to the increasing scarcity of farmyard manure in many districts, and the consequent use of mineral fertilisers to supply nitrogen, potash, and phosphate to the crop. A need has therefore arisen for a substitute for farmyard manure, by means of which the humus content of soils may be kept up in districts where natural manure is scarce.

"It is well known that if fresh unrotted manure or straw be added to the soil, it often produces harmful effects on the succeeding crop. The problem, therefore, was to develop a method by which fresh straw, before application to the soil, could be made to rot down to a mixture of humus compounds such as occur in well-rotted farmyard manure. The solution of this problem came as a result of an investigation by Hutchinson and Richards, at Rothamsted, into food requirements of the cellulose-decomposing bacteria. They realised that since more than 10 per cent of the dry weight of bacteria consists of nitrogen, it would be necessary to supply the cellulose-decomposing bacteria with a supply of nitrogen, in order that they should attain their greatest activity. Experiments with cultures of *Spirochaeta cytophaga* showed that the amount of cellulose decomposed depended upon an adequate supply of nitrogen for the organism. Similarly, materials such as straw will scarcely decompose at all if wetted with pure water. An adequate supply of nitrogen compounds is needed to enable decomposition to take place. Hutchinson and Richards tested the effect of ammonium sulphate, and discovered experimentally the proportion of ammonia to straw that produced the most rapid decomposition. They found that if a straw heap was treated with the correct proportion of ammonia, it decomposed into a brown substance having the appearance of well-rotted manure. This has resulted in the development of a commercial process for making synthetic farmyard manure from straw. The method of manufacture is as follows: A straw stack is made and thoroughly wetted with water. The correct amount of ammonium sulphate is then sprinkled on the top and wetted, so that the solution percolates through the straw. The cellulose bacteria attack the straw, breaking it down and assimilating the ammonia. This ammonia is not wasted, as it is converted into bacterial protoplasm that eventually decays in the soil. Field trials of this synthetic manure show that it produces an effect closely similar to that of natural farmyard manure," p. 29.

"The oxidation of ammonium carbonate by nitrosomonas results in the formation of nitrous acid. The organisms are very sensitive to acidity, and can only operate if the nitrous acid produced is neutralised by an available base. In normal soils calcium carbonate supplies this base, and in acid soils the formation of nitrite is, as a rule, increased by the addition of lime, or of calcium or magnesium carbonate. There is evidence that in the absence of calcium carbonate, other compounds can be used as a base. It was found by Hopkins and Whiting that in culture solution the nitrifying organisms could use insoluble rock phosphate as a base, producing therefrom the soluble acid phosphate. There is evidence, however, that in ordinary soil containing calcium carbonate very little solution of phosphate takes place in this way. The further oxidation of nitrite to nitrate by *Nitrobacter* does not produce acid, and requires no further neutralising base," p. 36.

"One organism studied by Waksman and Joffe is able to live in inorganic solution, deriving its carbon from carbon dioxide. The sulphur bacteria have recently come into prominence in America owing to their faculty for producing acid. Thus Thiospirillum will increase the acidity of its medium to a reaction of pH 1.0 before growth ceases. The potato scab disease in America is now treated by composting with sulphur. This treatment depends on the production of sulphuric acid by the sulphur-oxidising bacteria, which renders the soil too acid for the parasite. There is some evidence also that acid thus produced can be used to render insoluble phosphatic manures more available in the soil.

"Analogous to the sulphur organisms are certain bacteria isolated from sheep dip tanks in South Africa by Green, which can derive energy by the oxidation of sodium arsenite to arsenate," p. 37.

"A long controversy has been held as to whether the nodule organisms found in different host-plants all belong to one species, or whether there are a number of separate species, each capable of infecting a small group of host-plants. As the term "species" has at present no exact meaning when applied to bacteria, the discussion in this form is unlikely to reach a conclusion. The evidence seems to show that the nodule organisms form a group that is in a state of divergent specialisation to life in different host-plants, and that this specialisation has reached different degrees with different hosts. Thus the organisms from the nodule of the pea (*Pisum sativum*) will also produce nodules on vicia, Lathyrus, and Lens, but seem to have lost the ability normally to infect other legumes. On the other hand, the bacteria from the nodules of the Soy Bean (*Glycine hispida*) have become so specialised that they do not infect any other genus of host-plant, and soy beans are resistant to infection by other varieties of the nodule organism. Burrill and Hansen, after an extensive study, divided the nodule bacteria into eleven groups, within each of which the host-plants are interchangeable. The existence of different groups of nodule organisms has been confirmed by the separate evidence of sero-logical tests (Zipfel, Klimmer, and Kruger). The results of cross-inoculation tests have sometimes been conflicting. It seems, indeed, that the host-plant has a variable power of resisting infection, so that when its resistance is lowered it may be capable of infection by a strange variety of the nodule organism. The question that has thus arisen of the ability of the legume to resist infection is of fundamental importance, and its elucidation should throw light on the relation of plants to bacterial infection as a whole," p. 48.

"A great difficulty in applying quantitative methods to bacteria in the field is the great variation in the density of the bacterial population over a plot of field soil, which may be so great that a bacterial count from a single sample is quite valueless. For example, the distribution of bacterial numbers over a plot of arable soil near Northampton was studied by taking sixteen samples distributed over an area about 12 feet square. The result showed that in some cases the bacterial numbers in samples taken 6 inches apart differed by nearly 100 per cent. Fortunately, under favourable conditions, a remarkably uniform distribution of bacterial numbers over a plot of soil can be found.

"On such a plot it is possible to investigate the rapidity with which the numbers of the soil micro-organisms alter in point of time. For example, on the dunged plot of Barnfield, Rothamsted, which has been cropped with mangolds for forty-seven successive years, the area distribution of bacteria has been found to be so uniform that if a number of samples of soil are taken from the plot at the same time, the difference in bacterial numbers between the samples cannot be detected by means of the counting technique. The work of Cutler, Crump, and Sandon on this plot showed that the bacterial numbers vary very greatly from one day to the next, and that these fluctuations took place over the whole plot, since two series of samples taken in two rows 6 feet apart, showed similar fluctuations. The discovery of these big daily fluctuations in numbers led to an inquiry as to how quickly bacterial numbers change, and samples from Barnfield, taken at two-hourly intervals, showed that significant changes in numbers took place even at such short intervals.

"Since the bacteria involved in this fluctuation are of great importance to the crops, being for the most part ammonia-producing types, further knowledge as to the cause of this fluctuation and of its effect on the ammonia and nitrate in the soil is of fundamental importance. There is evidence, which will be discussed later, that the cause is connected with the changing activities of certain soil protozoa, since the daily changes in the numbers of active amoebae in the soil have been found to be in the reverse direction to those of the bacterial numbers. It appears, therefore, that we are dealing with an equilibrium between the various members of the soil population, the point of equilibrium changing at frequent intervals," p. 57.

"The majority of soil protozoa (like the fresh-water forms) appear to be quite cosmopolitan, for the species found in such widely separated localities as England, Spitsbergen, Africa, West Indies, Gough Island (in the South Atlantic) and Nauru (in the Pacific) are, with few exceptions, identical. This distribution indicates an ability to withstand an extremely wide range of conditions, for the same species occurring in Arctic soils, which are frozen for the greater part of the year, are found also in soils exposed to the direct rays of the tropical sun. Even sand from the Egyptian desert contains protozoa, though it seems probable that in such cases they must be present only in the encysted condition for the greater part of the time," p. 75.

"In the cultivation of rice the algae of the paddy field have been found to be of extreme importance. Brizi in Italy has shown that although rice is grown under swamp conditions yet the roots of the rice plant are typical of those of ordinary terrestrial plants and have none of the structural adaptation to aquatic life so characteristic of ordinary marsh plants. Hence the plants are entirely dependent for healthy growth upon an adequate supply of oxygen to their roots from the medium in which they are growing. A serious disease of the rice plant, characterised by the browning and dying off of the leaves, which was thought at first to be due to the attacks of fungi, was found to be the effect of the inadequate aeration of the roots, while the entry of the fungi was shown to be subsequent to the appearance of the physiological disease. The presence of algae in the swamp water was found to prevent the appearance of the disease, in that they unite with other organisms to form a more or less continuous stratum over the surface of the ground, and add to the gases which accumulate there large quantities of oxygen evolved during photosynthesis. The concentration of dissolved oxygen in the water percolating through the soil is thereby raised to a maximum, and the healthy growth of the crop ensured.

"This work has been corroborated by Harrison and Aiyer in India, and a sufficient supply of algae in the swamp water is now regarded as one of the essentials for the production of a good rice crop," p. 113.

"The great cycle of changes occurring in the soil whereby organic matter is gradually transformed and again made available as plant food is entirely dependent upon micro-organisms. Until a decade ago it was thought that bacteria were by far the most important group concerned in the bringing about of these changes, but recent studies have shown that, in at all events certain arcs of this great organic cycle, the fungi have, perhaps, an equal part to play. The life of fungi in the soil may, for our purposes, be considered from three points of view—their part in the decomposition of carbon compounds, their nitrogen relationships, and their work in the mineral transformations of the soil," p. 133.

"On the neutral grass plots at Rothamsted, the dead vegetation does not accumulate on the surface but is rapidly decomposed or drawn into the soil, leaving the surface of the earth bare and free for the growth of seedlings. On the acid plots dead vegetation remains long on the surface, blotting out all new growth excepting two or three grasses which form underground runners capable of penetrating the mat, and sorrel, the seedling roots of which seem to have the power of boring through a fibrous layer of this sort. It is possible to remove the mat entirely by bacterial action alone, if sufficient lime be added periodically to make the reaction neutral, but failing these repeated additions the mat persists," p. 165.

"The general relationship between plants and soil organisms is one of complete mutual interdependence. The growing plant fixes the sun's energy and converts it into a form utilisable by the soil organisms; without the plant they could not exist. The plant is equally dependent on the soil organisms in at least two directions: their scavenging action removes the dead vegetation which would, if accumulated on the surface of the soil, effectively prevent most plants from growing. Further, the plant is dependent on the soil population for supplies of nitrates. Nothing is known about the relative efficiencies of the various soil organisms as scavengers. Numerous fungi and bacteria are effective producers of ammonia, the precursor of nitrates; it is not known, however, whether flagellates and such higher forms of nematodes act in this way.

"This widespread power of producing ammonia makes it impossible in our present knowledge to regard any particular group of organisms as *par excellence* promoters of fertility. Indeed, it is safest not to attempt to do so. The primary purpose of the activities of a soil organism is to obtain energy and cell material for itself; any benefit to the plant is purely incidental. For cell material it must have nitrogen and phosphorus; here it competes with the plant. If it produces more ammonia than it utilises—in other words, if it is driven to nitrogen compounds for its energy, then the plant benefits. If, on the other hand, it absorbs more ammonia than it produces, as happens when it derives its energy from non-nitrogenous substances, the plant suffers. Thus, addition of peptone to the soil or an increase in bacterial numbers effected without addition of external energy (e.g. by partial sterilisation) leads to increased ammonia supply, and, therefore, to increased fertility. But addition of sugar to the soil causes so great an increase of numbers of bacteria and other organisms that considerable absorption of ammonia and nitrate occurs, and fertility is for a time depressed," p. 176.

Wilder D. Bancroft

The Science of Metals. *By Zay Jeffries and Robert S. Archer. 23×16 cm; pp. xvii+460. New York and London: McGraw-Hill Book Company, 1924. Price: $5.00.* As the authors point out in the preface, we have a great store of facts about the structure and properties of metals and alloys, and what we need is a better classification of this knowledge so that we can understand the underlying principles. This need has been supplied by Jeffries and Archer in a most logical and readable manner, and they are to be congratulated on giving us something well worth-while; something quite new and along original lines, and yet always essentially practical. It will appeal to the engineer in a way which previous books on metallography have failed to do. This book is not a composite of previous books, padded here and there with more or less new material—it is absolutely original from beginning to end. To the teacher of metallurgy who strives to something more than setting forth the facts accumulated since the art began, it will appeal as few books have done, because it gives the "reasons why" underlying the science of working in metals.

The treatment of the subject can be gathered from the titles of the twelve chapters. The introduction covers definitions of structure, physical properties and methods of testing metals and alloys. Then follow Electrons, Atoms and Molecules; the Crystalline Structure of Metals; the Amorphous Metal Hypothesis; Grain Growth and Recrystallization; Mechanical Properties of Metals; Compounds of Metals; Metallic Solid Solutions; Constitution of Alloys; Structure and Properties of Aggregates; Hardness of Metals; the Hardening of Steel.

To review this book as it deserves would mean writing an abridged edition, because it is all so new.

Discussing the role of science in metallurgical development, the authors point out that while such materials as high speed steel, stainless steel, alloys capable of resisting oxidation at high temperatures, light alloys of high tensile strength, have come largely from accidental discoveries and more or less empirical experiments, their full development is due in a great measure to the new science of metals.

We have known for sometime that the properties of metals are intimately related to the size and shape of their grains or crystals, and now, by means of the x-ray spectrometer, the actual arrangement of the atoms in crystals and even the distances between atom centers is being determined, and a new field of attack is being opened up. A very useful table of physical constants of the alloy-forming elements is given on pages 4 and 5. This covers: atomic weight; atomic volume; density, grams per c.c.; melting point; boiling point; linear coefficient of thermal expansion per degree centigrade 0°-100°; specific heat, calories per gram per degree centigrade at room temperature; thermal conductivity, calories per cm. cube per degree centigrade at room temperature; electrical resistivity, microhms per cm. cube; crystallization shrinkage, per cent; Young's Modulus, lbs. per square inch; latent heat of fusion, calories per gram; type of crystal lattice; axial ratio; lattice constant side of elementary cube or hexagon; closest approach of atoms.

Under the heading of "Mechanical Properties" stress, deformation, compressibility, Young's Modulus, etc., are all very clearly defined and the introduction ends with fatigue and impact tests.

Chapter II entitled "Electrons, Atoms and Molecules" might be considered as an introduction to the next chapter, in that the essential points covering the constitution of atoms are given in the simplest language and this is followed by the chapter entitled "The Crystalline Structure of Metals."

As the essence of crystallinity lies in regularity of internal structure, all metals are crystalline. This crystallinity depends on orderly arrangements of the molecule and hence the first point discussed is space lattices, which determine the orientation of crystal phases. Further, crystalline materials break easily along certain cleavage planes and deformation of metals takes place by sliding on slip planes. All of these planes pass through atomic centers in the space lattice. Most metals crystallize in the cubic system—tin and indium are tetragonal while magnesium, zinc and cadmium belong to the hexagonal system. When a metal is strained beyond its elastic limit, slip along crystallographic planes or slip planes produces block movement. The original equiaxed grains are drawn out and the change in external shape of each grain is compounded of a multitude of minute slips. With extreme cold work the metal takes on a fibrous appearance. If cold-worked metal is heated to the annealing or recrystallization temperature, a new system of equi-axed grains is produced. The higher the temperature, the coarser the grains. If, however, the work on a metal is done above the recrystallizing temperature, the metal anneals or recrystallizes during the process and is said to be hot worked. Such hot-worked or annealed metal usually shows twinning of the grains, as for example in brass and bronze.

The next point taken up is the x-ray analysis of metals, and an explanation of the three space lattices in which metals occur. Metals crystallizing in the face-centered cubic arrangement are ductile through a considerable range of temperature. They include all the noble metals—all the best electrical conductors and the best conductors of heat, and commonly show annealing twinning. They have four sets of planes of easy slip. Body-centered cubic metals may be ductile or brittle, though this system is less favorable to ductility. Annealing twins have not been observed, as for example, alpha iron, tungsten, molybdenum. Metals showing the hexagonal close-packed arrangement of the atoms have only one set of planes of easy slip and harden rapidly by cold work.

Chapter IV covers the amorphous metal hypothesis. Beilby set this forth in 1911, and his idea was that the hardening produced by cold work was due to films of amorphous material produced on the faces of slip. This was extended by Rosenhain who said that the grains of a metal are held together by similar amorphous cement.

The authors show that Beilby's original hypothesis is untenable and that strained hardness is caused by slip interference created by grain fragmentation of the original grains, the importance attached to the specific hardness of amorphous metal as a cause of hardening having been greatly exaggerated.

The chapter covering grain growth and recrystallization is perhaps the most interesting of all. The authors lay down certain laws of grain growth. While many of these have been taken for granted for a long time, some of them are not so well known in practice.

The grain size in cast metals which undergo no phase change in the solid state, cannot be changed by annealing. Grain growth in the solid state does occur in worked metals and compressed powders, as well as in electro-deposited metals, in iron when it changes its allotropic form, and in certain alloys in which a new phase is formed in the solid state. The recrystallization temperature is lower, the greater the amount of deformation, the smaller the grains prior to cold work, the purer the metal; the lower the temperature at which cold work is effected and the longer the time of heating.

In any given metal, the grain size after complete recrystallization, is normally smaller, the lower the recrystallization temperature. Certain conditions of non-uniformity sometimes give rise to abnormally large grains. This was investigated by Stead in low carbon steel and hence called Stead's brittleness. In general, it has been referred to as germination. These conditions are grain size contrast, strain gradients, temperature gradients, concentration gradients, obstruction gradients. The presence of foreign matter or a second phase causes mechanical obstruction to grain growth.

Chapter VI on the mechanical properties of metals, covers 72 pages. The summary of the properties of cold worked metals given on p. 201 may be startling to some of us who think we know all about the working of metals. Of course, we know that the hardness and strength of a metal increases with the amount of reduction by cold work while its plasticity decreases. In metals which become brittle on cooling because of inter-crystalline weakness, the cold-worked metal may possess considerable elongation at temperatures at which the equi-axed metal is brittle. The hardening effects of slight or moderate deformation are greater, the smaller the initial grain size of the metal. Again, the elongation of a cold-worked metal increases with respect to the elongation of annealed metal as the temperature of the test decreases below the working temperature, reaching a maximum value, after which further decrease in temperature produces a rapid decrease in elongation.

Cold work produces a structure which simulates in many respects that of a very fine grain metal. The main cause of strain hardening is the slip interference resulting from the disregistry of slip planes at the boundaries of grain fragments. An additional cause of strain hardening is the disorganized layer of atoms at self stopping slip planes, and the additional amorphous metal generated at the old grain boundaries.

Chapter VII deals with compounds of metals, while Chapter VIII covers metallicsoli d solutions and their physical properties.

The constitution of alloys in Chapter IX devotes barely ten pages to the phase rule, but this is quite enough. The type binary diagrams are explained with adequate examples.

Chapter X on the structure and properties of aggregates discusses eutectics and their properties; the effect of rate solidification of cast alloys; the effect of heat on solid alloys; commercial heat treatments; cold working on aggregates and their recrystallization.

On p. 370 the summary of the grain-size inheritance in iron and carbon steel is given, in which many new points are brought out, the most important of which is that the ferrite and pearlite grain size is not inherited from the original austenite. The austenite grain boundaries are nearly always effaced through the Ar transformation.

The slip-interference theory of hardness is illustrated in the case of Duralumin in which the hard particles of the copper-aluminum compound act as keys to the slip planes.

In Chapter XI the slip-interference theory of hardening is set forth. It is pointed out that the cohesion of pure metals is entirely sufficient to account for the maximum hardness of the alloys of the metals. Mechanical failure under stress is usually premature and due to potential slip planes which allow sliding of one crystal fragment on another at loads much lower than the absolute cohesion. Any structural condition which interferes with this slip increases the strength and hardness and every known method of hardening metals can be explained by this principle of slip interference. The effective hardness is obtained by slip interference of very fine particles of a hard constituent.

The effect of a given amount of this hard constituent increases with the fineness of subdivision reaching a maximum at what is called the critical dispersion and this is probably the particle size having the characteristic properties of the crystalline substance. The atomic dispersion of solid solutions is less conducive to hardness. The manner in which the greatest degree of dispersion is produced is the limited decomposition of solid solutions.

The hardening of steel in Chapter XII is also new. In the past the constitution of steel has been a closed book to many because the experts have continued to fight about the nature of austenite, martensite, troostite and sorbite. We have had half a dozen theories of hardening and not one of them has been satisfactory—in fact, many of them have been foolish.

The slip-interference theory applied to the hardening of steel is so simple that it seems almost astonishing that it was not put forth years ago, but steel was put in a class by itself, and the nature of its hardening was considered as something abnormal. The increased strength and hardness of pearlite compared with pure iron are largely due to the increased resistance to slip brought about by the hard cementite. Martensite, troostite and sorbite all consist of ferrite and finely dispersed carbide particles. Sorbite and troostite are harder than pearlite because of the refining of the ferrite grains and the greater dispersion of the cementite particles. The greatly increased hardness of martensite is due to a still greater refining of the ferrite grains and the critical dispersion of the cementite particles.

Austenite contains carbon in solution as such. It is not there as dissolved cementite. Cementite only exists by precipitation from austenite.

This chapter ends with a discussion of high-speed steel whose properties are just as easily explained as those of ordinary steel and are based on the excess carbide present. The reason why high-speed steel does not suffer from grain growth through hardening at a white heat is due to obstruction of the residual carbide particles. The reason for its retention of hardness to a red heat is two-fold. The iron-tungsten carbide particles reach approximately the size for critical dispersion at about 600°C. Within the grain growth temperature range the carbide particles are present to obstruct the growth, and small grains are therefore retained. The second re-hardening is the austenite transformation into martensite. At this temperature, the iron-tungsten carbide forms in critical dispersion and its presence helps to keep the grain size of the new martensite small and key the slip planes of the ferrite grains. As the temperature is raised above 600° C grain growth in the alpha and particle growth of the carbide produce rapid softening similar to the corresponding change in carbon steel at lower temperatures.

In the above, an attempt has been made to emphasize some of the important points brought out in this book. To cover them all would take pages. In the past our books on metallography have been mainly for the specialists, and the everyday engineer did not know the language. This book has only one prerequisite—the little chemistry and physics we remember from our school work. It contains nothing but common sense and clear thinking, and has succeeded in taking all the mystery out of the science of metals.

Wm. Campbell

Mikrochemisches Praktikum. *By Friedrich Emich. 23×16 cm; pp. xiii+174. Munich: J. F. Bergmann, 1924.* During the past few years much has been done in the direction of devising new methods, and improving older ones for use in connection with what may, perhaps, be termed Micro-analytical Chemistry, and it is of interest in this connection to note that recently a Nobel prize was awarded to Prof. Pregl, who may be regarded as one of the founders of the modern technique. Notwithstanding this, and although one of the earliest comprehensive works dealing with Micro-Chemical Methods (by Theodore G. Wormley) was published as long ago as 1867, it cannot be said that these methods are very extensively adopted in the great majority of chemical laboratories. This appears to the writer to be due mainly to the sound instinct of Chemists, who prefer to rely upon methods in which the sources of experimental error are fewer and in which the limits of those errors are, in most cases, accurately known. At the same time, there are unquestionably many cases in which the Chemist is compelled to have recourse to operations involving the use of very small quantities of material, and in such cases the reference to a work such as the one under review will prove exceedingly helpful. Prof. Emich is well known as one of the leaders in this branch of work, and the present volume may be said at once to be worthy of its Author. It is clearly written, the illustrations are numerous and good, and unlike many of the works which are being published in Germany at the present time it is printed on reasonably good paper.

The book is divided into two parts, the first being a general section devoted to an admirable description of apparatus and methods, and the second a special part dealing with the application of those methods to a considerable number of selected examples. The latter include exercises in both inorganic and organic analysis, as well as in organic preparations When it is remembered that in qualitative micro-analysis the Author deals with methods capable as a rule of working with an amount of material of the order of 1/1000th milligramme and that in the quantitative work quantities not exceeding 2 to 10 milligrammes give trustworthy results, it will be understood that the nature of the apparatus and the experience of the operator are both factors of supreme importance. The Author does well, therefore, to insist upon the need for such an amount of practice as will ensure absolute proficiency in the carrying out of the methods he describes. In his own words—it is better to repeat a single reaction until complete mastery has been gained than to cover a larger amount of ground superficially—and with this all chemists who have had any experience of micro-chemical analysis will cordially agree. A number of 'micro-methods' for the determination of physical properties such as densities, molecular weights, refractive indices, melting points, boiling points, etc., are also described.

This little work may be warmly commended to the attention of Chemists, the great majority of whom at one time or another find themselves compelled to work with very small quantities of material, and who might, perhaps, with advantage make more frequent incursions into this field of chemical procedure. *A. Chaston Chapman*

Einführung in die Chemie der Komplex-Verbindungen (Wernersche Koordinationlehre) in elementarer Darstellung. *By R. Weinland. Second edition. Stuttgart: F. Enke, 1924. Price: 24 gold marks.* The co-ordination theory of chemical combination and molecular structure first established by Alfred Werner on the basis of his comprehensive researches on metal-ammines and extended by him and by other contemporaneous investigators to the most diverse types of complex substances has now found general acceptance by chemists and physicists as a useful working hypothesis in the development of chemical science.

On the experimental side the advances have been so rapid and extensive that an authoritative treatise classifying and correlating this vast accumulation of complicated data has become essential to all students of the subject. This need is met by the treatise under review which after five years now appears in a second and considerably enlarged edition.

The opening section of the book, which is devoted to mononuclear compounds having the co-ordination number six, contains copious references to the new classical metal-ammines and their derivatives. In the following chapters are found a very full description of complex substances, having co-ordination numbers other than six. From this section it will be seen that the co-ordination viewpoint extends to many types not generally regarded as having the nuclear structure. A case in point is the discussion of the chemical constitution of acetic and other organic acids, these substances being regarded as equilibrium mixtures of pseudo-acids and true acids, the latter being co-ordination compounds in which carbon has its lower co-ordination number, three. Another typical exposition of co-ordination is revealed in a later chapter on a new theory of acids and bases.

The chapter on inner-metallic complexes also has a wide interest since it includes references to metallic acetyl acetones and to such analytical reagents as dimethylglyoxime, nitroso-β-naphthol and "cupferron."

Werner foresaw a useful extension of his theory in explaining the characteristic properties of the lakes of mordant dyes and later investigations have confirmed his anticipation. On the biochemical side it is suggested that the outstanding features of haemoglobin and chlorophyll are those of highly complex co-ordination compounds, and another physiological significance of the theory is seen in the biuret reaction.

The intricate structures of polynuclear cations receive a geometrical explanation on the basis of conjugated tetrahedral and octahedral units. The important group of complex heteropoly acids (e.g., phospho-molybdic and phospho-tungstic acids), long-known and frequently employed in analysis, are shown to be capable of formulation on a general co-ordination plan.

The foundations of this theory were laid down before the electronic structure of atoms was fully recognised but it has been shown by Kossel and others that the co-ordination and electronic conceptions of chemical valency are complementary and not contradictory. Interesting generalisations on the stability of co-ordination compounds have been deduced by Ephraim and Biltz from a study of the dissociation of metal ammines and related compounds. Investigations of the absorption spectra of organic acids and their derivatives have confirmed the above mentioned co-ordination hypothesis regarding the structure of these carbon derivatives.

These physical confirmations of Werner's theory are dealt with in special chapters and throughout the test there are references to the evidence derived from determinations of electric conductivity. The treatise, however, makes no mention of the application of X-ray analysis to co-ordination compounds embodying the work of the Braggs and their co-workers in England and of Wyckoff and others in America. Another defect of the work, which can hardly fail to be noticed by English-speaking chemists, is the paucity of references to the relevant researches of American and British investigators, although in this respect the present edition shows some improvement on the first. Nevertheless, even now, in the few citations given, the author's source of information still appears to be the Centralblatt and not the original communications in the Journals of the American and British Chemical Societies. These omissions detract from the value of the name-index; moreover, the subject-index is a very inadequate guide to the enormous store of useful information contained in this handbook. But in spite of these blemishes which might easily be remedied in future editions, the whole work is a valuable handbook to the study of a fascinating although intricate branch of chemistry. *G. T. Morgan*

Über Azo-Indikatoren vom Typus des Methylgelb, Methylorange und Methylrot. *By A. Thiel, A. Dassler and F. Wulffken. Berlin: Gebrüder Bornträger. Price: 9 shillings, 4 pence.* This monograph in the 'Fortschritte der Chemie, Physik und physikalischen Chemie' deals with the optical absorption coefficients 'e' of the azo- indicators as measured by the König-Martens spectro-photometer. The 'isobathms' or graphs of 'e' against λ for each pH may be compared with the well-known 'acid' and 'alkaline' absorption curves of methyl orange, etc., and also with some (at various values of pH) recently published by Brode: J. Am. Chem. Soc., **46**, 581 (1924).

The 18 substituted aminoazo-compounds usually show in the yellow alkaline solutions a weaker absorption, with a maximum near 450 $\mu\mu$ and in the red acid solutions a stronger absorption with a maximum near λ = 500 $\mu\mu$. These 'isobathmic' curves at intermediate values of pH cut one another at 'isosbestic' points, or values at which 'e' is the same for all values of pH, excepting in most cases very high or very low values at which secondary colour changes take place. The isosbestic 'e' is that of the half-way change. 'Isochromates' or pH 'e' graphs when carried to values of pH which are not too far from pH½ (halfway change) are straight lines inclined at various angles to the pH axis (of course parallel to it at the isosbestic λ). The degrees of transformation of the indicators at each pH may be calculated by linear formulae using the absorption e_x at each λ and in particular independent values of $pH^{\frac{1}{2}} = \frac{e_A - e_B}{2}$ can be obtained. But pH½ = − log k_A (pk_A) or, if we regard the colou change as determined by the basic (optical constant, pH½ = pk_B/pk_W. For helianthin pk_A is 3.32 to 3.35 and the weighted mean is 3.40.

The amphoteric and tautomeric equilibria of the indicators are fully discussed. The solubilities of the helianthins and methyl red were determined by optical methods in solutions of varying acidity. From these were deduced the isoelectric points pH and the minima of solubility which occur at these points.

		p.helianthin	o.helianthin	o. methyl red	
pH	=	1.71	1.93	3.70	
$C \times 10^6$	=	3.0	8.45	0.78	mols/litre

The absorption of azobenzene p.sulphonic acid is not affected by change of pH. It is isosbestic at all values of λ. This curve of absorption, although somewhat weaker, resembles the absorption curves, in alkaline solution, of substances like p.oxyazobenzene which do not show a great change in acid solution, and also the alkaline curves of p.aminoazobenzene p' sulphonic acid, monomethyl orange etc., which show the characteristic indicator change. The author considers this common absorption of the yellow solutions to be due to azoid forms and not to second quinoid forms as stated by Hantzsch: Ber. **46**, 1537 (1912).

E. B. R. Prideaux

Isotopes. *By F. S. Aston. Second Edition 21×15 cm; pp. xi+182. New York and London: Longmans, Green and Co., 1924. Price: $3.50.* In the preface the author says that "the number of non-radioactive elements on the constitution of which direct experimental evidence has been obtained has risen from twenty-seven to fifty-three, a welcome additional weapon has been provided by the quantum theory of band spectra, and the problem of the separation of isotopes has been attacked systematically from many new points of view."

The chapters are entitled: introduction; the radioactive isotopes; positive rays; neon; the mass-spectrograph; analysis of the elements; the electrical theory of matter; isotopes and atomic numbers; the spectra of isotopes; the separation of isotopes.

Aston points out, p. 2, that we now reject the second part of Dalton's postulate that "atoms of the same element are similar to one another and equal in weight." Chemists "had to decide which hypothesis, Dalton's or Prout's they would adopt. There was little doubt as to the result of the decision and in due course Prout's theory was abandoned. It is interesting to consider the reasons which led to a decision which the subsequent history of science proves to have been as wise in principle as it was wrong in fact. The alternative views were—either an element was composed of atoms of identically the same weight, when in certain elements the weights of the individual atoms must be fractional, or these particular elements were composed of atoms of different weights mixed together, so that though the individual weights of the atoms would still be whole numbers their mean would be a fraction. It is almost inconceivable that the second alternative never occurred to philosophers during the time when the decision hung in the balance—indeed it was far more likely to be considered then than years later when Dalton's view had been generally accepted—but the objections to it were immediate and formidable. The idea that particles could behave in a practically identical manner even though they had different weights is not one that commends itself, *a priori*, to common sense, and as a working hypothesis for chemists it is as hopeless and indefinite as the simpler alternative is distinct and inspiring. Also it could be urged that the objections to the fractional weights of atoms were rather philosophic than practical. They were concerned with the structure of individual atoms and so might be, and wisely were, set aside till the time, distant enough it would then have seemed, when these hypothetical entities could be dealt with experimentally."

"By far the most important result of the measurements detailed in the foregoing chapters is that, with the exception of hydrogen, the weights of the atoms of all the elements measured, and therefore almost certainly of all elements, are whole numbers to a considerable accuracy, in most cases about one part in a thousand. Of course, the error expressed in fractions of a unit increases with the weight measured, but with the lighter elements the divergence from the whole number rule is extremely small. This enables the most sweeping simplifications to be made in our ideas of mass, and removes the only serious objection to a unitary theory of matter.

"The discovery of the electron, the proof that it was the same whatever the atom from which it was detached and, most important of all, the demonstration by Sir J. J. Thomson and others that electrical charges always possess the property of mass, gave us the key to the riddle of what these primordial atoms really are. The only serious obstacle, the fractional atomic weights, has now been removed so that there is nothing to prevent us accepting the simple and fundamental conclusion:—The atoms of the elements are aggregations of atoms of positive and negative electricity," pp. 108, 109.

"The whole number rule may be translated simply into a statement that the mean packing effect in all atoms is approximately constant, and the unit of mass 1 when O = 16 will be (mass of a packed proton) + ½ (mass of free electron) + ½ (mass of packed electron). The whole number rule is not, and never was supposed to be, mathematically exact, for this would imply an identical packing effect in the case of all atoms, an exceedingly improbable supposition.

"From the above considerations we should expect that divergence from the integral relation of mass between one normal element and another would be less than between a normal element and hydrogen. The latter is less than one percent and as the limit of accuracy of the mass-spectrograph is about one part in 1,000 it did not seem probable that divergence from the whole number rule between normal elements would be detected with any degree of certainty by means of that instrument.

"That this has been done in the case of the elements tin and xenon is due to a somewhat fortunate chance. The evidence obtained is as follows: Measurements of the lines of tin show that while their masses are integral within experimental error with regard to each other, yet when compared with the other lines on the plate they give values *less than whole numbers by 2 to 3 parts in 1,000.* This result would certainly have been suspected of being an experimental error had it not been for the residual xenon lines on the plate, and the appearance of the lines of tin monomethide amongst them. There are two strong xenon lines at 134, 136 which have been compared with the lines of mercury in previous experiments, and there is no reason to doubt that they are integral to about 1 in 1,000 The strongest tin monomethide line $S_n^{120}CH_3$ should lie evenly between these two lines. It is very clear that it does not do so, but, on the contrary, is shifted so far to the left as to coalesce partically with Xe^{134} so that the latter appears broadened. This marked asymmetry is repeated in another part of the plate taken with a stronger magnetic field.

"It seems impossible to imagine any instrumental defect which could give rise to this shift. There appears, therefore, to be no escape from the conclusion that tin and xenon cannot both obey the whole number rule. It is somewhat surprising that elements only differing by three units in atomic number should show so large a divergence. It seems probable that the divergence from the mean (O = 16) is greater in the case of tin than in that of xenon, but since the arithmetic sum of the two (supposing them to be of opposite signs) is only about three times the experimental error, satisfactory settlement of this point will have to be deferred till an instrument of higher precision is available," p. 120.

The negative evidence from the study of the atomic weights of chlorine, nickel, boron, and nickel is impressive and "supports the idea already put forward by the writer that the evolution of the elements must have been such as to lead to a proportionality of isotopes of the same element which was constant from the start, and, since we know of no natural process of separation, has remained constant ever since. The isotopes of lead formed by radioactive disintegration are exceptional. These substances have been produced continuously during the history of the earth's crust and are being so produced today. Although ordinary lead may consist of isotopes—which is practically certain—and these isotopes may be identical in every respect with those produced in the last stage of radioactive disintegration, yet there is no reason whatever to assume that ordinary lead is itself the accumulated result of these processes. It takes its place among the other ordinary elements and would doubtless have done so had thorium and uranium never existed." p. 142.

Aston does not believe in calling each isotope, as it is discovered, a new element. He believes in fixing the word element "now and for the future, as meaning a substance with definite chemical and spectroscopic properties which may or may not be a mixture of isotopes—in other words to associate it exclusively with the conception of atomic number. On that view there would be, corresponding to Moseley's numbers ninety-two possible elements, of which eighty-seven are known," p. 145.

Wilder D. Bancroft

Inorganic Physical Chemistry. *By G. H. Cartledge. 21×15 cm; pp. xv+463. Boston: Ginn and Company, 1924. Price: $4.80.* The group of undergraduates for whom this book is intended at the Johns Hopkins University includes the premedical students, besides those majoring in chemistry with a view to graduate or technical work in the subject. The book is divided into four parts. The first is entitled the nature of matter and the chapters are: the study of chemical composition; the nature of gases—kinetic theory; the nature of gases—ultimate particles; the determination of atomic weights; the nature of the atom. The second part deals with the nature of solutions, with three chapters on the molecular properties of solutions—vapor pressure, boiling and freezing points, osmotic pressure— and one chapter on the electrical properties of solutions. The nature of reactions is discussed in the third part, with one chapter on the speed of reactions, four chapters on equilibrium—the distribution laws and phase rule, reactions involving gases, ionization, valence equilibrium—and one chapter on energy in chemical changes. The last division is on applications and the six chapters are entitled: precipitates; precipitation by weak acids and weak bases; acidity and indicators; hydrolysis and titration; complex ions; oxidation and reduction.

The theory of the porous-plug experiment is given well, p. 34. The reviewer was pleased to find the definite statement, p. 54, that we know there are twice as many hydrogen atoms in the hydrogen molecule as in the hydrogen chloride molecule; but that it is an arbitrary assumption that there is only one hydrogen atom in the latter molecule. The student will undoubtedly remember the statement, p. 64, that "in the best vacuum we have ever obtained, one cubic millimeter contains three times as many molecules as there are inhabitants in the whole United States. There is a clear statement, p. 131, of the merits of the Cottrell boiling-point apparatus although Menzies' modification is not mentioned.

Under cause of osmotic pressure, p. 149, we read that "the pressure due to the inherent molecular motion of the solute molecules is called diffusion pressure. It is sometimes stated that osmotic pressure *is* the pressure due to the bombardment of the membrane by the solute molecules; but the latter is really the diffusion pressure and is *inherent* in the solution whether we insert a membrane or not, whereas the osmotic pressure is not a real pressure necessarily existing in the solution. It is realized only when we insert a membrane and try to prevent diffusion of the pure solvent into the solution."

In order to show that semipermeability is not a question of molecular sieves, the author cites, p. 150, Raoult's experiment with mixtures of ether and methyl alcohol, where methyl alcohol alone goes through pig's bladder and ether alone through rubber.

On p. 194 the author says that "old glass when worked in the flame often crystallizes more or less suddenly, that is, devitrifies. This is an indication of the slow change taking place during the years." One would like to believe this.

On p. 197 the author calculates that the reversible equilibrium between nitric oxide and its constituent elements is reached in 0.0004 seconds at 3000° and in twelve days at 1500°, while we can detect no change whatever at room temperature. The reviewer was delighted with the frankness of two statements on successive pages, pp. 295, 296. "As already stated, the law of mass action is rigidly true when we use activity terms . . . The activity of a substance is such a quantity as will give a true constant in an equilibrium equation when the other quantities are all known."

The reviewer was also glad to note, p. 309, that the mercurous ion is given as $\overset{\cdot\cdot}{Hg_2}$, which means that the formula of mercurous chloride is Hg_2Cl_2. Even so good a man as Mellor slipped up on this point.

There are of course some points which the reviewer would like to have seen expressed differently. It does not seem wise to say, p. 67, that "the determination of true atomic weights involves two distinct quantities: namely, the combining, or equivalent, weight and the valence. Valence is most simply defined as the number of equivalent weights of a substance contained in one atomic weight. In the case of the elements the fundamental relation may be stated thus:

$$\text{atomic weight} = \text{equivalent weight} \times \text{valence."}$$

The reviewer believes that the difference between Tweedledum and Tweedledee is fundamental and he would like to see the atomic weight (or ratio) deduced first, regardless whether one can really do it or not; then should come the valence, which makes the conception of equivalent weight the secondary one, the fundamental relation as Mr. Cartledge calls it becoming:

$$\text{atomic weight} \div \text{valence} = \text{equivalent weight.}$$

It is very questionable whether one should give the student, p. 121, Raoult's formula $(p_o\text{-}p)/p_o = x$ when one knows it is not right. The modern answer is that it agrees with the experiments better than the van't Hoff formula does; but, assuming this to be true, this is all the worse for the experiments.

The author cannot have meant to say, p. 157, that we get copper at the cathode when we electrolyze aqueous cupric chloride solution. We get cuprous chloride. On p. 398 the author says that indicators are for the most part very weak acids. This is rather unfair to methyl orange which is a distinctly important indicator and is a weak base so far as the color change goes, although Ostwald has never admitted this officially.

Barring some natural faults this is an excellent book. The author has thought out clearly what he wanted to do and has kept that always in mind.

Wilder D. Bancroft

THE ELECTRONIC CONCEPTION OF VALENCE AND HEATS OF COMBUSTION OF ORGANIC COMPOUNDS*

BY MORRIS S. KHARASCH AND BEN SHER

(Preliminary Communication)[1]

Introduction

The relation between the amount of heat given off by a substance upon combustion and its chemical constitution appears from its very conception to be of fundamental importance. An enormous amount of experimental work has been carried out in thermochemistry There has also been no lack of attempts to correlate the heats of combustion of the compounds with their chemical constitution. It is, of course, beyond the scope of this preliminary paper to review, even briefly, the various works upon the subject. Sufficient to say, however, that these attempts have not led to any definite concept as to the correlation of valence notions and the heats of combustion of organic compounds. Even the most recent paper on the subject[2] falls short in that direction. The latter attributes different values for the carbon to carbon and carbon to hydrogen linkages. The equations he sets up are rather complicated[3] and thus obscure the main issues involved.

Furthermore, the constants are applicable only to hydrocarbons and cannot be extended very readily to include other types of organic compounds, such as the alcohols, aldehydes, ketones, nitrogen and sulfur derivatives, etc.

It seemed, therefore, highly desirable to consider this problem not from the mathematical standpoint, evaluation of constants from simultaneous equations, as it has been handled before, but from the standpoint of our modern conception of valence. A statement of some of the concepts involved is given below in the form of postulates.

Statement of Postulates

Postulate 1. Heat of combustion is due to the liberation of energy in the interdisplacement[4] or shift of electrons between atoms or molecules.

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* Contribution from the Department of Chemistry of the University of Maryland.

[1] Read before the Organic Division of the American Chemical Society at the New Haven Meeting, April, 1923 and the Division of Physical and Inorganic Chemistry at the Washington Meeting, April, 1924.

[2] Swietoslawski; J. Am. Chem. Soc. 42, 1312 (1920).

[3] Swictoslawski gives the following equation of combustion of any hydrocarbon, C_nH_m:

$$(2n - \frac{m}{2})(y - w - 2z) - m(x - w - z - u) - A = 0$$

Where $(y - w - 2z)$ and $(x - w - z - u)$ represent the thermochemical characteristics of the atomic linkages C-C and C-H respectively, A denotes the molar heat of combustion of C_nH_m. In these equations w,z,u are constants while x and y are variables, depending on the structure of the hydrocarbons.

[4] We are using this rather inaccurate expression of the "number of electrons interdisplaced" in the sense that the electrons are displaced in the direction of the oxygen atom, or atoms. Furthermore, a direct consequence of this notion is that any system in which the relative position of the electrons, with respect to carbon and oxygen, is the same as in carbon dioxide, will not furnish any heat upon combustion. Throughout the paper the word "interdisplaced" is to be assigned the above meaning.

The heat of combustion of a substance is usually defined as the heat evolved in the oxidation of unit mass of the substance. In terms of our modern conception of valence, oxidation means the removal or the displacement of electrons. It should thus be possible to correlate, at least empirically, the heat of combustion with the total number of electrons that have been displaced.

Postulate 2. The heat of combustion of a compound is a function of the total number of electrons interdisplaced, and must be an integral multiple of the heat value given by one electron.

Thus, if we ascribe the heat liberated in the combustion of methane to the displacement of the electrons between the carbon and oxygen atoms, then the molar heat of combustion of methane would be X times 8, if X is the amount of heat[1] liberated by the interdisplacement of an electron between the carbon and oxygen atoms.

Postulate 3. The net amount of energy in the form of heat liberated by the interdisplacement of an electron from an arrangement such as exists in a methane type of molecule to that of the carbon dioxide type is approximately 26.05 Kg. Cal. per mole per electron[2].

On the above basis, we have only to consider two types of systems, viz., the methane and carbon dioxide systems, provided other concomitant changes are included in the constant. The constant, considered above, is characteristic only when the electrons migrate from an arrangement such as exists in the methane type of molecule to that existing in the carbon dioxide type. Therefore, if a pair of electrons in methane are displaced from the carbon, the constant will be applicable only to the six electrons that have retained their position near the carbon, for the two displaced electrons will give off a different amount of heat than the others.

It is understood, of course, that the value of X is made up of different factors. Presumably, the methane carbon in giving up an electron would absorb a certain amount of heat, Y, while the oxygen molecule in taking up an electron would liberate an amount of heat, Z. The important point, however, is the difference $Z - Y = X$, which quantity is constant if the electrons always traverse the same distance between the carbon and oxygen atoms. This value of X can, therefore, be easily obtained by dividing the experimentally determined value of the heat of combustion of methane by eight, the number of electrons displaced. Or, if we make the simple assumption that all saturated hydrocarbons contain an arrangement of electrons with respect to the carbon

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[1] For those not versed in the electronic concepts the following may serve as a very simple guide in estimating the total number of electrons present. Write the ordinary structural formula, then designate all the hydrogen atoms as positive, oxygen negative; the carbon atom will then have the reverse sign of the element attached to it. The sign between two carbon atoms is of no consequence. Make any one of them positive, the other will then have the opposite sign. Count, then, the number of negative signs, multiply that number by two, for each bond corresponds to a pair of electrons, and the value thus obtained gives the total number of electrons that have to be multiplied by X in order to give the heat of combustion. (See also, for additional information, Postulate 3 and the discussion under each heading).

[2] The sum total of the energy in the form of heat evolved by the interdisplacement of *one* electron in ergs is readily obtained from the above value, i. e. $(26050 \times 4.185 \times 10^7) \div 6.06 \times 10^{23} = 1.79 \times 10^{-12}$ ergs.

atoms similar to that of methane (see Postulate 5), an assumption which is well justified by the excellent agreement of the calculated and the experimentally determined values, then the value of X could be obtained by dividing the heat of combustion of the hydrocarbon by the total number of electrons interdisplaced. In evaluating X we have used the mean of the values of the heat of combustion of normal octane, determined by T. W. Richards and Jesse and by Zubow, namely 1302.9 and divided that by 50, the number of electrons interdisplaced when octane burns to carbon dioxide and water. The value, thus obtained, of the heat supplied by the interdisplacement of one electron, namely 26.05 Kg. Cal. per mole per electron, should then be immediately applicable to the calculation of heats of combustion of all types of saturated hydrocarbons.

Postulate 4. The displacement of the electrons from the methane arrangement to that of the carbon dioxide type occurs in stages.

This postulate is merely a corollary to the Bohr conception that around each atomic center there exists a "particular" set of orbits. The postulate concerns itself only with those orbits that lie outside the "normal" valence orbit and the displacement of the electrons from the valence orbit into outside orbits. From this standpoint, therefore, when we speak of the eight electrons of methane we refer to the eight valence electrons located in the "normal" valence shell.

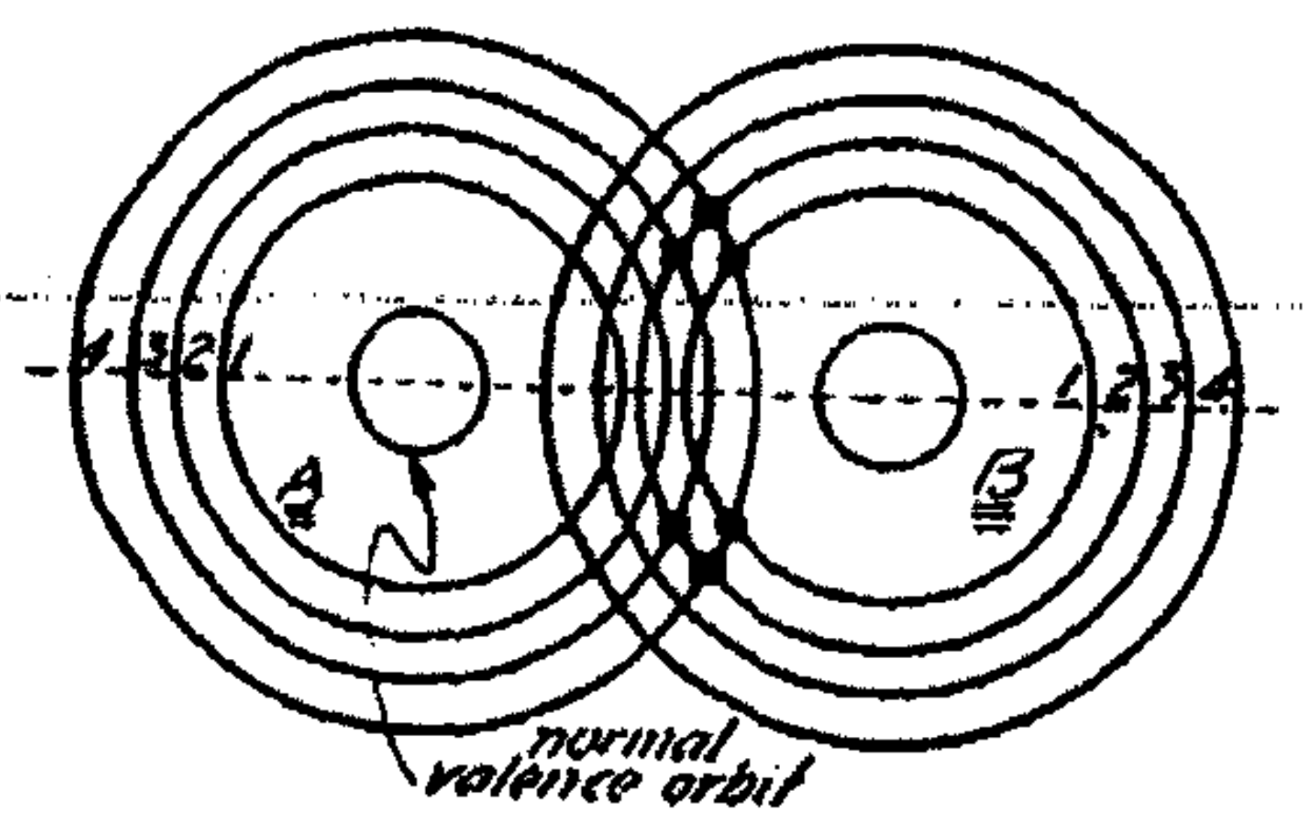

FIG. 1

The above postulate also implies that two atoms can share a pair of electrons in any of their respective orbits and that the kinetic and potential energy of the system will depend, therefore, upon the electronic structure of the molecule. To make clearer the meaning implied by this last statement let us consider the following case. Let Figures A and B represent only the orbits of two atoms, A and B, of a molecule.

The orbits intersect and the two atoms can hold a pair of electrons in common at the points of intersection of any two orbits. The position of these shared electrons with respect to their individual valence orbit will depend upon the affinity of the two atoms for electrons and the nature of the other atoms attached to A and B. Thus, if the atom B has a greater affinity for electrons than atom A, we may assume that the two electrons will be in the first orbit of B and the fourth orbit of A, as indicated by circles in the figure. Other positions are also possible, for instance, the second orbit of B and the fourth or third orbit of A, as indicated by squares on the figure. The two atoms may thus share a pair of electrons in such a way as to give rise to various degrees of polarity.

Presumably, the displacement of electrons from the valence orbit into outside orbits requires energy, while the reverse of this process liberates energy. The difference "X" (see Postulate 3) or the energy evolved in the interdisplacement of an electron from a valence orbit that it occupies in a methane carbon to that of a valence orbit that it occupies in carbon dioxide is thus really a summation of the energy differences evolved in the interdisplacement of the electrons through the various orbits. In the case of oxygen compounds, therefore, it is very easy to note that the farther the electrons are displaced from the carbon atom, the nearer they are to the oxygen atom, i. e., the nearer to an arrangement of a carbon dioxide type, and the smaller will be the energy liberated by the combustion of the compound. It is of great interest and importance that the different stages of polarity between atoms in organic compounds, as interpreted from the data on heats of combustion, can be readily correlated with the chemical properties of the compounds.

Postulate 5. The pair of electrons held together by two carbon atoms in saturated hydrocarbons may be considered midway between their respective normal valence shells and the orbit which the electrons occupy in carbon dioxide.

The total energy which they supply upon combustion is thus the same as if we had a pair of electrons held in the valence shell of one carbon atom of the methane type. (see Postulate 4.) This is a rather plausible assumption and one that is well justified by the agreement between calculated and observed values.

In all of our calculations, we shall treat, therefore, the pair of electrons held together by two carbon atoms as supplying the same amount of heat as a pair of electrons held in the valence shell of a methane carbon atom, and will refer to it in that sense.

Choice of data. It would be profitable now to examine the application of these simple postulates and see, first how they help to predict the heats of combustion of organic compounds, and secondly, how they supply an experimental basis for the determination of the factors that influence the chemical properties of the various types of organic molecules; for instance, the theoretical basis for the difference in the chemical properties of primary, secondary, and tertiary alcohols. The present paper will be devoted entirely to the first aspect of the problem, while a second paper by the one of us (Kh.) will be devoted to a correlation of heats of combustion and chemical properties of organic compounds. In choosing the experimental data for comparison with the calculated values of the heats of combustion, we were compelled to use only the data of a few observers; since the data of different observers do not agree well at all times. Whether the difference is due to faulty manipulation, such as incomplete combustion, impurities in the sample burned, etc., is not for us to decide. We have, therefore, been led to use only the data of the following observers: T. W. Richards and collaborators, Zubow (the corrected values given by Swietoslawski[1]), Stohmann and his collaborators, Roth, Fisher and Wrede, and a few others. Our calculations also refer to the amount of heat given off in Kg. Cal. per mole at constant pressure. All the data, except the results of Richards'

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[1] Swietoslawski: J. Am. Chem. Soc. 42, 1092 (1920).

investigations, and the data of Zubow, mentioned above, were taken from Landolt-Börnstein "Tabellen", 1912. The data are discussed under various heads such as saturated hydrocarbons, unsaturated hydrocarbons, primary alcohols, secondary alcohols, tertiary alcohols, acids, etc.

Saturated Hydrocarbons

The molecular heat of combustion of any saturated hydrocarbon is given by the formula: $H = 26.05 \times N$; where H is the heat of combustion in Kg. Cal. per mole of the substance; 26.05 Kg. Cal. represents the amount of heat liberated by the interdisplacement per electron per mole from an orbit of a methane type to that of a carbon dioxide type (see Postulates 2 and 3) and where N is the number of electrons in the molecule that have the same position around the carbon atoms as in methane. This exceedingly simple calculation is based upon the assumption that all saturated hydrocarbons have an arrangement of electrons with respect to the carbon atom similar to that of methane. (see Postulate 5.) This assumption is well justified by the excellent agreement between the calculated and experimentally determined values[1].

The molecular heats of combustion of eighteen saturated hydrocarbons are given in Table I. In no case, except the three compounds (15, 16, 17) does the difference between the calculated and observed values exceed 0.3 to 0.4 percent. We believe that the heats of combustion of these hydrocarbons would bear reinvestigation. Swietoslawski also recommends that in the article we have referred to previously.

Comparison of our formula for saturated hydrocarbons with the formulae of Clarke[2] and Swietoslawski[3]. It is not claimed by us that better agreement between the calculated and experimentally determined values for saturated hydrocarbons is obtained by the use of our formula over that of Swietoslawski, for the agreement in both cases is well within the limits of experimental error. We find also that the compounds 15, 16, 17 (Table I), which according to our

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[1] It is understood that this constant is applicable to combustions of carbon compounds in which the electrons are interdisplaced in the direction of the valence shells of oxygen atoms, but would not necessarily hold whenever other atoms are used as oxidizing agents. While the principle involved in the combustion of compounds with other oxidizing agents, say chlorine, is the same as with oxygen, a different amount of heat would presumably be evolved. It would be of great theoretical interest and significance to ascertain whether there is such a difference. The latter of course, would not invalidate any of the concepts developed, but, instead of 26.05 Kg. Cal. per electron per mole, some other constant would have to be used to designate the amount of heat evolved in the interdisplacement of one electron between the two atoms or molecules. Instead of actually determining the heats of combustion of compounds, in chlorine, one might attain the same results by the combustion of compounds containing what we ordinarily call "positive chlorine", namely chloramides, chloramines, etc., in oxygen. From the values thus obtained it would be a very simple matter to calculate the heat effect due to the interdisplacement of electrons between the carbon or nitrogen atoms and the chlorine atom acting as the oxidizing agent. This point will be discussed more thoroughly in a later paper by the one of us (Kh.).

[2] F. W. Clarke: Proc. Wash. Acad. Science, Vol. 5 (1903).

[3] $(2n - \frac{m}{2})(y - w - 2z) - m(x - w - z - u) - A = 0$

TABLE I

Saturated Hydrocarbons

Name	Number of Electrons	Calculated	Observed	% Difference
1 N. Hexane	38	989.9	992.4 St. Kl.	−0.3
			989.8 Zub.	0.0
2 N. Octane	50	1302.5	1302.7 Zub.	0.0
			1303.1 Rich., Je.	0.0
3 2-Methyl heptane	50	1302.5	1304.5 Rich., Je.	−0.2
4 2,5-Dimethyl hexane	50	1302.5	1301.7 Rich., Je.	+0.1
5 3,4-Dimethyl hexane	50	1302.5	1302.3 Rich., Je.	0.0
6 3-Ethyl hexane	50	1302.5	1300.9 Rich., Je.	+0.1
7 Hexadecane	98	2552.1	2562.7 St.	−0.4
8 N. Decane	62	1615.1	1610.2 Zub.	+0.3
9 Methyl cyclobutane	30	781.5	784.2 Zub.	−0.3
10 Methyl cyclopentane	36	937.8	937.9 Zub.	0.0
11 Cycloheptane	42	1094.1	1087.3 Zub.	+0.6
12 Cyclohexane	36	937.8	936.3 Zub.	+0.2
			937.5 Rich., Je.	0.0
			938.8 Rich., Je.	−0.1
13 Methyl cyclohexane	42	1094.1	1091.8 Zub.	+0.2
14 1,1-Dimethyl cyclohexane	48	1250.4	1242.5 Zub.	+0.7
15 1,3-Dimethyl cyclohexane	48	1250.4	1238.0 Zub.	+1.0
16 1,4-Dimethyl cyclohexane	48	1250.4	1228.8 Zub.	+2.5
17 1,3,3-Trimethyl cyclohexane	54	1406.7	1394.7 Zub.	+0.9
18 1,3-Dimethyl cyclopentane	42	1094.1	1090.7 Zub.	+0.3

calculation show a deviation of over one percent, show the same deviation according to Swietoslawski's formula, and Swietoslawski even states that the experimental values of these compounds must be in error. What we do wish to emphasize is that the formula employed by Swietoslawski is quite complicated, containing three constants and two variables, and also that there is no definite physical meaning to the terms in the equation. Furthermore, Swietoslawski's formula can be used only in the calculation of saturated hydrocarbons but cannot be extended to include other types of molecules, ethylene and acetylene compounds, etc.

The equation of Clarke is not only subject to the same objections as the equation of Swietoslawski, but to a number of others. Thus, Clarke gives the following equation for the heat of combustion of any hydrocarbon; saturated, ethylene, and acetylene:

$$\frac{4\,K}{12\,a + 6B - c - 8\,n} = \text{Constant}$$

where "K" represents the heat of combustion of any hydrocarbon; "a" the number of CO_2 molecules produced; "B" the number of molecules of gaseous H_2O; "C" the number of oxygen molecules dissociated during combustion, and "n" the number of atomic unions or likings in the single molecule of the compound burned. The rigid application of this equation to ethylene or acetylene compounds leads to an absurdity—for it is necessary to assume that only one bond evolves heat, the extra bonds "being in abeyance and thermally inoperative." It is impossible to reconcile our views of unsaturated derivatives with such an assumption. Furthermore, Clarke states that the important "fundamental fact throughout is the union of an atom with an atom, the mode of combination, the structure, being an entirely subordinate affair." In accordance with our postulates it is primarily this mode of combination, or structure, which determines the heat of combustion. Clarke's formula also is entirely too laborious and on the whole it gives a poorer agreement between calculated and experimentally determined values than our formula. Furthermore, as will be shown in a later paper, all of the factors used in our formulae, in contradistinction from that of the other investigators mentioned, have a physical interpretation and can be correlated with the chemical properties of the various classes of organic molecules. The premises upon which our formula rests are thus entirely different from either that of Clarke or Swietoslawski, and the superiority of it is readily seen from application of it in the calculation of combustion of other types of organic molecules.

Unsaturated hydrocarbons. From the standpoint of the data of the heats of combustion of unsaturated derivatives the latter may be divided into two classes. First, the class of unsaturated compounds which contain an arrangement of electrons around the carbon atoms similar to the saturated hydrocarbons, i. e., share the electrons in such a manner as to produce the same heat effect (Type I), Secondly, the class of unsaturated derivatives which contain a pair of displaced electrons. To the first class belong all of the benzene hydrocarbons and conjugated systems; to the second class, the ethylene derivatives.

TABLE II

Unsaturated hydrocarbons (Type I)

Name	Number of Electrons	Calculated	Observed	% Difference
1 Benzol	30	781.5	782.3 Roth., Au.	−0.1
			781.8 Rich., Ba.	0.0
2 1,3-Dimethyl-dihydrobenzene	44	1146.2	1148.2 Zub.—	−0.2
3 Cycloheptene	40	1042.0	1049.9 Zub.	−0.7
4 Methyl-l-cyclohexene-1	40	1042.0	1040.9 Zub.	+0.1
5 Methyl-l-cyclohexene-3	40	1042.0	1042.6 Zub.	−0.1
6 Toluene	36	937.8	936.9 Rich., Ba.	+0.2
7 Ethyl benzene	42	1094.1	1089.8 Rich, Ba.	+0.4
8 Xylene (ortho)	42	1094.1	1090.2 Rich., Ba.	+0.4
9 Xylene (meta)	42	1094.1	1090.2 Rich., Ba.	+0.4
10 Xylene (para)	42	1094.1	1086.4 Rich., Ba.	+0.8
11 Mesitylene	48	1250.4	1251.9 St., Ro.	0.0
			1241.7 Rich., Ba.	+0.7
12 Propyl benzene	48	1250.4	1250.0 Gen.	0.0
			1244.6 Rich., Ba.	+0.5
13 Isopropyl benzene	48	1250.4	1251.6 Gen.	−0.1
			1245.5 Rich., Ba.	+0.4
14 Pseudocumene	48	1250.4	1238.8 Rich., Ba.	+1.0
15 Butyl benzene (tert.)	54	1406.7	1398.4 Rich., Ba.	+0.6
16 Naphthalene	48	1250.4	1236.0 Rich., Je.	+1.2
			1236.7 Fi., Wr.	+1.2
			1234.2 St., Kl., La.	+1.3
17 Pentamethyl benzol	60	1563.0	1555.5 St., Kl., La.	+0.5
18 Diphenyl	58	1510.9	1495.0 St., La.	+1.0
19 Diphenyl methane	64	1666.8	1656.6 St., Kl.	+0.7
			1660.9 Schmdl.	+0.4
20 1,6-Diphenyl hexadien-1,5	90	2344.5	2344.9 Roth.	0.0

TABLE II (continued)

Name	Number of Electrons	Calculated	Observed	% Difference
21 Triphenyl methane	92	2396.4	2388.7 Schmdl.	+0.3
			2381.7 St. Kl.	+0.6
22 Triphenyl methyl	91	2370.4	2381.0 Schmdl.	−0.5
23 Tetrahydrobenzol	34	885.7	894.0 Roth.	−0.9
			892.8 St. Kl.	−0.8
			891.2 Zub.	−0.6
24 Dihydrobenzol	32	833.6	848.6 St. La.	−2.0
			833.2 Zub.	0.0
25 2,4-Hexadien	34	885.7	886.1 Roth., Moo.	0.0
26 Laurolene	46	1198.3	1194.5 Roth.	+0.4
27 1-Methyl-3-methane cyclohexene-1	44	1146.2	1150.8 Roth.	−0.4
28 1,5-Dimethyl-3-methene cyclohexene-1	50	1302.5	1299.1 Roth., Peters	+0.3
29 1, Ethyl-5-dimethyl cyclohexene-1	50	1510.9	1506.7 Roth.	+0.3
30 Isobutenyl cyclohexene-1	56	1458.8	1463.5 Roth., Ell.	−0.3
31 1,5-Dimethyl-3-ethene cyclohexene-1	56	1458.8	1457.4 A., R., E.	+0.1
32 1,5-Dimethyl-3-isopropene-cyclohexene-1	62	1615.1	1610.9 Roth., Peters	+0.3

TABLE IIa

Unsaturated hydrocarbons (Type II)

1 Trimethyl ethylene	30	794.5	796.0 Zub.	−0.2
2 Hexylene	36	950.8	952.6 Zub.	−0.2
3 Camphene	56	1471.8	1469.4 A.,R.,E.	+0.2
4 Methylene cyclohexene	40	1055.0	1052.0 Roth.	+0.3
5 Ethylene cyclohexene	46	1211.2	1209.2 Roth.	+0.2
6 Sylvestren	56	1471.8	1466.5 A.,R.,E.	+0.4

The formula used in the calculation of the heats of combustion of unsaturated derivatives of the first type is therefore, the same as in the saturated hydrocarbons, namely $H = 26.05 \times N$. Table II gives the values for thirty-two unsaturated hydrocarbons of this type. On the whole the agreement is very striking and satisfactory[1].

The heats of combustion of unsaturated derivatives of the second type indicate that they contain a pair of electrons displaced from the carbon atom or atoms. Reference to the diagram of Postulate 4 will help to make this clear. For, in these molecules, two carbon atoms share one pair of electrons in the same manner as two carbon atoms of saturated hydrocarbons, but the second pair of electrons is removed from both of the nuclei. Thus, it can be located in shell 3 of atom A and shell 4 of atom B. The molecule will thus have an electric moment in that part of the molecule. Furthermore, since energy is required to move electrons from the normal valence shell of the carbon atom to shells outside the valence shell, that amount of energy should be considered in the calculation of the ethylene derivatives. The formula for the calculation of ethylene derivatives is therefore $H = 26.05 \times N + A$, where A is the amount of energy necessary to move a pair of electrons from the normal valence shell to the position they occupy in ethylene derivatives. This value of A we find to be a fraction of the constant employed: namely, 13 Kg. Cal. per mole. The equation for ethylene derivatives therefore, becomes: $H = 26.05 \times N + 13$. The values, for seven unsaturated hydrocarbons of Type II, are given in Table II (a). The agreement between the calculated and experimentally determined values is most gratifying.

Primary Alcohols, Ethers, Esters

We find, from the close agreement of the predicted and calculated values for the saturated and unsaturated hydrocarbons, that the application of the notion of the non-polar conception of valence to the calculation of heats of combustion is a very useful one. However, unless it can be extended to include all types of compounds, it would hardly be very advantageous over other formulae. In the case of alcohols, we run into considerable difficulty if the completely non-polar structure is used. However, if we make use of the concepts developed in postulate 4, namely, that when two atoms share a pair of electrons in common, the position of the electrons in the respective orbits of the atoms depends upon the affinity of the two atoms for electrons, the calculation is simplified once more[2].

It is quite evident that, owing to the great affinity of oxygen atoms for electrons, the pair of electrons binding the carbon and oxygen atoms in primary

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[1] It is most significant that for most benzene hydrocarbons the calculated value is somewhat higher than the experimentally determined value. This is due to a diminution of the energy of the system due to the benzene nucleus. Once this is taken into account in the calculation of the heat of combustion the agreement is then even more striking. It is omitted here in order to avoid confusion and will be discussed in detail in a later publication.

[2] It is necessary to assume on this basis that intramolecular oxidation-reduction reactions are accompanied by the evolution of heat.

alcohols will be in the inner shell of the oxygen atom (close to the normal valence shell) and in the outer shell of the carbon atom. The energy liberated by the combustion of a molecule of this type should, therefore, be smaller than that for the hydrocarbons, which is in accord with the experimental facts. However, the two displaced electrons in the alcohols do not occupy the same position with respect to the carbon and oxygen atoms as they occupy in carbon dioxide—in order to obtain that condition they have to be displaced still further from the carbon atom and thereby put nearer to the oxygen atom. This process liberates heat and the amount of heat liberated should be the same for all primary alcohols, unless the other groups present in the molecule affect the position of these electrons. Take, for instance, the case of methyl alcohol. The difference between it and methane is that two of the electrons have been displaced in the direction of the oxygen atom. If these two displaced electrons occupy, with respect to carbon and oxygen atoms, the same position as in carbon dioxide the heat of combustion of methyl alcohol should be

$$6 \times 26.05 = 156.3 \text{ Kg. Cal. per mole}$$

The value obtained experimentally is 170 Kg. Cal. per mole. This shows that the two electrons binding the oxygen and carbon atoms do not occupy the same position as in carbon dioxide and that the amount of energy, in the form of heat, which they liberate in attaining that position is equal to about 13 Kg. Cal. per mole. This should, therefore, be the correction factor for all primary alcohols and the heat of combustion of any primary alcohol is given by the expression $H = 26.05 \times N + 13$. We find the same formula to hold for aliphatic ethers and esters, of course, in the case of the ethers the constant enters twice, for in these molecules there are two such pairs of displaced electrons.

In the case of the aromatic ethers the effect of the benzene ring on the position of the electron must be considered. The concepts involved, however, are too complicated to be taken up in this preliminary communication. A very good agreement with the experimentally determined values is obtained though by the use of the formula given for primary alcohols. The justification for the useof this formula can be readily inferred from the heats of combustion of phenols. The results indicate (at any rate for the purpose of calculation of heats of combustion) that the position of the shared electrons between the carbon and oxygen atoms in phenols is very nearly the same as in carbon dioxide[1].

Tables III, IV and V give the values of ten primary alcohols, fifteen others, and twenty-five esters calculated on this basis. It will be noted that the agreement is very close with the values actually obtained, except in the case of unsaturated derivatives of the ethylene series. They are given again in Table IVa, with the correction allowed for in the case of unsaturated derivatives (see Table IIa); namely, thirteen is added to the value calculated on the non-polar basis.

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[1] See discussion under tertiary alcohols.

TABLE III
Primary Alcohols

Name	Number of Electrons	Calculated	Observed	% Difference
1 Methyl alcohol	6	169.3	170.61 Rich., Da.	−0.8
2 Ethyl alcohol	12	325.6	327.04 Rich., Da.	−0.4
3 Propyl alcohol	18	481.7	485.8 Rich., Da.	−0.1
4 Butyl alcohol	24	638.0	638.3 Rich., Da.	−0.1
5 Isobutyl alcohol	24	638.0	637.1 Rich., Da.	+0.2
6 Heptyl alcohol	42	1107.1	1104.0 Zub.	+0.3
7 Benzyl alcohol	34	898.7	895.8 St., Ro.	+0.4
			895.2 St., Kl., La.	+0.4
			892.3 Schmdl.	+0.8
8 Cyclobutyl carbinol	28	742.4	747.8 Zub.	−0.8
9 Cyclohexyl carbinol	40	1055.2	1047.2 Zub.	+0.8
10 Saligenin	32	846.6	846.4 B. Rie.	0.0

TABLE IV
Aromatic Ethers

Name	Number of Electrons	Calculated	Observed	% Difference
1 Anisol	34	898.7	906.0 St., La.	−0.9
			901.8 St., Ro.	−0.4
2 Phenetole	40	1055.0	1057.9 St. Ro., H.	−0.2
3 M-Cresol methyl ether	40	1055.0	1058.0 St., Ro., H.	−0.3
4 Hydroquinone dimethyl ether	38	1016.0	1015.7 " " "	0.0
5 Resorcin dimethyl ether	38	1016.0	1023.6 " " "	−0.7
6 Phenyl propyl ether	46	1212.3	1214.3 " " "	−0.2

TABLE IV (continued)

Aromatic Ethers

Name	Number of Electrons	Calculated	Observed	% Difference
7 p-Cresol ethyl ether	46	1212.3	1214.0 St., Ro., H.	−0.2
8 m-Xylenyl methyl ether	46	1212.3	1214.6 " " "	−0.2
9 p-Xylenyl ethyl ether	52	1367.6	1369.9 " " "	−0.2
10 Thymol methyl ether	58	1523.9	1525.8 " " "	−0.2
11 Methyl chavicol*	50	1315.5	1335.9 St., La.	−1.5
12 Anethole*	50	1315.5	1325.1 St., La.	−0.8
13 α-Ethoxy styrol	50	1315.5	1316.2 Roth	−0.1
14 Eugenol*	48	1263.4	1287.8 St., La.	−1.8
15 Isoeugenol*	48	1263.4	1278.8 St., La.	−1.2

TABLE IVa

Aromatic Ethers

Name	Number of Electrons	Calculated	Observed	% Difference
1 Methyl chavicol	50	1328.5	1335.9 St., La.	−0.6
2 Anethole	50	1328.5	1325.1 St., La.	+0.3
3 Eugenol	48	1276.4	1287.8 St., La.	−0.9
4 Iso-eugenol	48	1276.4	1278.8 St., La.	−0.2

TABLE V

Esters

Name	Number of Electrons	Calculated	Observed	% Difference
1 Methyl iso-butyrate	26	690.3	693.4 Rich., Je.	−0.5
2 Dimethyl acrylic methyl ester*	30	794.5	805.2 Roth	−1.3
3 Methyl benzoate	36	950.8	944.4 St., Ro., H.	+0.7
4 Methyl p-oxybenzoate	34	898.7	896.3 St., Kl., La.	+0.2

TABLE V (continued)

Esters

Name	Number of Electrons	Calculated	Observed	% Difference
5 Methyl salicylate	34	898.7	899.2 St., Ro., H.	−0.2
6 Methyl anisate	40	1068	1069.8 St., Kl., La.	−0.2
7 Methyl ester cyclo-hexenyl-acetic acid	46	1211.3	1211.3 Roth., Ell.	0.0
8 Cyclohexylidene acetic methyl ester*	46	1224.3	1217.7 Roth., Ell.	+0.5
9 Methyl cinnamate	46	1211.3	1214.2 St., Kl., La.	−0.3
10 Methyl pinonate	56	1481.8	1478.8 Roth., O.	+0.2
11 Dimethyl carbonate	12	338.6	340.8 Zub.	−0.7
12 Diethyl carbonate	24	651.2	647.9 Zub.	+0.5
13 Ethyl sorbate*	38	1002.9	1013.0 Roth.	−1.0
14 Ethyl benzoate	42	1107.0	1099.8 St., Ro., H.	+0.6
15 Ethyl salicylate	40	1055.0	1052.3 St., Ro., H.	+0.3
16 Ethyl p-oxybenzoate	40	1055.0	1043.0 St., R., H.	+1.2
17 Cyclo hexenyl acetic ethyl ester	52	1367.6	1361.7 Roth.	+0.4
18 Propyl benzoate	48	1263.4	1255.8 St., Ro., H.	+0.6
19 Propyl p-oxybenzoate	46	1211.3	1201.8 St., Ro., H.	+0.8
20 Propyl salicylate	46	1211.3	1206.9 St., Ro., H.	+0.4
21 Iso butyl benzoate	54	1419.7	1412.8 St., Ro., H.	+0.5
22 Iso butyl salicylate	52	1367.6	1366.9 St., Ro., H.	+0.1
23 Amyl benzoate	60	1576.0	1571.1 St., Ro., H.	+0.3

Secondary and Tertiary Alcohols, Phenols, and Polyhydroxy Alcohols

On the basis of the same concept as that developed for primary alcohols, we estimate that the two electrons binding the carbon and oxygen atoms, in secondary alcohols, are not completely displaced in the direction of the oxygen atom, i. e., they do not occupy the same positive relation to the carbon and oxygen atoms as in carbon dioxide. In the combustion of the compound and the displacement of this pair of electrons in the direction of the oxygen atom a certain amount of heat is evolved. We find that amount to be equal to 6.5 Kg. Cal. per mole. The heat of combustion of secondary alcohols is, therefore, given by the expression $H = 26.05 \times N + 6.5$.

It is self-evident that for polyhydroxy alcohols a combination of the formula for primary and secondary alcohols should be used, namely

$$H = 26.05 \times N + 13a + 6.5b$$

where a and b are respectively the number of primary and secondary alcohol groups in the molecule.

In the case of tertiary alcohols and phenols the pair of electrons holding the carbon and oxygen atoms may be assumed, for the purpose of calculation of heats of combustion, to occupy the same relative position with respect to carbon and oxygen atoms as in carbon dioxide. This pair of electrons, therefore, does not supply any heat upon combustion. The authors appreciate the fact that this statement is not rigidly correct, since the data warrant such an assertion only to the extent that the displacement of the electrons toward the oxygen atom in tertiary alcohols is much more complete than in the case of primary or secondary alcohols. The results obtained, however, on the basis of a complete transfer of the electrons are quite satisfactory, although they do not preclude the possibility of a slight non-polarity (say three Kg. Cal. per mole). We have not made that correction, however, for the data in most cases are not sufficiently accurate, although we believe it should be applied. The heat of combustion of any tertiary alcohol or phenol[1] is, therefore, given by the expression (1) $H = 26.05 \times N$, or (2) $H = 26.05 \times N + 3.5$. In our calculations we made use of formula 1.

The values for a number of compounds are given in Tables VI, VII and VIII. The agreement between the calculated and observed values, in the case of the 35 compounds calculated, is good. In only a few cases does the error exceed five-tenths of one percent[2].

Ketones

In the case of ketones we find that the four electrons holding the carbon and oxygen atoms do not occupy relatively the same position as in carbon diox-

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[1] See footnote, p. 629. We might mention also that the numerical values obtained by the introduction of the new concept into the formula are better than those given in Table VII. As stated before, these points will be elaborated upon in a latter paper by Kharasch.

[2] Where the difference is rather large, one percent or so, it is evident from the structure of the compound that considerable difficulty would be experienced in obtaining it in pure condition.

TABLE Va

Esters

Name	Number of Electrons	Calculated	Observed	% Difference
1 Dimethyl acrylic methyl ester	30	807.5	805.2 Roth	+0.3
2 Cyclohexylidene acetic methyl ester	46	1224.3	1217.7 Roth	+0.6

TABLE VI

Secondary Alcohols

Name	Number of Electrons	Calculated	Observed	% Difference
1 Pinacoline alcohol	36	943.8	938.6 Zub.	+0.6
2 Diallyl carbinol*	38	995.9	1028.0 Zub.	−3.3
3 Cycloheptanol	40	1048.5	1050.2 Zub.	−0.2
4 β-methyl cyclopentanol	34	891.7	887.6 Zub.	+0.5
5 Cyclohexanol	34	891.7	889.8 Zub.	+0.2
6 1,3-Dimethyl cyclohexanol-2	46	1204.3	1196.0 Zub.	+0.7

TABLE VII

Tertiary Alcohols and Phenols

Name	Number of Electrons	Calculated	Observed	% Difference
1 Trimethyl carbinol	24	625	629.3 Zub.	−0.7
2 Dimethyl ethyl carbinol	30	781.5	784.6 Zub.	−0.4
3 Allyl methyl ethyl carbinol*	40	1042.0	1050.1 Zub.	−0.5
4 Triethyl carbinol	40	1094.1	1080.0 Zub..	+1.4
5 1,3-Dimethyl cyclohexanol (3)	46	1198.3	1192.5 Zub.	+0.5
6 Ethyl dipropyl carbinol	54	1406.7	1386.0 Zub.	+1.4
7 Phenol	28	729.4	732.9 St., La.	−0.5

TABLE VII (continued)

Tertiary Alcohols and Phenols

Name	Number of Electrons	Calculated	Observed		% Difference
8 Catechol	26	677.3	685.5	St., La.	−1.3
9 Resorcinol	26	677.3	683.7	St., La.	−1.0
10 Hydroquinone	26	677.3	683.6	St., La.	−1.0
11 Phloroglucinol	24	625.2	617.9	St., La.	+1.2
12 o-Cresol	34	885.7	883.5	St., Ro., H.	+0.3
13 m-Cresol	34	885.7	881.4	St., Ro., H.	+0.5
14 p-Cresol	34	885.7	883.4	St., Ro., H.	+0.3
15 o-Xylenol	40	1042.0	1036.1	St., Ro., H.	+0.6
16 m-Xylenol	40	1042.0	1038.4	St., Ro., H.	+0.4
17 p-Xylenol	40	1042.0	1036.3	St., Ro., H.	+0.6
18 Pseudocumenol	46	1198.3	1192.4	St., Ro., H.	+0.5
19 Thymol	52	1354.6	1354.1	St., Ro., H.	0.0
20 Carvacrol	52	1354.6	1355.8	St., Ro., H.	−0.1
21 Diphenyl carbinol	62	1615.1	1616.9	St., La., Kl.	−0.1
			1614.8	Schmdl.	+0.1
22 Triphenyl carbinol	90	2344.5	2343.0	St., Kl., La.	0.0

TABLE VIa

1 Diallyl carbinol	38	1021.9	1028.0	Zub.	−0.6

TABLE VIIa

1 Allyl methyl ethyl carbinol	40	1055.0	1050.1	Zub.	+0.5

TABLE VIII

Poly Hydroxy Alcohols

Name	Number of Electrons	Calculated	Observed	% Difference
1 Glycerine	14	396.7	397.3 St., La.	−0.2
2 Erythrit	18	508.9	504.8 St., La.	+0.4
3 Pentaerythrit	24	656.2	661.9 St., La.	−0.9
4 Arabit	22	617.1	612.4 St., La.	+0.8
5 Mannit-d	26	727.3	728.3 St., La.	−0.2
6 Dulcit	26	727.3	729.9 B., Vi.	−0.3
			724.4 St., La.	−0.5
7 Perseit	30	837.5	836.6 St., La.	+0.1

TABLE IX

Ketones

Name	Number of Electrons	Calculated	Observed	% Difference
1 Methyl ethyl ketone	22	579.1	582.3 Zub.	−0.6
2 Diethyl ketone	28	735.4	735.6 Zub.	0.0
3 Methyl propyl ketone	28	735.4	734.6 Zub.	+0.1
4 Methyl isopropyl ketone	28	735.4	733.9 Zub.	+0.2
5 Pinakoline	34	891.7	891.8 Zub.	0.0
6 Methyl butyl ketone	34	891.7	895.2 Zub.	−0.4

TABLE IX (continued)

Ketones

Name	Number of Electrons	Calculated	Observed	% Difference
7 Ethyl allyl ketone*	32	839.6	858.1 Roth.	
8 Allyl acetone*	32	839.6	857.7 Roth.	
9 Dipropyl ketone	40	1048.0	1050.5 Zub.	−0.2
10 Methyl hexyl ketone	46	1204.3	1205.1 Zub.	−0.1
11 Diallyl acetone*	48	1256.4	1282.3 Roth., Moo.	
12 Acetyl trimethylene*	26	683.3	691.0 Zub.	
13 β-methyl cyclo pentanone	32	839.6	833.4 Roth., Moo.	+0.8
14 Acetyl cyclo butane	32	839.6	856.8 Roth., Moo.	+1.9
15 β-methyl cyclo hexanone	38	995.9	994.8 Zub.	+0.1
16 Cyclo heptenone	38	995.9	996.7 Zub.	+0.1
17 Ethyl cyclo pentenone	38	995.9	990.4 Zub.	+0.5
18 1,3-Dimethyl cyclo pentenone	38	995.9	989.8 Zub.	+0.6
19 1,3-Dimethyl cyclo hexenone	42	1100.2	1102.2 Zub.	−0.2
20 1,3-Dimethyl cyclo hexanone	44	1152.7	1129.8 Zub.	+2.0
21 1,1,5-Trimethyl-cyclo hexanone	48	1256.4	1248.4 Zub.	+0.7

TABLE IXa

Name	Number of Electrons	Calculated	Observed	% Difference
1 Ethyl allyl ketone	32	852.6	858.1 Roth.	−0.7
2 Allyl acetone	32	852.6	857.7 Roth.	−0.6
3 Diallyl acetone	48	1282.4	1282.3 Roth.	0.0
4 Acetyl trimethylene	26	696.3	691.0 Zub.	+0.8

ide. The amount of heat liberated before that condition is attained is equal to 6.5 Kg. Cal. per mole. Whether this heat value is due to one or to two pairs of displaced electrons cannot be ascertained from the heat of combustion. The behaviour of ketones from a chemical standpoint, i. e., absorption reactions of different ketones, etc., throws considerable light upon this subject (See particularly postulates 4 and 5) and will be dealt with in a later paper.

The heat of combustion of ketones is, therefore, given by the formula

$$H = 26.05 \times N + 6.5$$

the same expression as used in the case of secondary alcohols.

The agreement is excellent in eighteen of the twenty-one ketones given. Those marked with an asterisk, namely, ethylene derivatives, are also given in Table IXa, with the usual correction for ethylene derivatives. A number of ketones given in the "Tabellen" have been omitted here, not because they do not agree with the calculated values, but merely on account of their compexity. It seemed to us that the chances of obtaining compounds in pure condition are greater for the simpler compounds than the very complex ones, and for the purpose of checking up on the hypothesis advanced, we have selected compounds with that end in view.

Acids

The heat of combustion of acids is given by the expression $H = 26.05 \times N$. This formula implies that the electrons binding the carbon and oxygen atoms in the carboxyl group have an arrangement of electrons similar to that existing in carbon dioxide and, therefore, do not supply any heat upon combustion. (See however, the discussion under tertiary alcohols.) It will also be noticed that in the case of the acids that are liquids the percent difference is negative, i. e., the calculated values are slightly lower than the experimentally determined values, while in the case of the acids that are solids the calculated values are higher than the experimentally determined values. The reason for this is fairly obvious: the constant used in the formula refers to the heat of combustion in the liquid state, and to obtain the heat of combustion of a solid the heat of fusion of the compound should be subtracted from the value calculated according to the formula. Unfortunately, the heats of fusion of most of the compounds given in the tables are unknown and thus, it is impossible to apply the correction. However, it has been noticed in the case of the acids whose heats of fusion have been determined experimentally, that the values of the heats of fusion of these compounds are approximately one half percent of their total heat of combustion. Once this fact is taken into account the already striking agreement between the calculated and experimentally determined values is brought out more conspicuously.

Some important relationships between cis and trans isomers from the standpoint of their energy values are also apparent. Thus, we find that the cis isomer has a heat of combustion larger than the trans isomer by 6.5 Kg. Cal. per mole. This important phase of cis-trans isomerism from the stand-

TABLE X
Acids

Name	Number of Electrons	Calculated	Observed		% Difference
1 Propionic	14	364.7	367.6	St., Kl., La., Off.	−1.0
2 Butyric	20	521.0	525.8	St., Kl., La., Off.	−0.8
3 N-valeric	26	677.3	682.3	St., Kl., La., Off.	−0.8
4 Caproic	32	837.6	839.2	Fi., Wr.	−0.3
			838.2	St., Kl., La., Off.	−0.2
5 Isobutyl acetic	32	833.6	838.2	St., Kl., La.	−0.5
6 Diethyl acetic	32	833.6	838.2	St., Kl., La.	−0.5
7 Ethyl propyl acetic	38	989.9	995.5	St., Kl., La.	−0.7
8 Dipropyl acetic	44	1146.2	1152.8	St., Kl., La.	−0.6
9 Lauric	68	1771.4	1773.5	St., La.	−0.1
10 Palmitic	92	2397.1	2400.8	St., Kl.	−0.2
11 Glycollic	6	169.3	166.8	St., Kl.	+1.5
12 Crotonic*	18	468.9	479.2	St., Kl.	
			478.2	St., Kl.	
13 Tiglic*	24	625.2	627.0	St., Kl.	
14 Angelic*	24	625.2	635.2	St., Kl.	
15 Allyl acetic*	24	625.2	642.3	Roth., Ell.	
16 Laevulinic	22	573.1	577.4	B., Thch.	−0.7
17 Hydrosorbic acid*	30	782.5	796.2	Fi., Wr.	
18 Sorbic*	28	729.4	743.7	St., La.	
			744.8	Fi., Wr.	
19 Geranic*	52	1365.6	1380.5	Roth., Moo.	
20 Oxalic	2	52.1	60.2	St., Kl., La.	

Table X (continued)

Acids

Name	Number of Electrons	Calculated	Observed	% Difference
21 Malonic	8	208.4	207.4 St., Kl., La.	+0.5
22 Succinic	14	364.7	357.0 St., Kl., La.	+2.0
23 Methyl malonic	14	364.7	362.6 St., Kl., La.	+0.7
24 Glutaric	20	521.0	515.2 St., Kl.	+1.1
25 Ethyl malonic	20	521.0	518.2 St., Kl., La.	+0.6
26 Diethyl malonic	32	833.6	833.4 St., Kl., La., Off.	0.0
27 Pimelic	32	833.6	823.1 St., Kl., La.	+1.2
			828.3 St., Kl.	+0.6
28 Citric	18	474.9	475.0 St., Kl., La.	0.0
29 Ethyl propyl malonic	38	989.9	989.5 St., Kl., La.	0.0
30 Azelaic	44	1146.2	1142.0 St., Kl., La.	+0.4
31 Dipropyl malonic	44	1146.2	1146.9 St., Kl., La., Off.	0.0
32 Heptyl malonic	50	1302.5	1303.7 St., Kl., La., Off.	−0.1
33 Fumaric*	12	312.6	320.3 St., Kl., La.	
			319.7 Roth.	
34 Maleic*	12	312.6	326.4 St., Kl., La.	
35 Itaconic*	18	463.9	476.1 St., Kl.	
36 Citraconic*	18	468.9	487.9 St., Kl.	
37 Mesaconic*	18	468.9	477.4 St., Kl.	
38 α,β-hydromuconic	24	625.2	629.4 St., Kl.	−0.7
39 β,γ-Hydromuconic	24	625.2	629.7 St., Kl.	−0.7
40 Allyl malonic*	24	625.2	638.4 St., Kl.	
41 Aconitic	18	468.9	475.6 St., Kl., La., Off.	−1.8
42 Capric (act)	32	833.6	831.0 Zub.	+0.3

TABLE X (continued)

Acids

Name	Number of Electrons	Calculated	Observed	% Difference
43 Cyclohexane-carbon acid	36	937.8	934.0 Zub.	+0.3
44 Hexahydro-m-tolyl acid	42	1094.1	1086.2 Zub.	+0.8
45 Cyclooctane acid (act)	42	1094.1	1089.2 Zub.	+0.5
46 Cycloheptane acid	42	1094.1	1087.9 Zub.	+0.6
47 Trimethylene-carbon acid*	18	468.9	483.7 Zub.	
48 Cyclobutane carbon acid*	24	625.2	639.2 Zub.	

TABLE Xa

Name	Number of Electrons	Calculated	Observed	% Difference
1 Crotonic	18	481.9	479.2 St., Kl.	+0.6
			478.2 St., Kl.	+0.7
2 Angelic	24	638.2	635.4 " "	+0.5
3 Allyl acetic	24	638.2	642.3 Roth., Ell.	−0.7
4 Hydrosorbic	30	795.5	796.2 Fi., Wr.	−0.1
5 Fumaric	12	325.6	319.7 Roth.	+1.8
			320.3 St., Kl., La.	+1.6
6 Maleic	12	325.6	326.4 St., Kl., La.	−0.3
7 Itaconic	18	481.9	476.1 St., Kl.	+1.2
8 Citraconic	18	481.9	487.9 St., Kl.	−1.0
9 Mesaconic	18	481.9	477.4 St., Kl.	+1.0
10 Allyl malonic	24	638.2	638.4 St., Kl., La.	0.0
11 Trimethylene carbon acid	18	481.9	483.7 Zub.	−0.4
12 Cyclobutane acid	24	638.2	639.2 Zub.	−0.2

point of the concept developed in postulate 4 will be dealt with in a later paper by Kharasch. In this preliminary communication no stress has been put upon that point in order not to complicate unduly the fundamental concepts developed.

Nitro Compounds

The close relationship between nitro compounds and amines, and the fact that the latter can be made from the former, prompts us to take up first the discussion of the nitro compounds. We have tacitly assumed, in all of our previous calculations, that the electrons holding atoms together can occupy any intermediate position between a "methane" arrangement of the electrons around the carbon to that of a "carbon dioxide" type. It is self-evident, that when two carbon atoms are concerned, the position of the two binding or valence electrons is immaterial from the standpoint of the total energy of the system. The heat of combustion of the system is the same irrespective of the position of the two electrons[1]. However, if an oxygen atom is introduced into the molecule then the position of the two electrons is of vital importance. If they are in the same position relative to the carbon atom as they were in the hydrocarbon, then we would expect that the heat of combustion of this system would be the same as that of the hydrocarbon. On the other hand, if they are displaced from that mean position in the direction of the oxygen atom—then the energy of the system should be lower. Thus, the heats of combustion of tertiary alcohols were found to be less than those of the corresponding hydrocarbons by an amount of heat corresponding to almost the complete displacement of two electrons from the carbon to the oxygen atom. In a sense, therefore, these compounds may be considered polar in that part of the molecule. In the case of primary alcohols, however, the electrons are not completely displaced in the direction of the oxygen atom. They can still give off 13 Kg. Cal. per mole before the displacement may be considered complete.

The considerations developed above are particularly instructive when one considers the case of nitro compounds. The nitrogen atom in these compounds does not evolve any heat upon combustion and we could omit it entirely from our calculations, if it were not for two factors involved: first, that the nitro group is attached to a carbon atom, and secondly, the fact that the nitro group acts as an oxidizing agent. The question then arises whether, when we treat, say, hexane with nitric acid to form nitro hexane, the two electrons, that held the hydrogen atom to the carbon atom have been displaced in the direction of the nitrogen atom. If they have been displaced in the nitration reaction a certain amount of heat must have been evolved and the heat of combustion of nitro hexane should be smaller than that of hexane. The experimental data point quite conclusively to the fact that such is the case, if we make the assumption that the sum total of heat evolved is the same when an electron is displaced from a carbon atom into the direction of the inner shells of an oxygen atom or a nitric acid nitrogen atom. This assumption is probably quantita-

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[1] See, however, footnote, p. 629.

tively incorrect, but perhaps within the limit of the error of the determination of heats of combustion of organic compounds. Once we accept this notion, however, our calculations indicate that the pair of electrons holding the carbon and nitrogen atoms together are not displaced completely in the direction of the nitrogen atom. Before they assume, with respect to the carbon atom, a position similar to the one they occupy in carbon dioxide, 13 additional Kg. Cal. per mole are evolved[1]. The heat of combustion of nitro compounds is, therefore, given by the formula: $H = 26.05 \times N + 13$.

The agreement of the calculated and experimentally determined values, although varying considerably is still sufficiently close to bear out the fundamental relationship involved. It should also be borne in mind that the constant, 26.05 is applicable to the combustion of liquid compounds, and that the heat of combustion of a solid would be smaller than that of the liquid by an amount corresponding to the heat of fusion. The only values of the heats of fusion of nitro compounds given in the literature are for m-dinitrobenzene and o-nitrophenol and in the case of m-dinitrobenzene once this is taken into account the difference instead of being 0.8% is only 0.1% while the o-nitrophenol is still within 0.3% of the calculated value. The correction should be applied and it is gratifying to note that our calculated values are larger than the experimentally determined ones. Once the heats of fusion of these compounds become available a still better check of the calculated values will then be possible. We also had to use the data of other observers than the ones mentioned in the introduction. A closer scrutiny of the data will be given in a subsequent paper with the correction that should be applied to the results of some investigators[2].

Primary Amines

The calculation of the heats of combustion of amines presents a very difficult problem from the quantitative standpoint of the heat contributed by the different groups in the molecule. The problem has two distinct features. In the first place, it is important to know the position of the pair of electrons binding the carbon and "NH_2" group nitrogen; secondly, since the "NH_2" group nitrogen is converted into nitrogen gas, it must have been oxidized by the oxygen, and thus it contributes a certain amount of heat. Of course, it is understood that a number of other factors enter into the mechanism, but it was thought well worth while not to burden this first publication with them.

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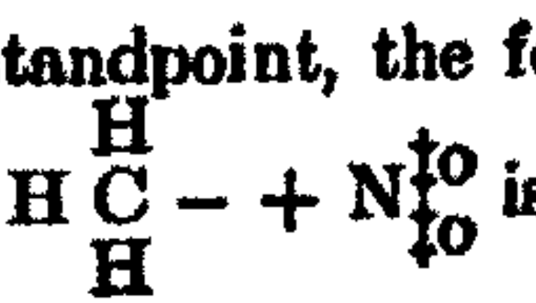
[1] From this standpoint, the formulae employed by various organic chemists for nitro compounds, viz:  $H\overset{H}{\underset{H}{C}} - + N^{\uparrow O}_{\downarrow O}$ is in error. The pair of binding electrons are nearer to the nitrogen atom than to the carbon atom, making the nitrogen almost negative and the carbon almost positive. (It all depends upon whether CO_2 is considered a polar or non-polar compound). This seems to be quite a plausible structure, since we would expect that such a powerful oxidizing agent as a nitric acid nitrogen would be capable of oxidizing the carbon atom. The reduction of the nitro compounds to the corresponding amines, does not then involve any additional postulate such as would be required, if the nitrogen were assumed to contain five positive charges in the nitro compounds.

[2] The data for the ketoximes will be discussed in the next paper. We might mention however, that the data throw considerable light on the electronic structure of these compounds.

Table XI

Nitro Compounds

Name	Number of Electrons	Calculated	Observed		% Difference
1 Nitro methane	6	169.3	169.6	Swi.	+0.2
			170.0	B., Ma.	−0.5
2 Nitro ethane	12	325.6	322.5	B., Ma.	+1.0
3 Nitro propane	18	481.9	478.3	Swi.	+0.7
4 o-Dinitrobenzene	26	703.4	703.7	B., Ma.	0.0
5 m-Dinitrobenzene	26	703.4	697.2	B., Ma.	+0.8
6 p-Dinitrobenzene	26	703.4	695.6	B., Ma.	+1.1
7 Sym. trinitrobenzene	24	664.2	664.0	B., Ma.	0.0
8 Unsym. trinitrobenzene	24	664.2	678.6	B., Ma.	−2.0
9 o-Nitrophenol	26	690.3	688.4	Mat. Del.	+0.3
10 m-Nitrophenol	26	690.3	688.4	Swartz	+0.3
11 p-Nitrophenol	26	690.3	689.3	Mat., Del.	+0.2
12 Nitrobenzene	28	742.4	734.7	Swartz	+1.0
13 m-Nitro toluene	34	898.7	889.5	Swartz	+1.0
14 o-Nitro ethoxy benzene	38	1016.0	1017.5	Swartz	+0.1
15 p-Nitro ethoxy benzene	38	1016.0	1006.0	Swartz	+1.0
16 m-Nitro ethoxy benzene	38	1016.0	1009.0	Swartz	+0.7

It has been our aim throughout to introduce as few assumptions as possible, and it seemed logical, therefore, to assume that the same amount of heat is evolved when an electron migrates from an "NH_2" nitrogen atom as from a methane carbon atom. This may be an erroneous assumption from a quantitative standpoint, and it probably is so, but perhaps within the limits of experimental error of the determination of heats of combustion. The second assumption is that the pair of electrons binding the carbon and "NH_2" group nitrogen has retained the same position it held in nitro compounds. This assumption is a rather plausible one and one that is in complete agreement with the mechanism of reduction of nitro compounds, and would mean that the position of the pair of electrons binding the carbon atom to other groups is not changed, when we go from a nitro compound to a primary amine and to the corresponding primary alcohol.

Once we make these assumptions the heat of combustion of primary amines is given by the expression $H = 26.05 \times N + 13$.

Upon this basis the aromatic and aliphatic amines exhibit a very interesting variation in the relative position of the electrons between the nitrogen and carbon atoms, if the heat of combustion is taken as a criterion. That such a difference is brought out by the calculation of heats of combustion is most gratifying for the difference in the properties of the two classes of amines is well known. Thus, we find that in the case of the aliphatic amines, the above formula gives a good agreement with the experimentally determined values, while in the case of the aromatic amines the following formula gives a better agreement, $H = 26.05 \times N$. It merely means that the pair of electrons binding the nitrogen and carbon atoms are more displaced from the carbon atom in the direction of the nitrogen atom in aromatic amines than in the aliphatic amines and therefore, no correction is necessary in the formula of the former compound. The case is analogous to the difference in the positions of the pair of electrons between the carbon and the oxygen atoms in primary and tertiary alcohols. (See discussion under tertiary alcohols and also footnote p. 629.)

The validity of the postulates advanced and other points of interest, namely the reason underlying the difference in chemical properties, particularly basicity of aliphatic and aromatic amines will be discussed later. We wish to emphasize once more that this is merely a preliminary paper, and that a number of other relationships will be pointed out in two papers in preparation at the present time by one of us (Kh.)

The data for primary aliphatic amines, with the correction allowed for, are given in Table XII, and that for the aromatic amines in Table XIII. The agreement on the whole is very satisfactory, the difference not exceeding one half percent, except in the case of methyl and ethyl amines. These compounds will be discussed more thoroughly in the next paper and the cause for the discrepancy pointed out.

Amides, Anilides and Amino Acids

On the basis of the method developed in the case of primary amines, the heats of combustion of a number of nitrogen derivatives have been calculated.

Table XII
Primary Amines (Aliphatic)

Name	Number of Electrons	Calculated	Observed		% Difference
1 Methyl amine	9	247.5	257.4	Lem.	−5.0
2 Ethyl amine	15	403.7	410.6	Lem.	−1.8
3 Propyl amine	21	560.0	561.2	"	−0.2
4 n-Butyl amine	27	716.3	717.3	"	+0.3
5 t-Butyl amine	27	716.3	717.3	"	−0.1
6 Isoamyl amine	33	872.6	871.3	"	+0.1
7 Hexyl amine	39	1029.0	1027.5	"	+0.1
8 Heptyl amine	45	1185.2	1185.0	"	0.0
9 Benzyl amine	37	976.8	970.8	"	+0.7

Table XIII
Primary Amines (Aromatic)

Name	Number of Electrons	Calculated	Observed		% Difference
1 Aniline	31	807.5	811.4	St., Hau	−0.5
			815.9	Lem.	−1.0
2 o-Toluidine	37	963.8	965.5	Pet.	−0.2
3 p-Toluidine	37	963.8	959.4	Pet.	+0.4
4 m-Toluidine	37	963.8	966.5	Pet.	−0.3
5 Pseudo cumidene	49	1276.4	1272.4	Lem.	+0.4
6 p-Anisidine	35	924.7	928.7	Lem.	−0.4

We find, also, that the pair of electrons binding the carbon and nitrogen atoms in amides, anilides and amino acids, occupy a different position than in the case of primary amines of the aliphatic series, if the heat of combustion is to be taken as the criterion. The pair of binding electrons may be considered completely displaced from the carbon atom, i. e., occupying the same relative position as in CO_2, in the direction of the nitrogen atom. (See, however, the discussion under tertiary alcohols—the same principle holds true in this case.) No correction is, therefore, necessary for this pair of electrons, and the formula for these types of compounds becomes: $H = 26.05 \times N$. In the table we are noting the total number of electrons interdisplaced, irrespective of whether the interdisplacement of electrons occurs between a carbon and an oxygen atom, or an oxygen and a nitrogen atom. The limitations of such a method of treatment are duly realized, and the point has been discussed already in the case of primary amines.

The agreement between the calculated and experimentally determined values is most gratifying, particularly in view of the fact that the constant employed, 26.05 Kg. Cal. per mole per electron, holds only for the heat of combustion of liquid compounds. The calculated values should, therefore, be larger than the experimentally determined values of the heat of combustion of those compounds which are solid. We find that to be the case. However, since the heats of fusion of these solids are presumably not very high, we should not expect the difference to be very large, but there should be that trend in the case of all of these compounds.

Of the forty-two compounds given in Table XIV, half of the compounds agree within four-tenths of one percent, while only eight compounds differ by more than one percent. That the data are of great significance is self-evident since it accounts for the combustion of the nitrogen derivatives on the same basis as that of the carbon compounds without any additional postulates. In some measure, it is thus a direct substantiation of the method and hypothesis employed in the calculation of the heats of combustion.

General Discussion

An attempt has been made in this paper to develop, on the basis of the non-polar conception of valence, the relation between the chemical constitution of a substance and the amount of heat liberated by it upon combustion. The notion of partial polarity had to be resorted to in order to explain the heats of combustion of unsaturated derivatives, alcohols, ketones, aldehydes, nitro compounds, amines, and other types of organic molecules not mentioned in this communication. The assumptions were made, however, not altogether unlikely; as a matter of fact they are included in the non-polar conception of valence[1].

There are two concepts that we consider most important from the standpoint of the calculation of heats of combustion and the elucidation of the chemical behavior of organic compounds. The first notion, which is rather

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[1] G. N. Lewis: J. Am. Chem. Soc. 35, 1448 (1913)

TABLE XIV

Amides

Name	Number of Electrons	Calculated	Observed	% Difference
1 Acetamide	11	286.5	289.2 St., Schm.	+1.5
			288.4 Be., Fo.	−1.0
2 Propionamide	17	442.8	440.3 St., Schm.	+0.5
			436.5 Ba., Fo.	+1.5
3 Malonamide	14	364.7	361.1 St., H.	+1.0
4 Butyramide	23	599.1	596.7 St., Schm.	+0.6
5 Isobutyramide	23	599.1	596.5 St., Schm.	+0.6
6 Succinamide	20	521.0	509.7 St., H.	+2.4
7 Succinamide	17	442.7	439.4 Be., Fo.	+0.7
			438.3 St., H.	+1.0
8 Isovaleramide	29	755.4	752.3 St., Schm.	+0.4
9 Dimethyl malonamide	26	677.3	686.5 St., Schm.	−1.5
10 Oxaminic acid	5	130.1	132.7 St., H.	−1.8
			128.8 Mat.	+1.0
11 Oxamide	8	208.1	203.4 St., H.	+2.5
12 Diethyl malonamide	38	989.9	995.8 St., H.	−0.7
13 Benzamide	33	859.5	853.0 Be., Fo.	+0.8
14 Phthalimide	33	859.5	850.4 St., Schm.	+1.1

TABLE XIV (continued)

Anilides—Amino Acids

Name	Number of Electrons	Calculated	Observed	% Difference
15 Urea	6	156.3	152.3 St., La.	−3.0
16 Glycocoll	9	234.3	233.4 Fi., Wr.	+0.4
			234.7 St., La.	−0.2
17 Alanin	15	390.6	388.1 St., La.	+0.7
			389.7 Fi., Wr.	+0.3
18 Isoserin	13	344.5	343.7 Fi., Wr.	+0.3
19 Aspartic acid	15	390.6	385.3 St., La.	+1.5
			385.9 Fi., Wr.	+1.5
20 Asparagine	18	468.8	463.8 St., La.	+1.2
21 Glycyl glycine	18	468.9	471.1 St., La.	−0.5
22 Barbituric acid	14	364.7	359.0 Fi., Wr.	+1.5
23 Uric acid	18	468.6	461.4 Mat.	+1.8
			460.7 St., La.	+2.0
24 Methyl hydrouracil	24	625.2	618.2 Fi., Wr.	+1.2
25 4-Methyl uracil	22	573.1	566.1 Fi., Wr.	+1.4
26 Leucine	33	859.5	858.0 R., A.	+0.2
			856.5 St., La.	+0.4
			857.8 Wr.	+0.2
27 Veronal	38	989.4	984.0 Fi., Wr.	+0.5
28 Acetanilide	39	1015.8	1017.5 B., Fo.	−0.2
			1011.4 St., Schm.	+0.4

TABLE XIV (continued)

Anilides—Amino Acids

Name	Number of Electrons	Calculated	Observed	% Difference
29 Propionanilide	45	1172.1	1168.8 St., Schm.	+0.4
30 Hippuric acid	39	1015.8	1013.6 B., A.	+0.2
			1013.4 St., Schm.	+0.2
31 Skatol	45	1172.1	1171.4 B., A.	+0.1
32 α-Methyl indol	45	1179.1	1169.6 B., A.	+0.2
33 Benzoyl alanine	45	1172.1	1169.3 St., Schm.	+0.3
34 Benzoyl sarcosine	45	1172.1	1181.0 St., Schm.	+0.8
35 Hemipinamide	42	1093.9	1100.1 St., Lie.	−0.6
			1099.3 Roth.	−0.5
36 Benzanilide	61	1588.9	1577.1 St., Schm.	+0.8
37 Phenacyl amino acetic acid	45	1172.2	1166.1 St., Schm.	+0.6
38 o-Methyl hippuric	45	1172.2	1168.9 St., Schm.	+0.4
39 m-Methyl hippuric	45	1172.2	1168.2 St., Schm.	+0.4
40 p-Methyl hippuric	45	1172.2	1168.7 St., Schm.	+0.3
41 p-Methoxy hippuric	43	1133.1	1136.3 St., Schm.	−0.3
42 Leucyl glycyl glycine	51	1328.5	1339.9 Fi., Wr.	−0.9
43 4-Phenyl uracil	43	1133.1	1132.2 Fi., Wr.	−0.1
44 o-Tolyl alanine	51	1328.5	1323.0 St., Schm.	−0.4
45 p-Tolyl-alanine	51	1328.5	1320.8 St., Schm.	−0.6

fundamental, is, that in oxidation reactions of carbon compounds, electrons are displaced from the carbon atom only in pairs, and furthermore the displacement occurs in definite stages from the normal valence shell until an arrangement of a carbon dioxide type is attained. The second notion, that when two carbon atoms share two pairs of electrons in common one pair occupies the same position as in the saturated hydrocarbon molecule, while the other pair is displaced from this normal valence shell into outer shells. The molecule may be considered, then, to have an electric moment in that part of it owing to this pair of displaced electrons. Furthermore, the extent of this displacement depends upon the other groups attached to the two carbon atoms. Reference to the postulates 3, 4 and 5 will help to clarify considerably these fundamental concepts[1].

The agreement between the calculated and experimentally determined values is very striking. Preliminary calculation of the heats of combustion of other types of compounds besides those mentioned in this paper, viz., oximes, chlorine, bromine, fluorine, and all sulfur derivatives, have also been made. The agreement is sufficiently close to bear out the fact that the fundamental concept of combustion, in the sense developed, is correct.

The possibilities of applying the heats of combustion to the elucidation of the electronic structures of organic compounds if self-evident. Thus, a number of important theoretical deductions such as the electronic structure of acetylenes, ethylenes, conjugated systems, cyclic structures, benzene, substitution in the benzene ring, etc., agree very well with the known experimental facts. We hope to discuss this prediction of chemical properties from the standpoint of the electronic structure of organic compounds in a future paper. We might add that, on the whole, this hypothesis gives us an excellent insight into the chemistry of organic reactions, and, that the knowledge gained of the electronic structures of the molecules helps us to interpret a number of now considered abnormal, interesting and bewildering reactions which are so abundant in our literature.

Summary

1. The hypothesis has been advanced that heat of combustion is due to an interdisplacement of electrons between atoms and molecules.

2. It has been assumed that, in the combustion of carbon compounds with oxygen, when an electron is displaced from the "methane arrangement" to that of the "carbon dioxide type" heat is evolved to the extent of 26.05.Kg. Cal. per mole.

3. It has been assumed that intramolecular oxidation-reduction reactions are accompanied by the evolution of heat.

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[1] It is extremely instructive to examine our present day concepts of heats of formation of organic compounds from the standpoint of the views developed in this paper. We see at once the ambiguity involved in the concept, as applied to all classes of organic molecules. This point will be discussed in a later paper by one of us.

4. It has been necessary to assume that, in nitro compounds, the two valence electrons which hold the nitrogen and carbon atoms are displaced in the direction of the nitrogen atom.

5. The two valence electrons which hold the nitrogen and carbon atoms retain their relative positions in going from the nitro compounds to amines and alcohols in the aliphatic but not in the aromatic series.

6. The heats of combustion of 278 compounds have been calculated on the basis of the concepts developed in this paper. The agreement, on the whole, is very striking.

7. The prediction of the chemical properties and reactions of organic compounds from the standpoint of the electronic structure of these molecules will be given in subsequent papers.

8. The postulates underlying the calculation of heats of combustion are very readily extended to the calculation of other physical constants and will be discussed in later papers by us.

College Park, Md.

STUDIES IN ADSORPTION. XI

Influence of ions carrying the same charge as the sol on the coagulation of sols of (i) prussian blue and of (ii) positive ferric hydroxide

BY S. GHOSH AND N. R. DHAR

In the foregoing papers of this series[1] the influence of ions carrying the same charge as the colloid particles on the coagulation of sols has been studied and its importance in the explanation of various phenomena in colloid chemistry has been emphasized. In the previous paper of this series[2] we have arrived at the following conclusions:—

i. The abnormal dilution effect shown by such sols as As_2S_3. Sb_2S_3, mastic, etc., when coagulated by monovalent electrolytes like KCl, LiCl, etc., (viz., more of these electrolytes is necessary to coagulate a dilute sol than a concentrated one has been attributed to the fact that these sols can adsorb the ions carrying the same charge as the colloid particles.

ii. The abnormal behaviour shown by these colloidal sols with mixtures of electrolytes (viz., the precipitation values of mixture of electrolytes of widely varying precipitating powers are greater than the additive values) is also explained from the same point of view so that a sol is partially stabilised by the adsorption of ions carrying the same charge as the colloid particles.

iii. The phenomenon of acclimatization has been explained from the point of view that colloidal particles can adsorb ions carrying the same charge as the colloid. It follows therefore that such sols as As_2S_3, Sb_2S_3, mastic, etc., which are known to adsorb negative ions show this phenomenon more markedly than $Fe(OH)_3$ positive and negative, $Cr(OH)_3$ positive and negative, etc., which hardly adsorb monovalent ions carrying the same charge as that on the sols.

We are of the opinion that the three phenomena (a) abnormality of sols to follow the general dilution rule, (b) abnormal behaviour with a mixture of electrolytes of widely varying precipitating values, and (c) the phenomenon of acclimatization are essentially connected and are mainly due to the adsorption of ions carrying the same charge as the sol. From all the data available from our experiments as well as those of other workers in this line it has been found that those sols, which are normal towards a mixture of electrolytes also show normal behaviour on dilution. Moreover it has been proved that mastic sol[3] and arsenic trisulphide sol[4] which show abnormal behaviour towards dilution when coagulated by KCl, LiCl, etc., and towards a mixture of electrolytes, also show the phenomenon of acclimatization more markedly than positively charged ferric hydroxide (Freundlich: loc. cit. and Weiser: loc. cit.) and negatively charged ferric hydroxide.

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[1] Sen, Ganguly and Dhar: J. Phys. Chem. 28, 313 (1924); Dhar, Sen and Ghosh: J. Phys. Chem. 28, 457 (1924); Sen and Dhar: Kolloid-Z. 34, 262 (1924); Ghosh and Dhar: Kolloid-Z. 35, 144 (1924); J. Phys. Chem. 29, 435 (1925).

[2] Ghosh and Dhar: J. Phys. Chem. 29, 435 (1925).

[3] Ghosh and Dhar: loc. cit.

[4] Freundlich: Z. physik. Chem. 44, 143 (1903); Weiser: J. Phys. Chem. 25, 399 (1921).

From a few preliminary experiments on prussian blue, we concluded that the sol behaves abnormally towards KCl, LiCl, etc., on dilution and is also abnormal towards a mixture of electrolytes. On the other hand, Weiser and Nicholas[1] have observed that this sol shows a normal behaviour towards KCl on dilution. It will be observed from their data that the amounts of a monovalent electrolyte necessary to coagulate strong and dilute sols of prussian blue are not very different when compared with the amounts of electrolytes like KCl, $KBrO_3$, etc., necessary to coagulate concentrated and dilute sols of positively charged ferric hydroxide, which may be considered as one of the typical normally behaving colloidal solution.

TABLE I

Precipitation of prussian blue colloid

Concentration of colloid	Precipitation values of		
	KCl	$BaCl_2$	$AlCl_3$
100% (8 grs. per litre	89.6	4.25	2.200
75%	87.5	3.33	1.625
50%	85.4	2.75	1.125
25%	81.2	2.16	0.500
10%	77.1	1.67	0.208

TABLE II

Precipitation of ferric oxide colloid

Concentration of colloid	Precipitation values of		
	$KBrO_3$	K_2SO_4	$K_4Fe(CN)_6$
100% (1.70 grms. per litre)	40.1	0.68	0.57
50%	34.4	0.41	0.30
25%	28.8	0.25	0.16
12.5%	25.0	0.16	0.08

It will be observed that the amount of the monovalent electrolyte KCl necessary to coagulate prussian blue decreases to the extent of about 10% when the sol is diluted four times, whilst the amount of monovalent electrolyte $KBrO_3$ necessary to coagulate positively charged ferric hydroxide decreases to more than 25% for the same dilution.

In this paper we have carefully investigated the dilution effect, the phenomenon of acclimatization, and action of mixed electrolytes with prussian blue. We have also investigated the influence of stabilising ions on the coagulation of positively charged $Fe(OH)_3$. Moreover we have also observed the effect of NaOH and several non-electrolytes on the coagulation of arsenious and antimony sulphide sols by electrolytes. It is well known that freshly precipitated ferric hydroxide, chromium hydroxide etc., can be peptised by

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[1] J. Phys. Chem. **25**, 743 (1921).

the specific adsorption of ferric, chromic, aluminium ions, etc., by the hydroxides from solutions of ferric chloride, chromium chloride, etc. It seems probable, therefore, that the adsorption of these ions should follow the ordinary adsorption laws. Now when $FeCl_3$ is first added in small quantities to a $Fe(OH)_3$ sol, the colloid particles due to chemical affinity will adsorb similarly charged Fe^{+++} ions. The percentage of adsorption is high as the solution of $FeCl_3$ is very dilute so that an equivalent amount of oppositely charged ions (Cl') has practically no precipitating action. Now as the amount of $FeCl_3$ is gradually increased, the adsorption of positively charged ferric ion reaches a saturation limit and the precipitating ion (Cl'), which also increases in concentration, tends to overcome the peptising effect of Fe^{+++} ions and coagulates the sol.

If the sol is now diluted, say twice, the amount of adsorption of Fe^{+++} ion by the sol is not actually halved; on the other hand, the amount of the adsorption of chlorine ions by the colloidal particles is practically halved, as this adsorption is mainly due to electrical attraction. Consequently the total effect of Fe^{+++} ion shows a greater peptising effect than the precipitating effect of the oppositely charged chloride ion, when the same amount of ferric chloride is added to a diluted sol of ferric hydroxide than to a concentrated sol. Hence more of $FeCl_3$ is necessary to coagulate the dilute sol than a stronger one. When ferric chloride is added to a sol of ferric hydroxide it will adsorb both the ions, but the chlorine ion is adsorbed more than the ferric ion because the sol is actually coagulated by the electrolyte. It seems very likely that the ratio of the adsorption of negative to that of the positive ion gradually becomes smaller and smaller and approaches unity as the sol is diluted, and in certain cases the ratio may be less than unity. That is why more and more $FeCl_3$ is necessary to coagulate a dilute sol of $Fe(OH)_3$ than a concentrated one.

Ferric hydroxide has chemical affinity for Fe^{+++} ions and can readily adsorb them. It is possible that when small quantities of $FeCl_3$ are added to a sol of $Fe(OH)_3$ such that no coagulation takes place, the amount of ferric ion adsorbed is slightly greater than that of chlorine ion and hence the sol becomes more stable towards KCl. This effect will be greatly diminished if the adsorption of ions carrying the same charge as the colloid particles is extremely small or the precipitating effect of the oppositely charged ions is very great. A similar line of argument was advanced in the explanation of the abnormal dilution effect of sols like As_2S_3, Sb_2S_3, etc., towards KCl, LiCl, etc.[1] It is known that sols of As_2S_3, Sb_2S_3, etc., adsorb appreciable amounts of chloride, nitrate, sulphate ions, etc., so that more of monovalent K from KCl is necessary to coagulate a dilute sol than a stronger one; on the other hand, the effect is not so marked with electrolytes of bivalent cations like $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, etc., and less so with trivalent cations like $Al^{\cdot\cdot\cdot}$, $La^{\cdot\cdot\cdot}$, $Ce^{\cdot\cdot\cdot}$, etc., where very small quantities of electrolytes bring about the coagulation and the stabilising action of Cl', SO_4'', NO_3', etc., is compensated by the greater precipitating action of $Ba^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, etc., than that of monovalent $K^{\cdot}$, $Li^{\cdot}$, etc. Consequently it

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[1] See Sen and Dhar: loc. cit.

seems probable that when coagulation of sols is effected by electrolytes of which both the ions can be adsorbed by the sols we are likely to get (i) abnormal dilution effect (ii) abnormal behaviour towards a mixture of electrolytes and (iii) the phenomenon of acclimatization.

In the following experiments we will show that $Fe(OH)_3$ which behaves normally in its coagulation by KCl, $KBrO_3$, etc., is abnormal when coagulated by $FeCl_3$, $Al(NO_3)_3$, etc., because from these electrolytes both the positive and the negative ions are appreciably adsorbed and the ratio of the adsorption of negative ion to that of positive ion decreases with the decreasing concentration of the sol just as in the coagulation of As_2S_3, Sb_2S_3, mastic, etc., by KCl, LiCl, etc., the ratio of adsorption of positive to that of negative ion decreases with the decreasing concentration of the sol.

On the other hand, sols like As_2S_3, Sb_2S_3, etc., which behave abnormally on dilution when coagulated by KCl, NaCl, etc., should behave normally when coagulated by an electrolyte of which mainly the positive ion is adsorbed by the sol. Our results of the coagulation of As_2S_3 sol by $AgNO_3$ prove that the coagulation of this sol follows the general dilution rule, because the $Ag^{\cdot}$ ions are highly absorbed by the sulphide in preference to NO'_3 ions.

Experimental

Prussian blue:—

The sol is prepared by precipitating prussian blue from a solution of $FeCl_3$ by potassium ferrocyanide and washing the precipitated mass with distilled water. The sol is obtained as a filtrate and can be made a concentrated one. The sol is dialysed through a parchment paper for seven days when it is free from ferrocyanide. The sol made up to 5 cc in clean tubes, is mixed with the electrolyte made up to 5 cc in another tube and kept for two hours when complete coagulation and clearing at the top of the mixture are observed. A series of experiments were carried out by the addition of electrolytes near the precipitation value and the exact precipitation value is found out with great care. It will be very interesting to note that this sol even after coagulation can again pass into the colloidal state on dilution and is extremely sensitive to shaking. With special care coagulation and complete clearing at the top of the mixture in a definite time can be reproduced with the same concentration of the precipitating electrolyte and the sol.

TABLE III

Strength of the prussian blue sol = 2.88 grams
Sol A = 1 cc of the original sol per litre made up to 20 cc
Volume = 10 cc Time = 2 hrs.

Concentration of the sol	Amounts of electrolyte necessary to coagulate		
	KCl N/4	$BaCl_2$ N/50	$Al(NO_3)_3$ N/400
A	1.70 cc	1.05	0.90 cc
A/2	1.80 cc	0.95 cc	0.50 cc
A/10	2.00 cc	0.80 cc	0.20 cc

In order to be absolutely certain that the results given in the previous table are reproducible and are valid for all samples of prussian blue sols, a fresh sol of prussian blue was prepared. This sol was dialysed for a week and freed from electrolytes. The sol was coagulated by KCl at two different dilutions and the following results are obtained:—

Table IV

Strength of the prussian blue sol = 2.76 grms.
Sol A = 1 cc of the original sol per litre made up to 10 cc
Volume = 10 cc Time = 20 hrs.

Concentration of the colloid	Amount of KCl N/4 to complete coagulation
A	2.30 cc
A/2	2.40 cc

Hence with this sample of the sol also we find that the diluted sol takes more of KCl for coagulation than a concentrated one.

Weiser and Nicholas (loc. cit.) have reported that the sol of prussian blue prepared by them contained free potassium ferrocyanide. We are trying to find out whether the difference between our results and those obtained by above authors can be attributed to free potassium ferrocyanide.

In Tables V-X the results are given as obtained when prussian blue is coagulated by a mixture of various electrolytes.

Table V

Precipitation of prussian blue colloid with a mixture of KCl and $BaCl_2$
Amount of sol taken each time = 1 cc (of 2.88 grs. of prussian blue per litre).
Volume = 10cc Time = 2 hrs.

KCl N/4	Amount of $BaCl_2$ N/50 to complete coagulation			
added cc	taken cc	Calculated	Difference	Difference percent
1.80	0			
0	1.05			
0.1	1.25	0.98	+0.27	28
0.3	1.35	0.88	+0.47	54
0.6	1.30	0.70	+0.60	86
0.8	1.15	0.58	+0.57	98
1.0	0.80	0.47	+0.33	70
1.4	0.45	0.23	+0.22	96

Table VI

Precipitation of prussian blue colloid with a mixture of HCl and KCl

HCl N/5	Amount of KCl N/4 to complete coagulation			
added cc	taken cc	Calculated cc	Difference	Difference percent
0	1.80			
1.9	0			
0.1	1.20	1.71	−0.51	30
0.5	0.75	1.33	−0.58	43
1.0	0.50	0.85	−0.35	41
1.7	0.10	0.19	−0.09	46

TABLE VII

Precipitation of prussian blue colloid with a mixture of HNO_3 and KNO_3

HNO_3 N/5	Amount of KNO_3 N/4 to complete coagulation			
	taken cc	Calculated cc	Difference	Difference percent
0	2.00			
1.90	0			
0.1	1.30	1.89	−0.59	31
0.5	0.75	1.37	−0.62	45

TABLE VIII

Precipitation of prussian blue colloid with a mixture of KCl and KNO_3

KNO_3 N/4	Amount of KCl N/4 to complete coagulation			
	taken cc	Calculated cc	Difference	Difference percent
0	1.80			
2.0	0			
0.5	1.45	1.35	+0.10	7
1.0	0.90	0.90	0.0	0
1.5	0.40	0.45	−0.05	11
1.9	0.10	0.09	+0.01	11

TABLE IX

Precipitation of prussian blue colloid with a mixture of $MgCl_2$ and $BaCl_2$

$MgCl_2$ N/50	Amount of BaCl N/250 to complete coagulation			
	taken cc	Calculated cc	Difference	Difference percent
0	1.05			
2.70	0			
0.2	1.00	0.97	+0.03	3
0.8	0.8	0.74	+0.06	8
1.40	0.6	0.51	+0.09	17

TABLE X

Precipitation of prussian blue colloid with a mixture of $BaCl_2$ and $Al(NO_3)_3$

$BaCl_2$ N/50	Amount of $Al(NO_3)_3$ N/400 to complete coagulation			
	taken cc	Calculated cc	Difference	Difference percent
0	0.90			
1.05	0			
0.1	0.90	0.82	+0.08	10
0.3	0.75	0.64	+0.11	17
0.5	0.55	0.47	+0.08	17
0.7	0.30	0.25	+0.05	20

Positively charged ferric hydroxide sol.

The sol was prepared according to the method of Krecke[1] by the gradual addition of a concentrated solution of $FeCl_3$ to a large volume of boiling water,

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[1] J. prakt. Chem. (2) 3, 286 (1871).

which was kept well stirred. The sol did not give any coloration with potassium ferrocyanide even before dialysis. The sol, however, contained enough of free hydrochloric acid and it was removed by dialysis for nine days. The sol was practically free from electrolyte and contained only traces of chloride.

Experiments on the coagulation of this sol were made exactly in the same way as already described under prussian blue. In determining the precipitation values the immediate turbidity was noted on adding the electrolyte. The following tables give the results obtained with positively charged ferric hydroxide sol:—

TABLE XI

Strength of sol = 3.62 grms. of Fe_2O_3 per litre
Sol A = 2 cc of the sol made up to 10 cc
Volume = 10 cc

Concentration of colloid	Amounts required to coagulate		
	KCl N	$Al(NO_3)_3$ N	$FeCl_3$ 3/2N
A	1.10 cc	2.30 cc	3.2 cc
A/4	0.9 cc	2.50 cc	3.3 cc
A/10	0.7 cc	2.70 cc	3.4 cc

TABLE XII

Coagulation of positive ferric hydroxide sol with a mixture of $Al(NO_3)_3$ and K_2SO_4
Amount of sol taken each time = 2 cc
Volume = 10 cc Immediate turbidity is observed

$Al(NO_3)_3$ N/1	Amount of K_2SO_4 N/400 to make the sol turbid			
	Taken cc	Calculated cc	Difference	Difference percent
0	1.45			
2.3	0			
0.2	1.80	1.32	+0.48	36
0.5	1.75	1.13	+0.62	57
0.8	1.65	0.95	+0.70	74
1.6	1.35	0.44	+0.91	207

Acclimatization of prussian blue colloid and positively charged ferric hydroxide sol.

The following results were obtained on the acclimatization of prussian blue colloid towards KCl and $BaCl_2$:—

When 1.80 cc of N/4 KCl is added all at once complete coagulation of the prussian blue colloid (1 cc sol containing 2.88 grms. per litre made up to 8 cc) occurs within 2 hours. The precipitation is however not complete in 2 hours after the last addition of the electrolyte, when 1.8 cc of KCl N/4 was added in 70 hours, 0.2 cc of the electrolyte being added at a time. By adding 0.4 cc of KCl N/4 more and allowing the sol to stand undistrubed for two hours complete coagulation occurs.

When 1.05 cc of $BaCl_2$ N/50 is added all at once complete coagulation of the sol of prussian blue (1 cc of the sol made up to 9 cc) occurs within 2 hours.

If, however, the addition of the electrolyte is very slow and 1 cc of $BaCl_2$ N/50 is added in 70 hours, 0.1 cc of the electrolyte being mixed with the sol at a time, the precipitation is not complete in 2 hours after the last addition of the electrolyte. By adding 0.1 cc of $BaCl_2$ N/50 more and allowing the sol to stand undisturbed for two hours, complete coagulation occurs.

From the above results on the acclimatization of the prussian blue colloid we find that the phenomenon is more marked when it is coagulated with potassium chloride than that observed when the sol is coagulated with barium chloride.

The following results were obtained on the acclimatization of positive ferric hydroxide sol towards $Al(NO_3)_3$ and $KBrO_3$:—

When 5 cc of N $Al(NO_3)_3$ is added all at once to 7 cc of the ferric hydroxide sol containing 1.034 grms. of Fe_2O_3 per litre complete coagulation of the sol occurs after twenty-four hours, whilst the same amount of the sol requires 5.40 cc N $Al(NO_3)_3$ to completely coagulate the sol, when the electrolyte is added very slowly and the addition is effected in 120 hours, 0.3 cc of the electrolyte being added at a time.

When the sol of ferric hydroxide is coagulated by N/5 $KBrO_3$, 7 cc of the sol containing 1.034 grms. per litre takes 2.1 cc to be completely precipitated in 24 hours. It has, however, been observed that if the addition of the electrolyte is very slow and 2.1 cc N/5 $KBrO_3$ is added in 72 hours, 0.2 cc of the electrolyte being added at a time, the sol is completely coagulated in 24 hours.

A very interesting fact can be observed here that positively charged $Fe(OH)_3$ sol shows the phenomenon of acclimatization markedly when coagulated by $Al(NO_3)_3$ but does not show any acclimatization towards $KBrO_3$.

Effect of dilution on the coagulation of As_2S_3 *sol with* $AgNO_3$

As_2S_3 sol is prepared and coagulated by the method already given in a previous communication (Ghosh and Dhar: loc. cit.). The following table gives the results, when the sol is coagulated by $AgNO_3$ at the various dilutions of the sol.

TABLE XIII

Strength of the sol (A) = 0.41 gr. per litre

Volume = 10 cc Immediate coagulation is observed

Concentration of sol	Amount of $AgNO_3$ N/4.88 to coagulate
A	0.70 cc
A/4	0.20
A/10	0.10

It has been already remarked in this paper that As_2S_3 sol requires for coagulation more of univalent electrolytes like KCl, LiCl, etc., as the sol is diluted, whilst it will be interesting to observe from the above table that the amount of $AgNO_3$ required for complete coagulation decreases with the decreasing concentration of the sol.

Freundlich[1] has shown that univalent organic cations of morphine hydrochloride, aniline hydrochloride, etc., behave as a far better coagulating agent

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[1] "Kapillarchemie", 576 (1922).

than KCl, LiCl, etc., in the coagulation of As_2S_3. Many of these organic cations behave as bivalent ions like $Ba^{\cdot\cdot}$, $Sr^{\cdot\cdot}$, etc. It is apparent, therefore, that all these ions are more preferentially adsorbed than $K^{\cdot}$, $Li^{\cdot}$ ions, etc., by As_2S_3. It seems very likely that these univalent organic cations will behave normally towards dilution in the coagulation of As_2S_3 sol, just as highly adsorbed univalent Ag ions show normal behaviour towards dilution in the coagulation of As_2S_3 sol. Experiments in this line are in progress in this laboratory.

In this connection it will be interesting to observe that Freundlich and Buchler[1] have studied the charge reversal of gold and As_2S_3 sol by several dye stuffs and monovalent organic cations. Consequently the phenomenon of charge reversal essentially depends on the amount of the preferential adsorption of ions carrying the opposite charge to that of the sol, as has been emphasised in previous papers of this series.

Coagulation of As_2S_3 sol and Sb_2S_3 sol in presence of KOH and several non-electrolytes.

In Tables XIV-XXI results will be given to show the effect of various non-electrolytes and KOH on the coagulation of antimony trisulphide and arsenic trisulphide sols with various electrolytes:—

TABLE XIV

Coagulation of Sb_2S_3 sol in presence of cane sugar
Strength of Sb_2S_3 sol = 3.7157 grs. of potassium antimony tartrate per litre
Amount of sol taken each time = 4 cc
Volume = 8 cc; Time = 1/2 hour

	Amount necessary to coagulate		
Cane sugar M/10 added	HCl N/5	KCl N/4	$BaCl_2$ N/125
0	1.30 cc	1.20 cc	0.95 cc
1.0 cc	1.30 cc	1.10 cc	0.90 cc
2.0 cc	1.30 cc	1.10 cc	

TABLE XV

Coagulation of Sb_2S_3 sol in presence of ethyl alcohol

Ethyl alcohol (98%)	Amount necessary to coagulate		
added	KCl N/4	$BaCl_2$ N/125	$Al_2(SO_4)_3$ N/166.6
0	1.20 cc	0.95 cc	1.15 cc
0.5 cc	1.20 cc	1.00 cc	1.25 cc
1.0 cc		1.05 cc	

TABLE XVI

Coagulation of Sb_2S_3 sol in presence of propyl alcohol

Propyl alcohol	Amount necessary to coagulate		
added	KCl N/4	$BaCl_2$ N/125	$Al_2(SO_4)_3$ N/166.6
0	1.20 cc	0.95 cc	1.15 cc
1.0 cc	1.25 cc	1.10	1.75 cc

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[1] Kolloid-Z. 32, 305 (1923).

TABLE XVII

Coagulation of Sb_2S_3 sol in presence of urea

M Urea added	Amount necessary to coagulate	
	KCl N/4	$BaCl_2$ N/125
0	1.20 cc	0.95 cc
2 cc	1.10 cc	0.85 cc

TABLE XVIII

Coagulation of Sb_2S_3 sol in presence of KOH

A fresh sample of Sb_2S_3 sol is prepared of the same strength as used in the previous experiments.

N/7.35 K(OH) added	Amount necessary to coagulate		
	KCl N/4	$BaCl_2$ N/125	$Al_2(SO_4)_3$ N/166.6
0 cc	1.25 cc	0.95 cc	1.10 cc
0.1 cc (no antimony in the filtrate)	1.25 cc	1.10 cc	did not coagulate with 1.10 cc
0.5 cc (antimony in the filtrate)	1.35 cc	0.85 cc	Do

TABLE XIX

Coagulation of As_2S_3 sol in presence of cane sugar

Strength of As_2S_3 sol = 3.134 grms. per litre

Amount of the sol taken each time = 4 cc

Volume = 8 cc. Time 1/2 hour

Cane Sugar M/10 added	Amount necessary to coagulate	
	KCl N/2	$BaCl_2$ N/125
0	1.40 cc	1.75 cc
1.0 cc	1.30 cc	1.70 cc

TABLE XX

Coagulation of As_2S_3 sol in presence of urea

Urea M added	Amount necessary to coagulate	
	KCl N/2	$BaCl_2$ N/125
0	1.40 cc	1.75 cc
2.0 cc	1.40 cc	1.60 cc

TABLE XXI

Coagulation of As_2S_3 sol in presence of ethyl alcohol

Ethyl alcohol 98% added	Amount necessary to coagulate	
	KCl N/2	$BaCl_2$ N/125
0	1.40	1.75
0.5 cc	1.40	2.00
1.0 cc	1.50	2.20

Coagulation of positively charged $Fe(OH)_3$ by barium sulphate

In a previous communication[1] it has been observed that freshly precipitated $BaSO_4$ can coagulate $Fe(OH)_3$ sol. In this paper we have determined the influence of the change in concentration of $Fe(OH)_3$ sol on its coagulation by $BaSO_4$. The following table gives the results.

TABLE XXII

Concentration of the Sol	Amount of $BaSO_4$ in grms.
A	0.8648
A/2	0.5596
A/5	0.3664

It will be seen from the table that the amount of $BaSO_4$ necessary to coagulate a sol of $Fe(OH_3)$ decreases with the decreasing concentration of the sol.

Coagulation of arsenious sulphide by barium sulphate

In a previous paper[2] we have determined the coagulation of sulphides of arsenic and antimony by freshly precipitated $BaSO_4$ free from electrolytes. In this paper we have investigated the influence of the change of concentration on the coagulation of As_2S_3 sol by $BaSO_4$ and the following results are obtained.

TABLE XXIII

Original concentration of As_2S_3 sol = 0.81 grm. As_2S_3 per litre
Sol A = 0.5 cc made up to 8 cc
Volume = 8 cc Time = 1/2 hr.

Concentration of the sol	Amount of $BaSO_4$ in grams.
A	0.4578
A/2	0.2645
A/4	0.1323

This result proves conclusively that in the coagulation of As_2S_3 sol by $BaSO_4$, the greater the concentration of the sol the greater is the amount of $BaSO_4$ necessary for coagulation. It will be evident from Fig. 1 that the amount of $BaSO_4$ necessary to coagulate As_2S_3, and $Fe(OH)_3$ varies practically directly with the concentration of As_2S_3, $Fe(OH)_3$ sols.

Coagulation of arsenious sulphide by positively charged $Fe(OH)_3$ sol.

Moreover we have determined the coagulation of As_2S_3 sol by a positively charged ferric hydroxide sol and the following results were obtained:—

TABLE XXIV

Strength of As_2S_3 sol = 0.81 grm. per litre
Strength of $Fe(OH)_3$ sol = 3.62 grms. per litre
Sol A = 0.5 cc As_2S_3 sol made up to 8 cc
Immediate coagulation is observed

Concentration of sol	Amount of $Fe(OH)_3$ sol to coagulate
2A	0.55 cc
A	0.35
A/2	0.20

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[1] Ghosh and Dhar: loc. cit.

[2] Ghosh and Dhar: loc. cit.

From the above results it is clear that in this case also the greater the concentration of As_2S_3 sol the greater is the amount of positively charged $Fe(OH)_3$ necessary for coagulation.

Consequently the coagulation of As_2S_3 sol by barium sulphate and by positively charged ferric hydroxide is normal towards dilution, whilst this sol behaves abnormally towards dilution when coagulated by KCl, LiCl, etc.

Discussion

These results on the coagulation of prussian blue confirm our preliminary results already published in the previous paper of this series. In other words this sol behaves abnormally towards dilution and towards a mixture of electrolytes. The behaviour of this sol is exactly like that of As_2S_3 sol; just as a dilute sol of arsenic sulphide takes more electrolyte of the type KCl, LiCl, etc., for coagulation than concentrated sols, similarly a dilute sol of prussian blue takes more KCl for coagulation than a concentrated sol. Our results do not agree with those obtained by Weiser and Nicholas, who observed normal behaviour on dilution in the coagulation of prussian blue. The coagulation of prussian blue by a mixture of electrolytes also behaves exactly in the same way as the coagulation of arsenious sulphide. Some very peculiar results have been obtained in the coagulation of prussian blue by mixtures of KCl and HCl, and KNO_3 and HNO_3. From our experiments we find that the precipitation values are not additive. In presence of HCl, the amount of KCl necessary to coagulate prussian blue is much less than the calculated amount of KCl necessary for coagulation. Exactly similar results have been obtained by us in the coagulation of prussian blue by a mixture of HNO_3 and KNO_3. On consulting the literature we find that more or less similar results have been obtained by Linder and Picton[1] in the coagulation of As_2S_3 sol by mixtures of electrolytes. Their results are given in the following tables:—

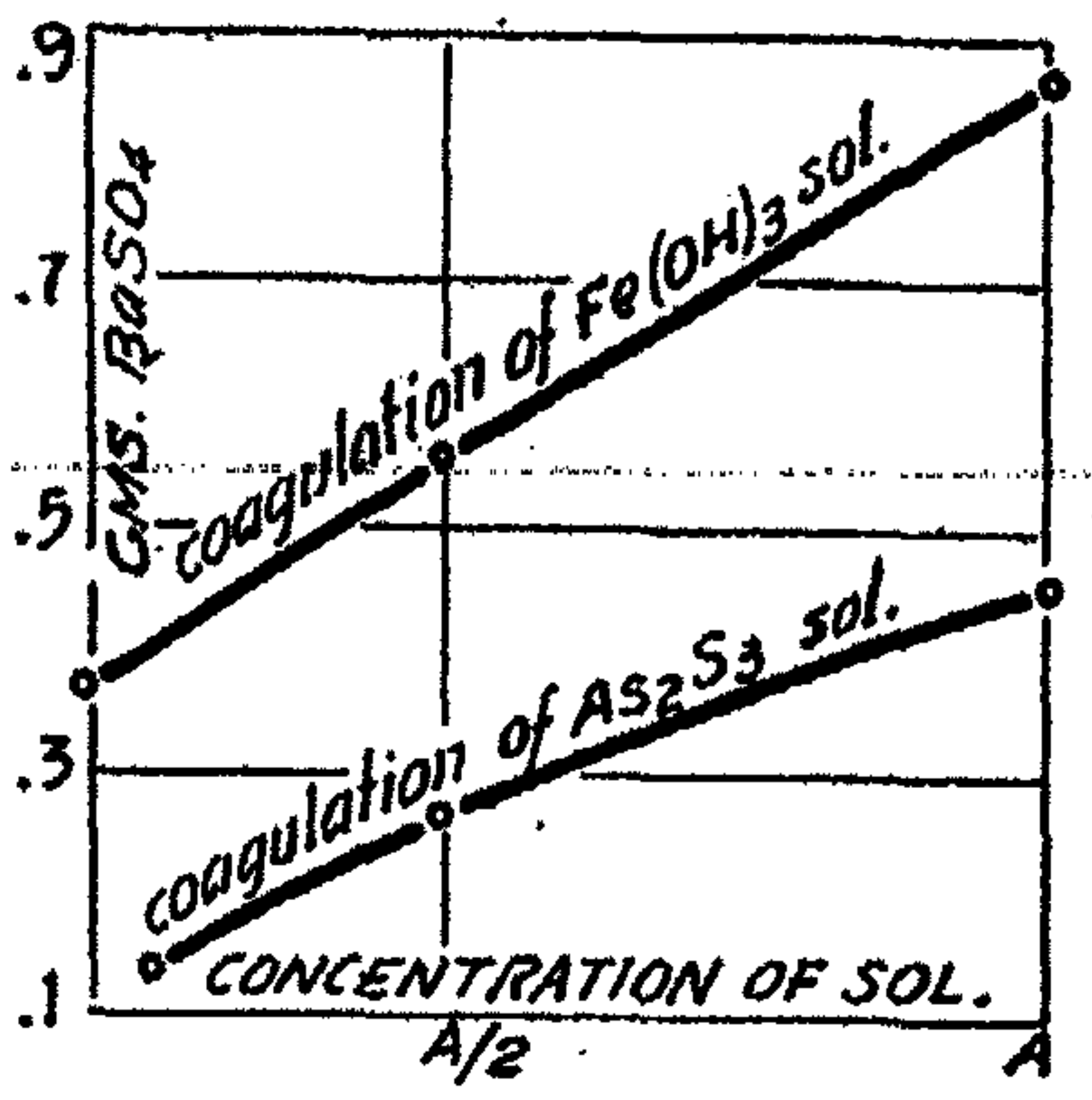

Fig. 1

Table XXV

SaltA	Volume A	Salt B	Volume B to complete coagulation determined	calculated	difference
NH_4Cl	4.90	0			
0		HCl	4.20		
NH_4Cl	2.00	HCl	2.40	2.50	−0.10
HCl	2.60	NH_4Cl	1.75	1.85	−0.10
		HNO_3	4.10		
HCl	2.35	HNO_3	1.97	1.80	+0.17
		K_2SO_4	4.40		
HNO_3	2.00	K_2SO_4	1.95	2.25	−0.30

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[1] J. Chem. Soc. 67, 67 (1895).

It will be seen that in presence of HCl quantities of NH_4Cl smaller than the calculated amounts are necessary to coagulate the sol. Similarly in presence of HNO_3 smaller quantities of K_2SO_4 than the calculated amounts are required to precipitate the sol, whilst more or less additive amounts of HNO_3 and HCl coagulate the sol.

Our results on prussian blue as well as those of Linder and Picton on As_2S_3 can be explained from the following considerations:—

Prussian blue can be hydrolysed according to the equation

$$Fe_4[Fe(CN)_6]_3 + 12H_2O \rightleftarrows 4\ Fe(OH)_3 + 3H_4\ Fe(CN)_6.$$

This hydrolysis will be checked by the presence of acids. The sol of prussian blue will apparently be stabilised by its hydrolysis, specially due to the adsorption of $Fe(CN)_6''''$ ion. Now checking the hydrolysis of the sol due to the presence of the acids means rendering the sol unstable towards electrolytes. Consequently in presence of small quantities of HCl or HNO_3 the sol would require smaller quantities of KCl or KNO_3 than in the absence of acids. From our experience on the phenomenon of hydrolysis of substances like anilin hydrochloride, urea nitrate, etc., we know that the checking of hydrolysis by the addition of an acid or a base is not directly proportional to the amounts of acid or base added; in other words, the checking of hydrolysis by the addition of a small amount of an acid or base is more marked than when larger amounts are added to check the hydrolysis. Thus it has been shown by Dhar[1] that on adding 13.0358 grams of urea to 125 cc M/15.16 urea nitrate solution, the hydrolysis is checked to an extent of about 4.6% per gram of urea present, whilst it is checked to an extent of only 1.33% per gram of urea when 63.7416 grams of urea are added to the same amount of urea nitrate solution. Consequently when, say, 0.1 cc of HCl is added to a sol of prussian blue the checking of the hydrolysis of a sol will be more marked than when 1.70 cc of HCl is added to the same volume of the sol, when we are considering the checking of hydrolysis by a definite amount of HCl; in other words, in presence of HCl the amount of KCl smaller than the calculated quantity will be required to coagulate the sol, and this effect will be more marked when smaller quantities of HCl are added. Exactly similar explanation is applicable to the results obtained with HNO_3 and KNO_3 in the coagulation of prussian blue. Moreover, there is the possibility that the activity of hydrogen ions of HCl or HNO_3 is increased in presence of KCl or KNO_3.

The results of Linder and Picton on the coagulation of As_2S_3 sol by a mixture of an acid and its salt can also be similarly explained. It is well known that As_2S_3 sol is hydrolysed as in the equation

$$As_2S_3 + 3\ H_2O \rightleftarrows As_2O_3 + 3H_2S,$$

and this hydrolysis is also checked by the presence of acids. In a foregoing paper (loc. cit.) we have proved that this hydrolysis makes the sol more stable towards KCl. Consequently by the presence of acids like HCl, HNO_3, etc., smaller quantities of KCl, KNO_3, etc., would be required to coagulate the sol of As_2S_3.

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[1] Z. anorg. Chem. **85**, 198 (1914).

In our experiments on the coagulation of prussian blue by a mixture of KCl and $BaCl_2$ it will be seen that the amount of $BaCl_2$ necessary for complete coagulation goes on increasing with the increase in the concentration of KCl up to a limiting value. After this limiting value is attained if the concentration of KCl is increased the amount of $BaCl_2$ necessary for complete coagulation goes on decreasing. Exactly similar behaviour was observed by Linder and Picton with As_2S_3 sol when coagulated by a mixture of KCl and $SrCl_2$, and by Weiser[1] in the coagulation of the same sol by KCl and $BaCl_2$, LiCl and $BaCl_2$, etc.

From these results a very interesting point can be drawn out. It is well known that keeping the amount of adsorbent constant, the greater the concentration of the electrolyte which will be adsorbed the greater is the amount of adsorption. Now as the concentration of KCl, LiCl, etc., is increased the amount of adsorption due to chemical attraction of Cl′ ions goes on increasing and consequently the sols like As_2S_3, Sb_2S_3, and prussian blue become more and more stable and thus take more and more $BaCl_2$, $SrCl_2$, etc., for complete coagulation. The adsorption of chlorine ions by As_2S_3, prussian blue, etc., follows the general exponential formula of Freundlich. We have drawn graphs with our results on prussian blue as well as from the results of Linder and Picton on arsenious sulphide. In these graphs the logarithims of the difference between the observed and calculated values are plotted as the amounts adsorbed (ordinates) whilst the concentration of KCl is plotted as abscissae. It will be seen from Figs. 2 and 3 that they are more or less straight lines

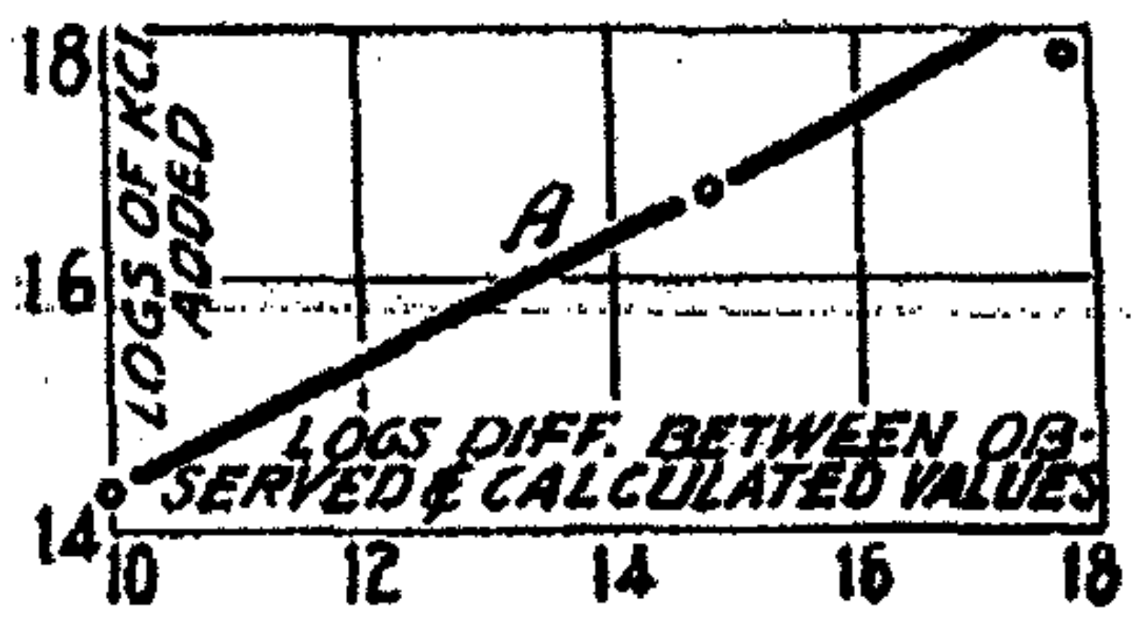

FIG. 2

Coagulation of prussian blue sol by a mixture of KCl and $BaCl_2$.

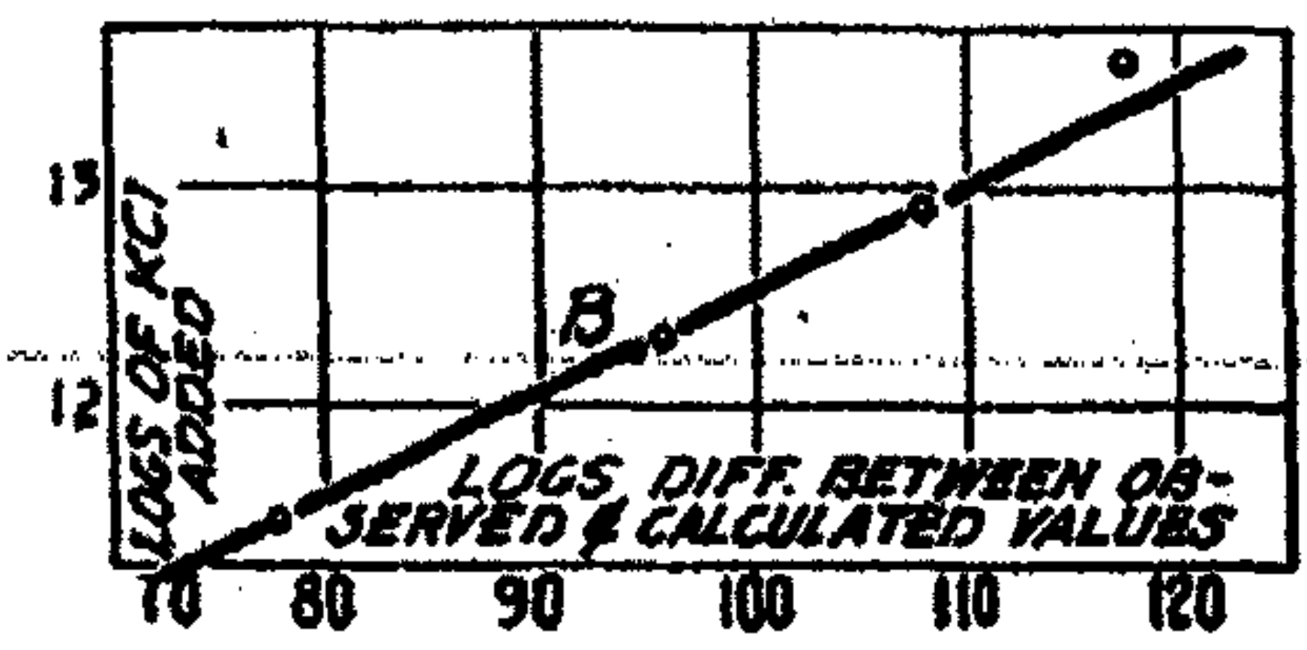

FIG. 3

Coagulation of As_2S_3 sol by a mixture of KCl and $SrCl_2$ (Linder and Picton).

In this paper we have been able to establish a very important point on the coagulation of a sol by electrolytes and this will throw a flood of light on the coagulation of sols by different electrolytes. It is very interesting to observe that positively charged ferric hydroxide, which behaves normally towards dilution when coagulated by KCl, $KBrO_3$, etc., behaves abnormally towards dilution when coagulated by $FeCl_3$, $Al(NO_3)_3$, etc. Moreover ferric hydroxide is normal when coagulated by a mixture of KCl and K_2SO_4 whilst it behaves abnormally when coagulated by $Al(NO_3)_3$ and K_2SO_4. Also this sol hardly shows any acclimatization with $KBrO_3$, whilst it shows markedly the phenomenon of acclimatization when coagulated by $Al(NO_3)_3$. Consequently our

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[1] J. Phys. Chem. 25, 665 (1921); 28, 232 (1924).

proposition, advanced in the previous paper in which it was stated, that abnormal behaviour towards dilution and towards electrolytes and the phenomenon of acclimatization are essentially connected and go hand in hand and are mainly due to the adsorption of ions carrying the same change as the sol, is highly strengthened by these researches.

The coagulation of As_2S_3 sol by KCl, LiCl, etc., is abnormal towards dilution and we have already indicated that this sol is abnormal towards a mixture of electrolytes and markedly shows the phenomenon of acclimatization; but with $AgNO_3$ we have proved that the sol behaves normally on dilution. Consequently it seems very likely that even this sol will behave normally towards mixtures of $AgNO_3$ and $Ba(NO_3)_2$ or $Ag(NO_3)$ and $Al(NO_3)_3$. Moreover this sol will not show the phenomenon of acclimatization with $AgNO_3$, $Pb(NO_3)_2$, etc. Of course, we do not ignore the possibility of the chemical reaction between these electrolytes and the sol.

In a previous paper[1] we have obtained the following results in the coagulation of Sb_2S_3 sol by $Ba(NO_3)_2$ and $Pb(NO_3)_2$.

TABLE XXVI

Strength of antimony sulphide sol (4A) = 4 grms. of pot. antimony tartrate per litre

Concentration of the colloid	Amounts necessary to coagulate $Ba(NO_3)_2$ N/100	 $Pb(NO_3)_2$ N/100
4A	0.45 cc	1.20 cc
2A	0.50 cc	0.80 cc
A	0.50 cc	0.60 cc

It will be evident from the above results that the precipitation value of $Ba(NO_3)_2$ is practically constant when Sb_2S_3 sol is diluted, whilst that of $Pb(NO_3)_2$ is practically directly proportional to the concentration of the sol; in other words, more concentrated sols require greater quantities of $Pb(NO_3)_2$ than diluted ones. This difference in the behaviour of $Pb(NO_3)_2$ and $Ba(NO_3)_2$ is due to the more marked adsorption of $Pb^{\cdot\cdot}$ ions than that of $Ba^{\cdot\cdot}$ ions by Sb_2S_3 sol; in other words the ratio of the adsorption of $Ba^{\cdot\cdot}$ ion to that of NO'_3 ion is less than that of $Pb^{\cdot\cdot}$ ion to NO'_3 ion by Sb_2S_3. This behavicur of $Pb(NO_3)_2$ with Sb_2S_3 is more or less allied to that of Ag NO_3 towards As_2S_3 sol as investigated in this paper. Consequently it is very likely that in the coagulation of Sb_2S_3 by a mixture of electrolytes like $Pb(N)_3)_2$ and $Al(NO_3)_3$, more or less additive relationship would be obtained and no marked acclimatization would be observed with Sb_2S_3 sol and $Pb(NO_3)_2$.

In a recent paper Freundlich and Wosnessensky[2] have observed the coagulation of $Fe(OH)_3$ sol obtained (i) by the oxidation of $Fe(CO)_5$ by H_2O_2 and (ii) by hydrolysis of $FeCl_3$ solution. The following results have been obtained by them:—

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[1] Sen, Ganguly and Dhar: J. Phys. Chem. 28, 313 (1924).

[2] Kolloid-Z. 33, 222 (1923).

TABLE XXVII

Electrolyte	Precipitation value with $Fe(OH)_3$ sol from $Fe(CO)_4$	Precipitation value with $Fe(OH)_3$ sol from $FeCl_3$
KCl	5.4	240
$\frac{MgCl_2}{2}$	5.6	250
$\frac{BaCl_2}{2}$	6.4	280
$\frac{AlCl_3}{3}$	>200	500
$\frac{FeCl_3}{3}$	>200	>400

It is evident from the above table that more of $FeCl_3$, $AlCl_3$, etc., are necessary to coagulate a sol of $Fe(OH)_3$ than an equivalent amount of KCl. This is certainly due to the fact that the sol is peptised by the adsorption of $Fe^{\cdots}$, $Al^{\cdots}$ ions, etc.

Some more interesting results have been obtained by the above authors in their investigation on the coagulation of $Fe(OH)_3$ sol by mixtures like $FeCl_3$ and KCl, $AlCl_3$ and KCl, $La(NO_3)_3$ and KCl, etc. Their results are as follows:

TABLE XXVIII

Amount of $FeCl_3$ millimoles per litre	Amount of KCl millimoles per litre to coagulate
0	11.5
0.076	29.0
0	
0.200	85.5
0.400	241.0

TABLE XXIX

Amount of $AlCl_3$ millimoles per litre	Amount of KCl millimoles per litre to coagulate
0	8.4
0.2	41.0
0.5	95.5
1.0	140.0
5.0	295.0

TABLE XXX

Amount of $La(NO_3)$ millimoles per litre	Amount of KCl millimoles per litre to coagulate
0	8.5
2.5	27
5.0	36
25	41

From the above data it will be evident that the sol gets stabilised by the adsorption of $Fe^{\cdots}$, $Al^{\cdots}$, $La^{\cdots}$, etc., and consequently more and more of KCl is necessary for complete coagulation, when the concentration of substances like $FeCl_3$, etc., are increased. It will be evident from Figs. 4 and 5 that the adsorption of $Al^{\cdots}$, $Fe^{\cdots}$ and $La^{\cdots}$ ions by a sol of $Fe(OH)_3$ follow the general adsorption formula and straight lines are obtained when the logarithms of the differences in the amount of KCl necessary for coagulation of the sol are plotted as ordinates and the logarithms of the concentrations of $FeCl_3$ and $AlCl_3$ added as abscissae. These results obtained by Freundlich and Wosnessensky (loc, cit.) corroborate our view on the subject and we are strongly of the opinion that sols like As_2S_3, Sb_2S_3, mastic, etc., are stabilised by the adsorption of the negatively charged ions and show abnormal behaviour on dilution when coagulated by KCl, LiCl, etc., and are abnormal towards a mixture of electrolytes, and show the phenomenon of acclimatization markedly. Similarly sols like $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, etc., behave normally towards dilution, towards mixture of electrolytes and do not show the phenomenon of acclimatization when coagulated by K BrO_3, KCl, K_2SO_4, etc. On the other hand these very sols show abnormal behaviour on dilution when coagulated by $FeCl_3$, $AlCl_3$, $Al(NO_3)_3$, etc., and behave abnormally towards mixtures of electrolytes like $Al(NO_3)_3$ and K_2SO_4, $FeCl_3$ and K_2SO_4, and show the phenomenon of acclimatization markedly when coagulated by $FeCl_3$, $Al(NO_3)_3$ $La(NO_3)_3$, etc. This is due to the stabilisation of the sol by the adsorption of ions carrying the same charge as the sol, and this adsorption follows the ordinary exponential formula of Freundlich.

The coagulations of As_2S_3 and of $Fe(OH)_3$ have been effected by $BaSO_4$ at various dilutions of the sols and it will be seen that in both these cases the greater the concentration of the sol the greater is the amount of $BaSO_4$ necessary for coagulation. This is because the question of the adsorption of ions carrying the same charge as the sol does not enter in the coagulation of sols by freshly precipitated $BaSO_4$. Similarly we have proved experimentally that in the coagulation of As_2S_3 by positively charged $Fe(OH)_3$ sol the greater the concentration of As_2S_3 the greater is the amount of $Fe(OH)_3$ necessary for coagulation.

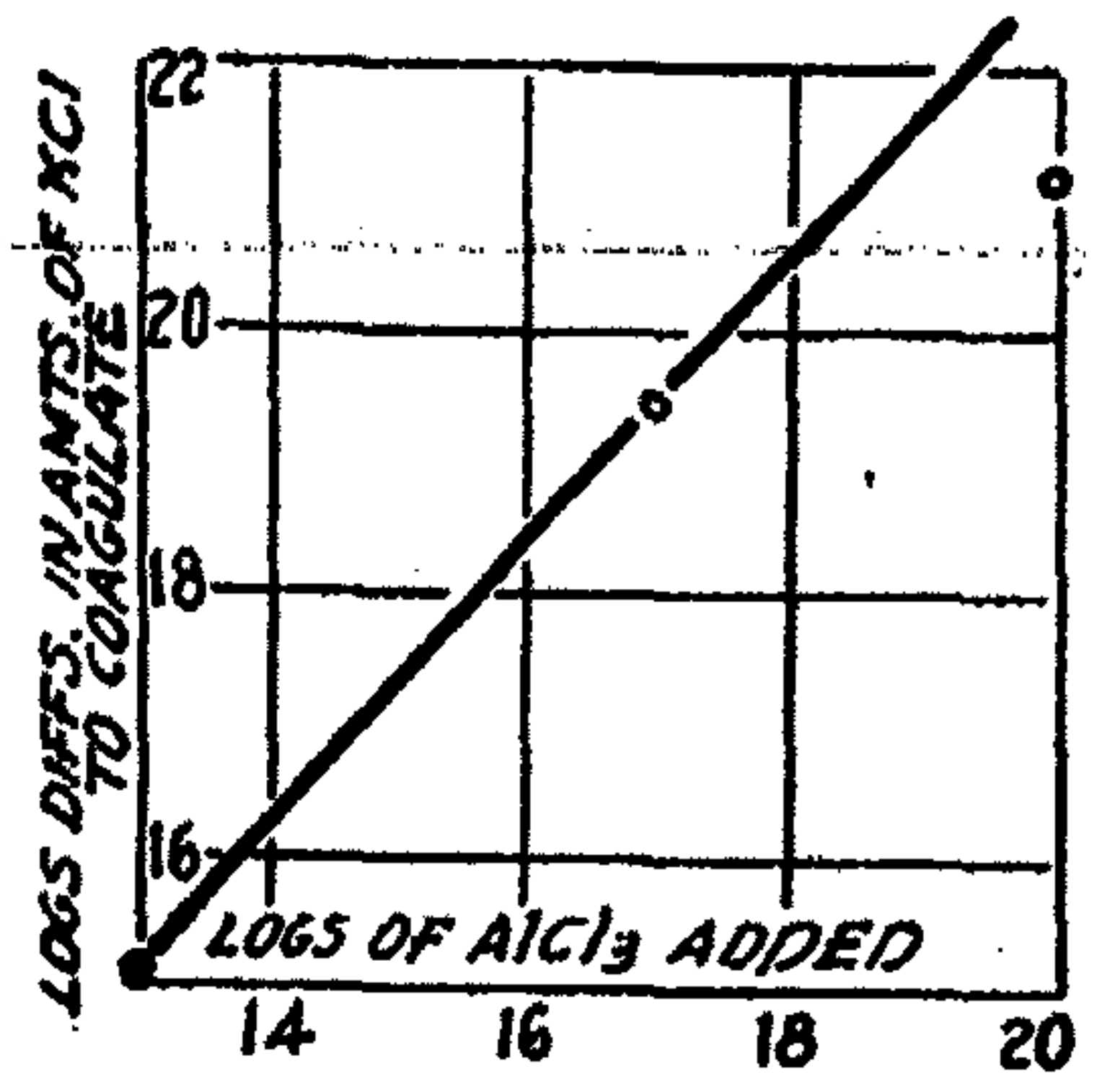

FIG. 4

Coagulation of $Fe(OH)_3$ sol in presence of $AlCl_3$ by KCl (Freundlich and Wosnessensky).

In a previous paper[1] we have shown that when KCl is used as the coagulating agent diluted sols of As_2S_3 and Sb_2S_3 do not coagulate even after the lapse of 16 hours when sufficient electrolyte is added to coagulate the concentrated sols in an hour. In the same paper we came to the conclusion that the view advanced by Kruyt and Spek[2], and Mukerji and Sen[3], that the decreased chance of collision amongst the colloidal particles is an important factor that prevents a weaker sol of arsenious sulphide from coagulating is not corroborated by experiments.

From the results obtained in this paper on the coagulation of sols by freshly precipitated $BaSO_4$, where the coagulation is more or less of a mechanical nature, and is caused by the collision of colloid particles with the particles of barium sulphate, we have observed that the amount of $BaSO_4$ necessary for complete clearing (coagulation) of a sol decreases with the decreasing concentration of the sol. Similarly from our experiments on the coagulation of As_2S_3

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[1] Ghosh and Dhar: Kolloid-Z. (1924).

[2] Kolloid-Z. 25, 3 (1919).

[3] J. Chem. Soc. 115, 461 (1919).

sol by $Fe(OH)_3$ sol we find that the less the concentration of As_2S_3 the less is the amount of $Fe(OH)_3$ necessary for coagulation.

According to Kruyt and Spek, and Mukherji and Sen, dilution of a sol of As_2S_3 leads to its stabilisation due to the decreased chance of collision amongst the colloidal particles and the precipitants; if such is the case, then more of the precipitants like freshly precipitated $BaSO_4$, positively charged $Fe(OH)_3$, etc., would be necessary to coagulate a dilute sol of As_2S_3 than a concentrated one, but as a matter of fact experimental results show that the greater the concentration of As_2S_3 sol the greater is the amount of $BaSO_4$ or $Fe(OH)_3$ sol necessary for coagulation. Consequently the dilution rule based on the phenomenon of adsorption that the greater the concentration of a sol the greater is the amount of precipitant necessary for coagulation has a general application. Our results on the coagulation of Sb_2S_3 sulphide sol in presence of KOH show that in general as the concentration of KOH is increased greater quantities of univalent, bivalent, and trivalent electrolytes are necessary to coagulate the sol.

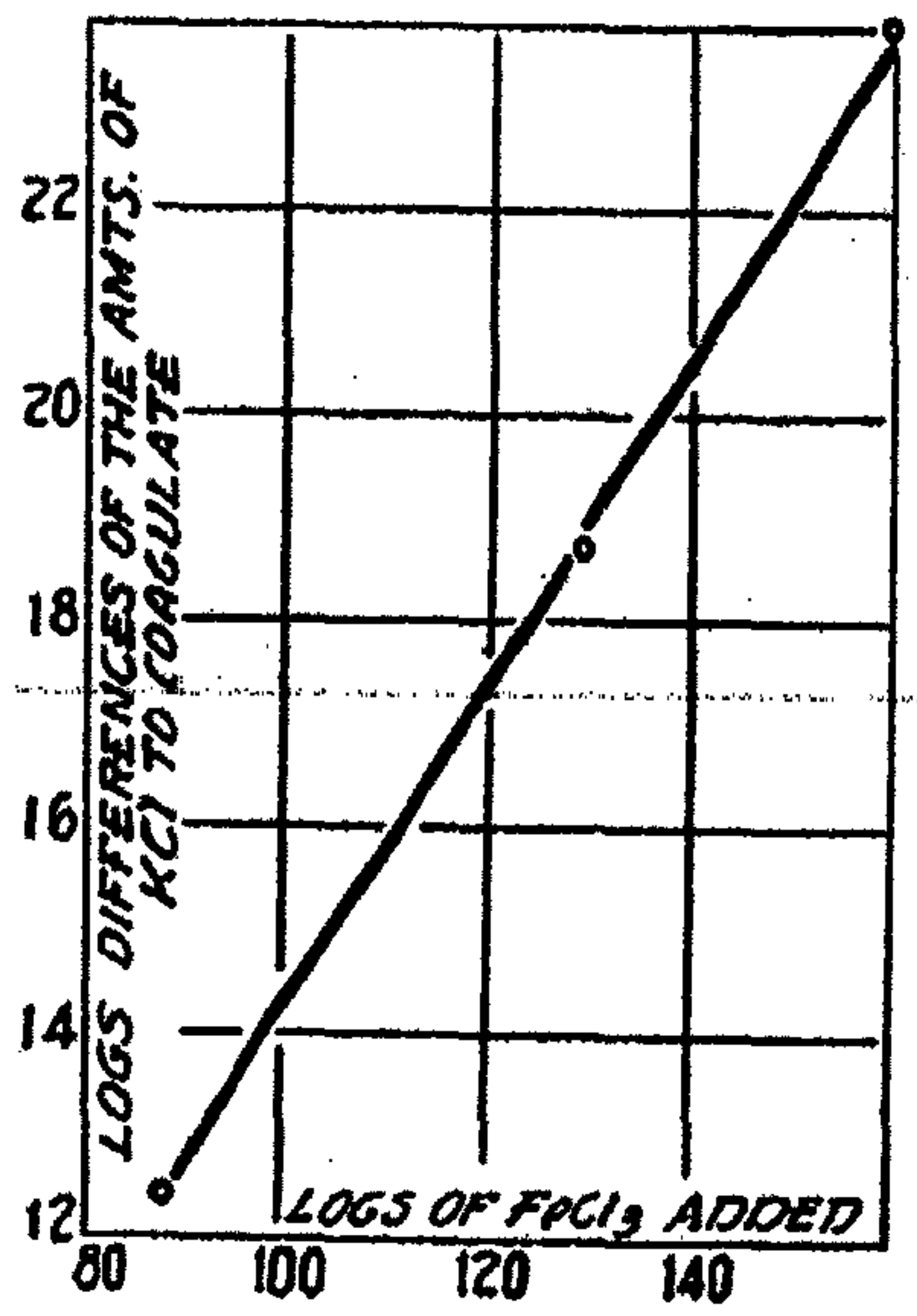

Fig. 5

Coagulation of $Fe(OH)_3$ sol in presence of $FeCl_3$ by KCl (Freundlich and Wosnessensky).

It has been observed in a previous paper[1] that OH ions even in traces exert great peptising effect on Sb_2S_3, As_2S_3, SnS_2, etc. Thus 5 cc NaOH N/100 solution is sufficient to convert 1 gram of freshly precipitated As_2S_3 to the colloidal condition. Similar results were obtained with Sb_2S_3, SnS_2, etc. It is well known that OH ions have a great chemical affinity for these sulphides and exert solvent action on them, and hence the sols become stable towards all electrolytes when KOH is added to the sulphide sol.

From our experiments on the coagulation of As_2S_3 and Sb_2S_3 by electrolytes in presence of non-electrolytes like ethyl alcohol, propyl alcohol, urea and cane sugar we observe that both the sols become more stable towards all electrolytes in presence of ethyl and propyl alcohols. The stabilising influence of these alcohols on As_2S_3 and Sb_2S_3 sols is more pronounced when the above sols are coagulated by bi- and trivalent ions than when the sols are coagulated with monovalent electrolytes. With urea and cane sugar both the above sols become unstable towards all electrolytes.

In this connection it will be interesting to discuss the works of other investigators on the influence of non-electrolytes on the coagulation of sols. Kruyt

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[1] Kolloid-Z. (1924).

and Duin[1] have shown that As_2S_3 becomes unstable towards uni- and tri-valent cations and becomes stable towards bi- and quadri-valent cations in presence of non-electrolytes like ethyl, propyl and iso-amyl alcohols, etc., whilst with $Fe(OH)_3$ they have observed that the sol becomes unstable when coagulated by KCl, K_2SO_4, etc., in presence of phenol and iso-amyl alcohol. Gold sol is stabilised by ether and iso-amyl alcohol. On the other hand, Freundlich and Rona[2] have shown that $Fe(OH)_3$ becomes unstable towards KCl, KBr, etc., but not with K_2SO_4 and K_3 citrate in presence of urethanes, camphor, amyl-alcohol, thymol, etc. They have also shown that such substances as thymol, camphor, etc., diminish the rate of movement of $Fe(OH)_3$ sol in an electric field, and they explain this behaviour on the view of the adsorption of the substances on the surface of the colloid particles and the diminution in the dielectric constant of the medium.

Rona and Gyorgi[3] have shown that a suspension of kaolin becomes unstable towards electrolytes in presence of several alcohols, chloroform, camphor, thymol, etc.

From the above results it is difficult to draw any definite conclusion with regard to the coagulation of sols by electrolytes in presence of non-electrolytes. We have observed that the presence of alcohols makes the sols of Sb_2S_3 and As_2S_3 stable towards electrolytes especially bi- and tri-valent cations, whilst Kruyt and Duin have observed the stabilising influence of non-electrolytes towards the coagulation of As_2S_3 by bi- and tetra-valent ions. With gold they have shown that the sol becomes stable, towards uni- and tri-valent ions and unstable towards bivalent cations in presence of ether and amyl alcohol.

It will be interesting to observe that we have shown that in presence of H_2S both Sb_2S_3 and As_2S_3 sols become stable towards uni- and tri-valent cations and unstable towards bi-valent cations. It is apparent, therefore, that the results on the influence of non-electrolytes on the coagulation of sols are rather discordant and insufficient for a satisfactory explanation to be advanced.

Summary

1. In this paper further evidence has been brought forward in favour of the view that (1) abnormal behaviour on dilution (2) abnormality towards a mixture of electrolytes and (3) the phenomenon of acclimatization are essentially connected and go hand in hand. A dilute sol of Prussian blue takes up more KCl than a concentrated one for coagulation. This sol does not show additive relationship when coagulated by a mixture of electrolytes of varying valency and it also shows the phenomenon of acclimatization markedly. In these respects this sol behaves exactly like arsenious sulphide sol.

2. Smaller quantities of KCl and KNO_3 are required when prussian blue is coagulated in presence of HCl or HNO_3. An explanation based on the phenomenon of hydrolysis has been advanced.

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[1] Kolloidchem. Beihefte, 5, 269 (1914).

[2] Biochem. Z. 81, 87 (1917).

[3] Biochem. Z., 105, 133 (1920).

3. When positively charged ferric hydroxide sol is coagulated by $Al(NO_3)_3$, $FeCl_3$, etc., the dilute sol takes up more electrolyte than the concentrated one. Moreover this sol behaves abnormally when coagulated by a mixture of electrolytes like $Al(NO_3)_3$ and K_2SO_4, $FeCl_3$ and K_2SO_4, etc. Ferric hydroxide sol shows the phenomenon of acclimatization markedly when coagulated by $Al(NO_3)_3$, $FeCl_3$, etc.

On the other hand, this sol is normal towards dilution when coagulated by KCl, $KBrO_3$ and is also normal towards a mixture of electrolytes like $KBrO_3$ and $K_2C_2O_4$, KCl and K_2SO_4, etc.

An explanation of these results based on the phenomenon of the adsorption of ions carrying the same charge as the sol has been advanced.

4. More of univalent $Ag^{\cdot}$ ion and other univalent organic cations from aniline hydrochloride, morphine hydrochloride, etc., are required to coagulate a stronger sol of As_2S_3 than a diluted one.

5. The influence of several non-electrolytes on the coagulation of As_2S_3, and Sb_2S_3 has been investigated. It is not yet possible to put forward a satisfactory explanation of the influence of non-electrolytes on the coagulation of sols.

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November 20, 1924.

ON THE MECHANISM OF THE ACTION OF PROMOTERS IN CATALYSIS

BY M. C. BOSWELL AND C. H. BAYLEY

A theory has been developed by the senior author with regard to the mechanism of catalysis by partially reduced oxides and by platinum black.[1] According to this theory the catalyst consists of particles of unreduced oxide surrounded by a layer of reduced metal or lower oxide carrying positively charged hydrogens and negatively charged hydroxyls, and this surface layer of dissociated water molecules is the seat of the catalysis of oxidation, of reduction and of hydrolysis observed with these partially reduced oxides. This is clearly seen in Fig. 1 which should be compared with Figs. 2-4.

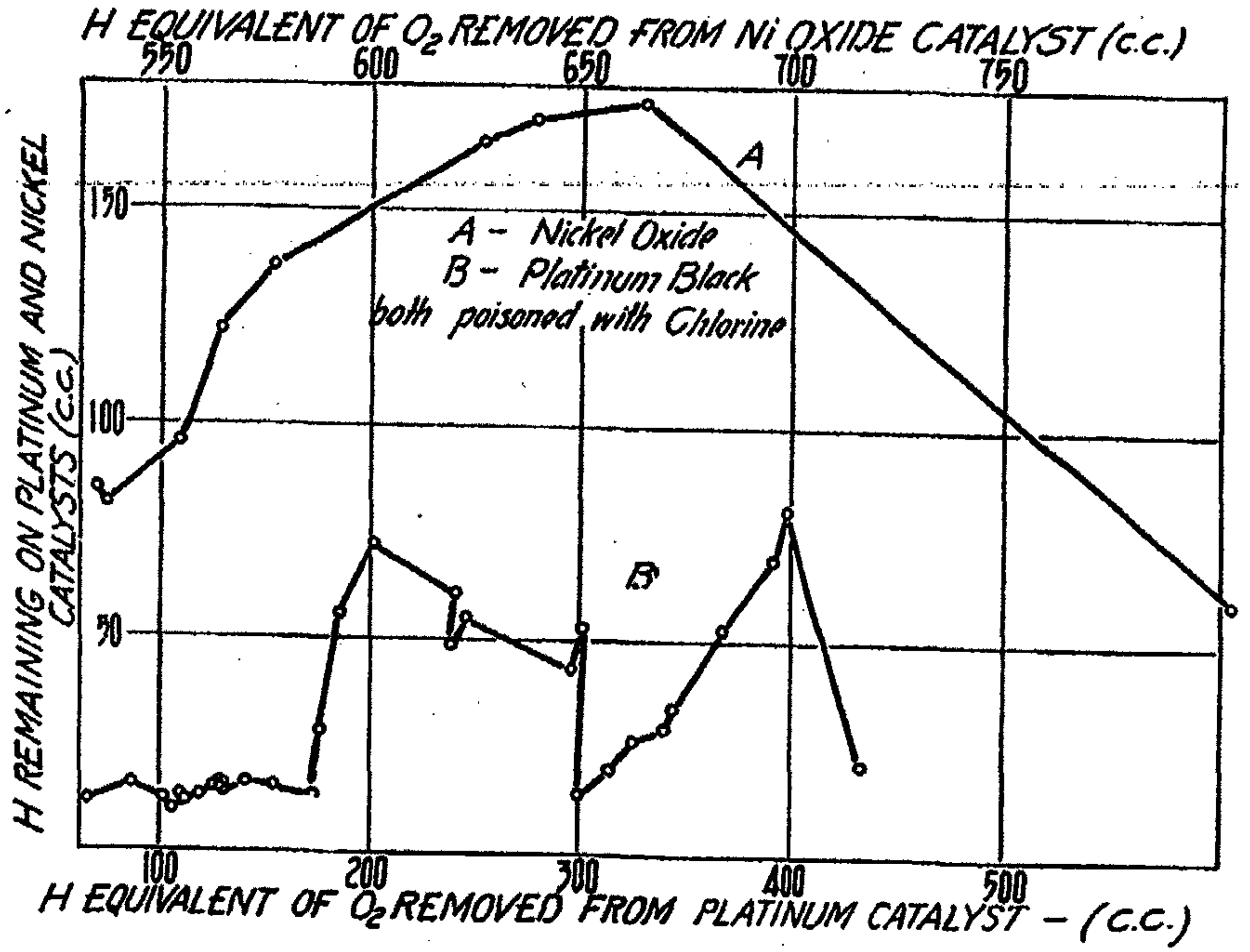

FIG. 1

More recently the authors have shown[2] that this theory gives a very satisfactory picture, in harmony with the facts, of the so-called poisoning of catalysts. The poisoning is due to the destruction of the surface film which is the real seat of the catalytic properties. The charged hydrogens and hydroxyls lose their charges and pass off as free water. Thus, the complex loses the very

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[1] Boswell: Proc. Roy. Soc. Canada, 16, III (1922); Boswell and McLaughlin: 17, III (1923).

[2] Boswell and Bayley: J. Phys. Chem. 29, 11-19 (1925).

effective protection afforded by this surface for the underlying interior content of oxygen. Accordingly, if the catalyst, in this condition, is brought into contact with free hydrogen, the interior oxygen content of the complex is rapidly removed as water, the poison still present (it has regenerated in a cycle of reactions) preventing the re-establishment of the catalytic film.

If this view of the mechanism of the action of catalysts and of catalytic poisons is correct, then the action of the so-called "promoters" in still further enhancing the activity of catalysts, is immediately suggested by the theory.

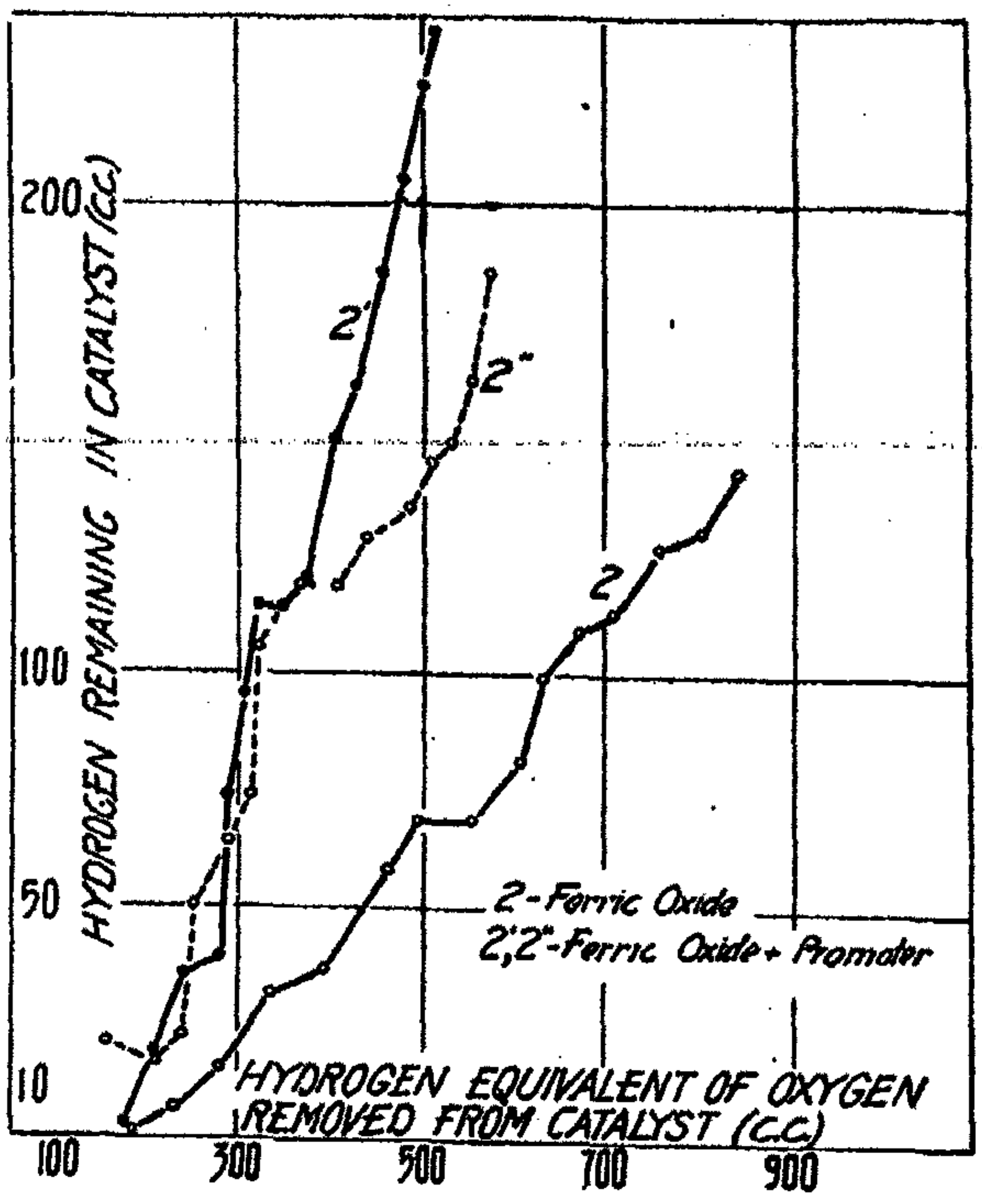

FIG. 2

For if the activity of the catalysts depends on these surface films of dissociated water, and if the poisoning of the catalyst is due to the destruction of these films and the prevention of their re-formation, then the action of promoters is probably due to the increased concentration of charged hydrogens and hydroxyls in the surface film. That is, the promoter enables the catalyst to hold more charged hydrogens and hydroxyls in the surface films per gram of catalyst than the catalyst alone can hold. Working with the well known cases of promoter action, viz cerium oxide as promoter of partially reduced ferric oxide and potassium hydroxide as promoter of platinum black, we have found that the above conclusions of the theory are strikingly verified by the facts. Iron oxide was reduced in hydrogen at 275°C. The hydrogen remaining on the catalyst was plotted against oxygen removed from the catalyst as free water.

Curve 2, Fig. 2, represents this action in the case of oxide alone, and curves $2'$ and $2''$ represent the action where 0.5% cerium oxide was present uniformly distributed throughout the iron oxide. It will be seen that the amount of hydrogen remaining on the catalyst for any given amount of oxygen removed, is greater in the presence of the promoter than in its absence. Also that the rate at which oxygen is removed as free water from the oxide layer is very much slower in the presence of the promoter. That is, in terms of the theory, for any given amount of oxygen removed as water from the catalyst, the catalyst is able to hold a very much greater amount of water as charged hydrogens and hydroxyls on the surface, in the case where the promoter is used. It will also be observed that the general form of the curve indicates that the ratio of hydrogen remaining on the catalyst to oxygen removed from the catalyst is a constant.

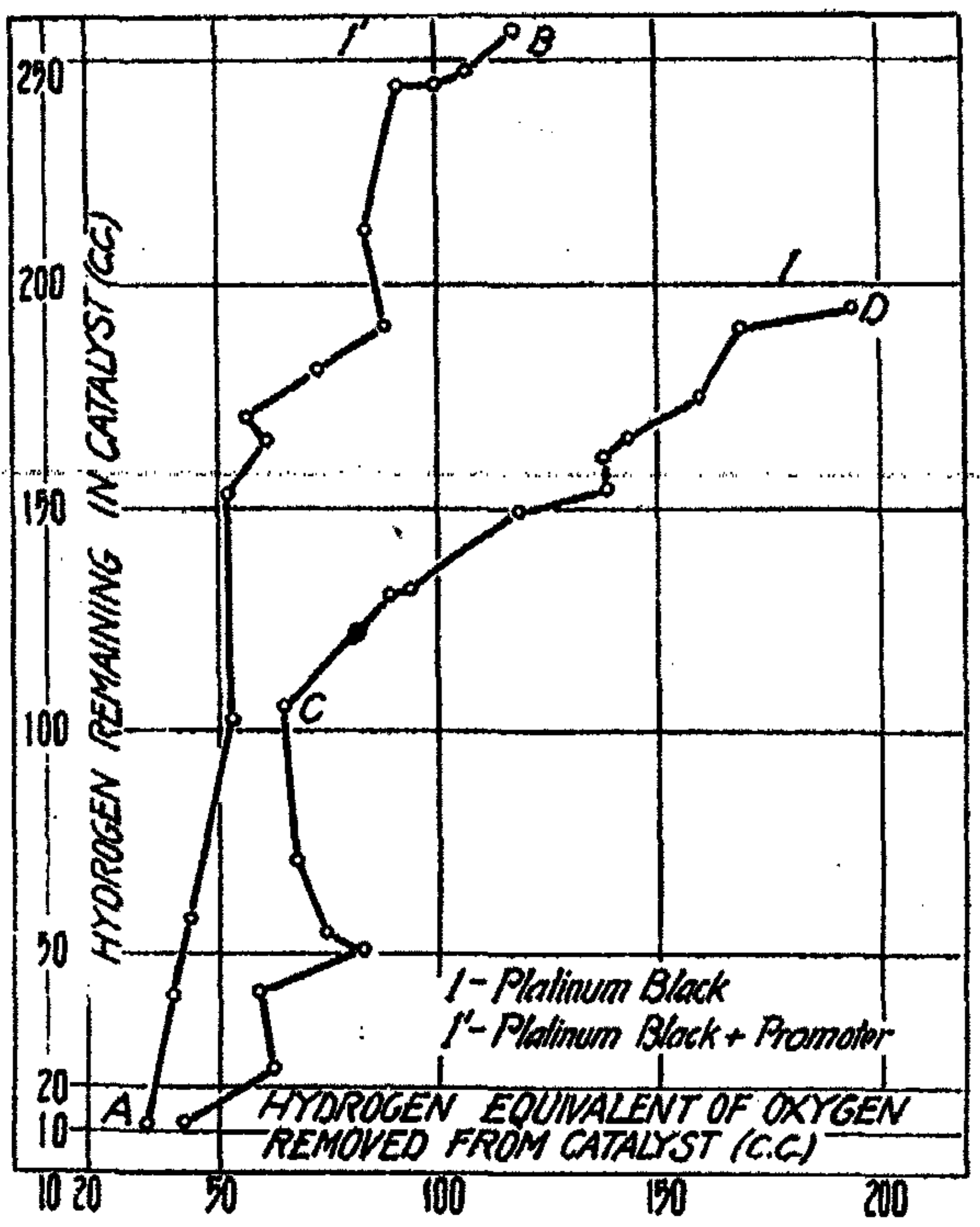

FIG. 3

Likewise, in the case of platinum black, using potassium hydroxide as promoter (see Fig. 3), the same increased concentration of dissociated water in the surface film, and slowness in the loss of interior oxygen is found in the presence of the promoter. In this case, where the promoter is absent, there is a distinct change of direction of the curve at the point C, the general form from C to D being approximately a straight line. That is, at the point C the rate of loss of oxygen is markedly increased and is constant to the point D, whereas where the promoter is present in the platinum black this sudden break in the curve is not found, the general direction of the curve from A to B being approximately a straight line. That is, the loss of oxygen in the former case, where the promoter was absent, is much greater than when the promoter was present.

Fig. 4 represents the behaviour of platinum black with and without promoter, identical in all respects with the platinum black experiments represented in Fig. 3 with the exception that in the former the platinum black stood in the reaction tubes in an atmosphere of nitrogen for eight weeks. It will be seen that in general the same statements hold in the two cases, and that the action of the promoter is to increase the amount of hydrogen on the catalyst for any given amount of oxygen removed. The chief difference is that in the case of the platinum samples which stood for 8 weeks, the amount of hydrogen remaining on the catalyst for a given amount of oxygen removed is greater than in the freshly prepared platinum, both where the promoter is present and where it is absent. This may possibly be due to the reduction in size of the platinum particles on standing, thus presenting a larger surface and enabling a larger amount of hydrogen and hydroxyl to be held on the surface.

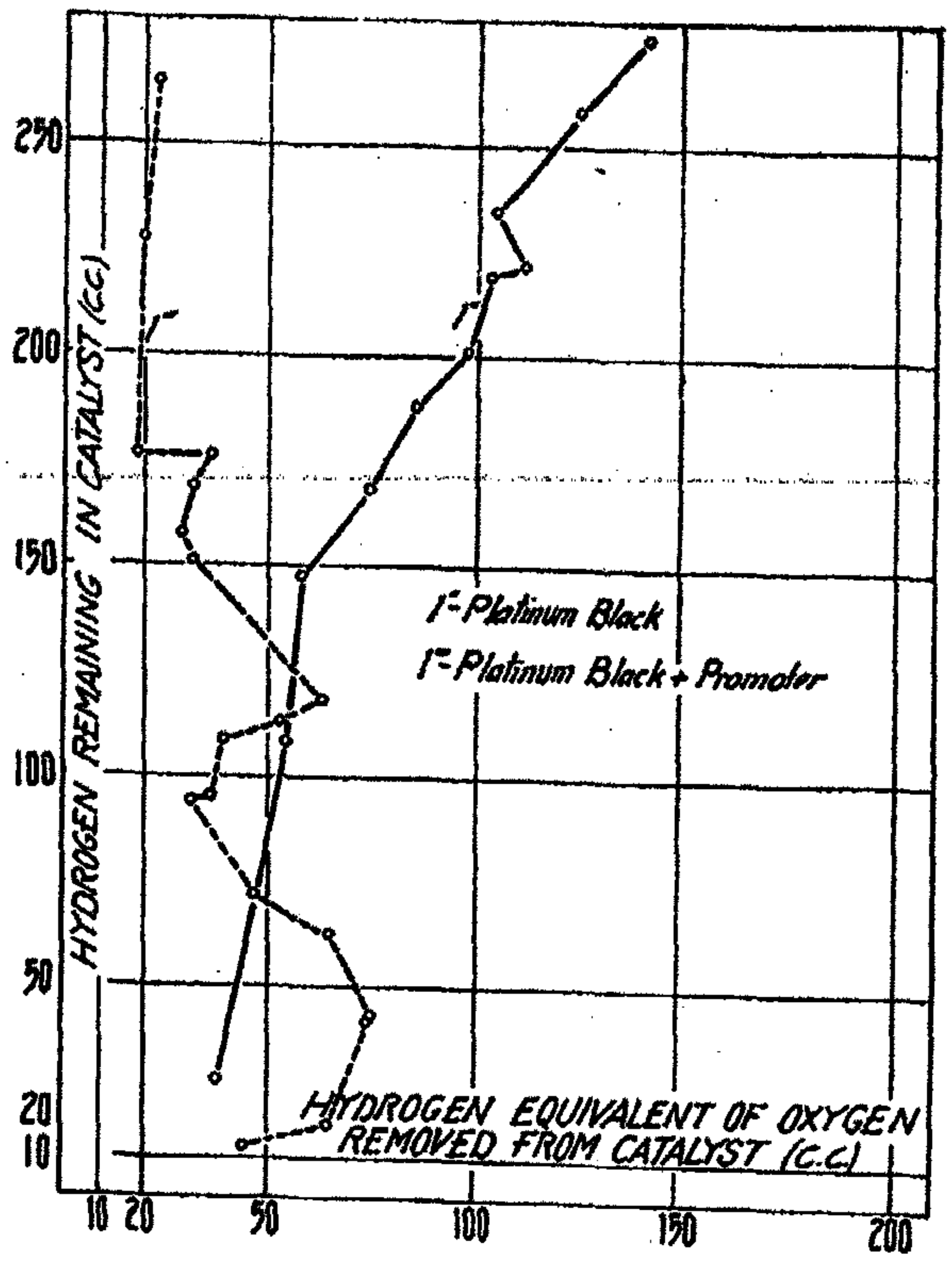

FIG. 4

That this hydrogen left on reduced oxide catalysts is present in the form of charged hydrogens and hydroxyls is supported by the experimental evidence already presented in the papers above referred to, and is corroborated by more recent evidence which will be presented by us in the near future. There it will be shown: (1) that the total hydrogen remaining on a partially reduced oxide catalyst is present only to a very slight extent in the form of free dissolved gas; (2) that a large part of this hydrogen is associated with oxygen in an external layer; (3) that the interior content of oxygen is vital for the maintainance of these partially reduced oxides as catalysts; and (4) that platinum black has a large interior oxygen content. This latter fact is of considerable importance to organic chemists who use platinum black as catalyst for hydrogenation. It has been the custom for organic chemists to use platinum black as a hydrogen carrier without regard to the fact that prior oxidation by the high oxygen content of the platinum black may interfere, with the result that, instead of simple hydrogenation, the actions in reality have consisted of oxidation by the platinum black, followed by reduction by hydrogen and further hydrogenation of the reduction product. Pummerer's hydrogenation of rubber[1] using platinum black, as has been shown in this laboratory, falls in this category.

EXPERIMENTAL

Influence of Cerium Oxide on the Reduction of Ferric Oxide

Preparation of Catalyst.

A quantity of Kahlbaum's ferric nitrate crystals were recrystallized from distilled water containing a little nitric acid, to prevent the formation of the basic salt. The crystals were cubical, corresponding to the formula

$$Fe(NO_3)_3 6H_2O.$$

150 grams of the dry crystals were dissolved in 600 cc. water, and the solution divided into 6 portions of 100 cc. each. 5 grams of ceric oxalate were ignited to the oxide and 0.75 gram of this was dissolved in 30 cc. nitric acid (50%). One third of this solution was added to each of three of the ferric nitrate portions—this giving 6 solutions in all—3 containing ferric nitrate alone and 3 containing the ferric and cerium nitrates. The 6 solutions were poured into 6 200 cc. crucibles and evaporated to small bulk on the water bath. 2.5 grams of Kahlbaum's C.P. acid washed asbestos were added to the contents of each crucible, and the evaporation carried on to dryness. The residues were ignited simultaneously in an electric muffle at 750°C. The asbestos bearing the oxide was then scraped out and placed into 6 reaction tubes 40 cm. long and 18 mm. in diameter.

Reduction of Catalyst.

The apparatus used was similar to the one used in the previously described papers on platinum and nickel. The apparatus train consisted of a 400 cc. chaduated and water jacketted gas burette, two U tubes containing concentrated sulphuric acid on pumice, the reaction tube containing the catalyst,

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[1] Pummerer: Ber. 55, 3458 (1922).

passing through an electric tube furnace, two U tubes containing sulphuric acid on pumice, a small mercury manometer and a 400 cc. gas burette similar to the first one.

The experiments were all run at 275°C. Before the reduction was begun the catalyst tube was thoroughly dried out. This was done by passing nitrogen free from oxygen through the tube heated to 275°C. until no further increase in weight was noticed in the U tube immediately following the catalyst tube.

TABLE I

Iron Oxide without Promoter. Fig. 2

Treatment	Hydrogen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	182.9	180.9	180.9	2.0
*—	—	2.0	182.9	0.0
2	55.5	47.9	230.8	7.6
—	—	2.4	233.2	5.2
3	55.5	44.7	277.9	16.0
—	—	1.2	279.1	14.8
4	70.0	52.4	331.5	32.4
—	—	4.8	336.3	27.6
5	69.1	59.3	395.6	37.4
—	—	5.3	400.9	32.1
6	79.2	53.3	454.2	58.0
—	—	0.3	454.5	57.7
7	49.1	38.2	492.7	68.6
—	—	8.9	501.6	59.7
8	59.2	50.3	551.9	68.6
—	—	0.0	551.9	68.6
9	64.6	50.5	602.4	82.7
—	—	0.8	603.2	81.9
10	45.5	28.6	631.8	98.8
—	—	1.7	633.5	97.1
11	50.0	38.0	671.5	109.1
—	—	4.8	676.3	104.3
12	41.8	32.3	708.6	113.8
—	—	1.3	709.9	112.5
13	59.1	44.1	754.0	127.5
—	—	2.7	756.7	124.8
14	53.7	47.8	804.5	130.7
—	—	1.4	805.9	129.3
15	61.0	36.4	842.3	153.9

*After standing over night in nitrogen, nitrogen was passed and the temperature raised to 275°C. and maintained at this temperature for a quarter of an hour, and the water weighed.

The method of carrying out the reduction was as follows:

Nitrogen free from oxygen was passed through the train of tubes and through the catalyst tube for half an hour, in order to expel any air present. The apparatus was now closed and hydrogen introduced into the right hand burette. It was then brought to atmospheric pressure by means of a levelling tube and the volume read. It was then passed over the catalyst and back into the burette, the volume being read after each passage, and the passages being

TABLE II

Iron Oxide with Promoter. Fig. 2

Treatment	Hydrogen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	175.6	155.1	155.1	20.5
*—	—	5.0	160.1	15.5
2	49.1	47.5	207.6	17.1
—	—	2.1	209.7	15.0
3	41.9	34.1	243.8	22.8
—	—	3.1	246.9	19.7
4	34.6	4.2	251.1	50.1
—	—	1.2	252.3	48.9
5	45.5	30.8	283.1	63.6
—	—	0.0	283.1	63.6
6	40.0	30.1	313.2	73.5
—	—	4.8	318.0	68.7
7	39.1	2.8	320.8	105.0
—	—	5.6	326.4	99.4
8	58.2	38.5	364.9	119.1
—	—	5.6	370.5	113.5
9	41.0	36.4	406.9	118.1
—	—	5.7	412.6	112.4
10	46.4	29.8	442.4	129.0
—	—	6.0	448.4	123.0
11	47.3	35.3	483.7	135.0
—	—	0.2	483.9	134.8
12	32.8	22.2	506.1	145.4
—	—	2.6	508.7	142.8
13	30.9	23.9	532.6	149.8
—	—	1.6	534.2	148.2
14	33.7	19.1	553.3	162.8
—	—	0.0	553.3	162.8
15	46.4	22.5	575.8	186.7

*After standing over night in nitrogen, nitrogen was passed and the temperature raised to 275°C. and maintained at this temperature for a quarter of an hour, and the water weighed.

repeated until there was no further diminution in volume. Nitrogen free from oxygen was now passed through the apparatus for half an hour in order to expel all the free hydrogen (it has been shown that no hydrogen is removed from the catalyst during this process). The catalyst tube was now closed at both ends and the water absorption tubes disconnected and weighed in order to determine the water formed during the reduction. The catalyst tube was again connected to the nitrogen supply and allowed to cool in a current of nitrogen.

TABLE III

Iron Oxide with Promoter. Fig. 2

Treatment	Hydrogen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	175.6	171.6	171.6	4.0
*—	—	3.8	175.4	0.2
2	59.1	39.5	214.9	19.8
—	—	5.0	219.9	14.8
3	43.7	21.5	241.4	37.0
—	—	5.3	246.7	31.7
4	38.2	31.1	277.8	38.8
—	—	1.4	279.2	37.4
5	42.8	6.6	285.8	73.6
—	—	2.2	288.0	71.4
6	37.3	12.8	300.8	95.9
—	—	3.4	304.2	92.5
7	39.1	16.0	320.2	115.6
—	—	6.2	326.4	109.4
8	25.5	20.4	346.8	114.5
—	—	2.6	349.4	111.9
9	29.1	20.9	370.3	120.1
—	—	2.5	372.8	117.6
10	65.5	32.3	405.1	150.8
—	—	1.7	406.8	149.1
11	31.8	18.8	425.6	162.1
—	—	1.1	426.7	161.0
12	51.9	26.7	453.4	186.2
—	—	0.0	453.4	186.2
13	44.6	25.2	478.6	205.6
—	—	0.6	479.2	205.0
14	42.8	22.4	501.6	225.4
—	—	0.1	501.7	225.3
15	26.4	13.7	515.4	238.0

*After standing over night in nitrogen, nitrogen was passed and the temperature raised to 275°C. and maintained at this temperature for a quarter of an hour, and the water weighed.

It was securely closed and allowed to remain over night in an atmosphere of nitrogen. Next morning the water absorption tubes were inserted and nitrogen passed at 275°C. for fifteen minutes in order to sweep over the water formed over night, which was then weighed. The cycle of operations was now repeated.

Tables I-III show the results of the measurements.

TABLE IV

Platinum Black without Promoter. Fig. 3

Treatment	Hydrogen used up cc.	Oxygen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	54.6	—	42.0	42.0	12.6
	—	0	2.8	44.8	—
2	35.5	—	18.8	63.6	26.5
	—	11.8	1.2	41.2	—
3	32.8	—	17.3	58.5	40.8
	—	0	4.2	62.7	—
4	34.6	—	20.1	82.8	51.1
	—	11.8	0.7	59.9	—
5	20.0	—	14.2	74.1	56.2
	—	11.8	2.4	52.9	—
6	31.8	—	14.5	67.4	71.1
	—	8.1	3.0	54.2	—
7	48.2	—	9.9	64.1	106.4
	—	3.6	3.7	60.6	—
8	55.5	—	27.7	88.3	130.5
	—	4.5	1.2	80.5	—
9	15.5	—	13.0	93.5	131.8
	—	4.5	5.0	89.5	—
10	51.0	—	28.1	117.6	149.7
	—	0	1.2	118.8	—
11	26.3	—	19.9	138.7	154.9
	—	10.0	3.3	122.0	—
12	26.4	—	16.0	138.0	162.0
	—	7.3	1.4	124.8	—
13	25.5	—	18.7	143.5	167.4
	—	0	1.4	144.9	—
14	24.5	—	14.8	159.7	175.7
	—	5.6	2.7	151.2	—
15	35.5	—	17.6	168.8	190.9
	—	0	2.2	171.0	—
16	19.1	—	12.4	183.4	195.4

TABLE V

Platinum Black with Promoter. Fig. 3

Treatment	Hydrogen used up	Oxygen used up	Hydrogen equivalent of water formed	Hydrogen equivalent of oxygen removed	Hydrogen remaining on catalyst
	cc.	cc.	cc.	cc.	cc.
1	45.5	—	33.7	33.7	11.8
	—	6.4	0.8	21.7	
2	48.2	—	17.9	39.6	41.3
	—	6.4	2.3	29.1	
3	33.7	—	14.0	43.1	58.7
	—	6.4	0.0	30.3	
4	67.3	—	23.0	53.3	103.0
	—	16.4	1.3	21.8	
5	82.0	—	29.7	51.5	154.0
	—	6.4	0.4	39.1	
6	34.6	—	21.6	60.7	166.6
	—	12.7	3.1	38.4	
7	26.3	—	18.5	56.9	171.3
	—	6.4	0.0	44.1	
8	12.8	—	12.8	56.9	171.3
	—	4.5	0.0	47.9	
9	33.7	—	24.2	72.1	180.8
	—	2.7	0.0	66.7	
10	30.9	—	21.6	88.3	190.1
	—	8.2	1.5	73.4	
11	36.4	—	10.8	84.2	214.2
	—	3.6	1.1	78.1	
12	46.4	—	13.5	91.6	246.0
	—	4.5	1.9	84.5	
13	16.5	—	15.2	99.7	245.4
	—	2.7	1.5	95.8	
14	15.5	—	11.2	107.0	248.2
	—	3.6	4.0	103.8	
15	27.3	—	13.4	117.2	258.1

Influence of Potassium Hydroxide on the Reduction of Platinum Black

The eight grams of platinum black used in these experiments were prepared by a modification of the method of Loew[1] and described in the above-mentioned paper on the "Mechanism of Catalysis by Platinum"[2].

2 grams of this platinum black were used in each experiment. This was placed in a porcelain boat 7 cm. × 8 mm. and heated to 150°C. in a tube of

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[1] Loew: Ber. **23**, 289 (1890).

[2] Proc. Roy. Soc. Canada, **16**, III (1922).

Jena glass 40 cm. x 18 mm. until there was no further increase in the weight of the U tube—indicating that no more water was being evolved.

Platinum Black without Promoter.

2 grams of the platinum black were dried at 150°C. to constant weight and treated alternately with H_2 and O_2 in the same apparatus as used in the experiments with ferric oxide.

Table IV gives the measurements obtained.

TABLE VI

Platinum Black which stood in Nitrogen for eight weeks. Fig. 4

The following measurements were obtained:

Treatment	Hydrogen used up cc.	Oxygen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	65.5	—	37.0	37.0	28.5
	—	2.7	3.1	34.7	25.4
2	101.9	—	19.3	54.0	108.0
	—	5.5	4.0	47.0	104.0
3	54.6	—	11.1	58.1	147.5
	—	1.8	0.4	54.9	147.1
4	40.9	—	19.4	74.3	168.6
	—	3.6	3.0	70.1	165.6
5	36.4	—	14.5	84.6	187.5
	—	4.5	4.0	79.6	183.5
6	35.5	—	17.3	96.9	201.7
	—	3.6	0.0	89.7	201.7
7	30.9	—	13.4	103.1	219.2
	—	2.7	0.0	97.7	219.2
8	15.5	—	13.5	111.2	221.2
	—	10.0	0.0	91.2	221.2
9	26.4	—	13.4	104.6	234.2
	—	4.5	2.2	97.8	232.0
10	54.6	—	28.8	126.6	257.8
	—	3.6	0.0	119.4	257.8
11	41.0	—	22.1	141.5	276.7

Platinum Black with Promoter.

To the 2 grams of platinum black contained in the boat were added 2 cc. of N/10 KOH solution. The amount of KOH added was, therefore, approximately 0.5% of the weight of platinum. The boat was heated to 125°C. in a stream of nitrogen until no more water was evolved. The temperature was then raised to 150°C. and nitrogen passed at this temperature until no more moisture was evolved. The data are given in Tables V-VII.

TABLE VII

Platinum Black which stood in Nitrogen for eight weeks and Promoter added as in previous set of platinum experiments: Fig. 4

Treatment	Hydrogen used up cc.	Oxygen used up cc.	Hydrogen equivalent of water formed cc.	Hydrogen equivalent of oxygen removed cc.	Hydrogen remaining on catalyst cc.
1	58.0	—	44.5	44.5	13.5
	—	0.0	0.0	44.5	13.5
2	24.6	—	20.5	65.0	17.6
	—	6.4	1.7	53.9	15.9
3	49.1	—	20.4	74.3	44.6
	—	9.4	3.8	59.3	40.8
4	16.8	—	14.8	74.1	42.8
	—	19.1	3.4	39.3	39.4
5	49.1	—	26.1	65.4	62.4
	—	20.9	4.8	28.4	57.6
6	32.8	—	18.7	47.1	71.7
	—	19.1	2.4	11.3	69.3
7	44.6	—	20.1	31.4	93.8
	—	6.4	0.0	18.6	93.8
8	17.3	—	16.9	35.5	94.2
	—	7.3	0.0	20.9	94.2
9	32.8	—	18.3	39.2	108.7
	—	4.6	1.2	31.2	107.5
10	28.2	—	21.9	53.1	113.8
	—	5.5	4.2	46.3	109.6
11	25.5	—	16.2	62.5	118.9
	—	27.3	1.3	9.2	117.6
12	58.8	—	22.8	32.0	150.4
	—	10.0	1.6	13.6	148.8
13	23.7	—	14.9	28.5	157.6
	—	7.3	0.0	13.9	157.6
14	30.0	—	18.4	32.3	169.2
	—	5.5	1.2	22.5	168.0
15	21.8	—	13.6	36.1	176.2
	—	19.1	5.0	2.9	171.2
16	19.1	—	14.7	17.6	175.6
	—	5.5	2.5	9.1	173.1
17	64.6	—	10.6	19.7	227.1
	—	6.4	2.4	9.3	224.7
18	54.6	—	13.4	22.7	265.9

The question naturally arises, why do these promoters cause this large increase in concentration of dissociated water in the surface films of the catalysts. Aluminum oxide and cerium oxide, when heated to temperatures up to 450°C., have a capacity of holding very considerable amounts of water on their surfaces. Likewise the alkali hydroxides lose all their water only at very high temperatures. It seems, then, that at the temperatures at which iron oxide is used as a catalyst (around 550°C. in the ammonia synthesis) and the temperature at which nickel oxide is used as a catalyst (around 150°C. in hydrogenations) and the temperature at which platinum black is used as a catalyst (around 450°C. in the ammonia synthesis), the particles of aluminum oxide, cerium oxide and potassium hydroxide disseminated throughout the catalysts hold the charged hydrogens and hydroxyls in larger concentration in the reduced layer surrounding the catalyst. Another and perhaps more important reason for this enhanced capacity for holding dissociated water in the reduced layer, is to be found in the fact that in the presence of the promoter a transfer is more quickly made of oxygen from the interior of the catalyst to the surface layer.

Thus, the promoter probably exerts its influence: (1) by enabling the catalytic surface film to form more rapidly on reduction in hydrogen; (2) by acting as particles scattered through the reduced layer, around which dissociated water can accumulate at higher concentrations; (3) by increasing the stability of the catalytic film so that it is not lost, at elevated temperatures, as free water.

In connection with the general theory of catalysis developed in this laboratory it may be pointed out that just as metallic oxides and platinum black upon reduction at low temperatures yield complexes having a high hydrogen content (which hydrogen we believe is present in the form of charged hydrogens and hydroxyls constituting the surface film, which is responsible for the catalytic properties of these catalysts) so it has been found in this laboratory that some chlorides, nitrides and sulphides, upon reduction in hydrogen at low temperatures, likewise form complexes containing a relatively large amount of hydrogen in some special form, probably in a form analogous to the charged hydrogens and hydroxyls in the case of partially reduced oxides. This is indicated by the fact that these complexes formed from nitrides, chlorides and sulphides also possess the catalytic properties one would expect to find in complexes having surface films of analogous constitutions. The facts and arguments will be presented in detail in the near future.

Summary

The theory of catalytic action by partially reduced oxides and by platinum black and of the mechanism of the action of catalytic poisons of these catalysts developed in this laboratory, is here expanded to include the mechanism of promoter action.

It has been shown that the theory indicates that the probable function of promoters is to increase the concentration of charged hydrogens and hydroxyls

in the catalytic surface layer. The experimental data are entirely in harmony with this theory.

An explanation of the inner mechanism of this process is suggested.

Nitrides, chlorides and sulphides, on reduction in hydrogen form complexes having relatively large amounts of hydrogen remaining on them and having the catalytic properties indicated by the general theory of catalysis developed in this laboratory.

NOTE. The following corrections should be made in the paper of Boswell and Bayley: J. Phys. Chem. **29**, 11 (1925).

page 14 line 7 for .0001 read .01
page 14 line 8 for 33.0 read 24.5
page 14 line 10 for 173.9 read 174.9
page 14 line 35 for 173.9 read 174.9

In the experiment recorded on page eighteen, 0.0164 grams of water was given off during the intermediate passage of nitrogen after the ninth passage of oxygen (line 18) and before the tenth passage of hydrogen (line 19). This measurement was taken into account in the calculation, although it was omitted in the table.

University of Toronto,
School of Engineering Research,
February 12, 1926.

SOLARIZATION, AND PHOTOGRAPHIC REVERSAL BY DESENSITIZERS*

BY B. H. CARROLL

Several times in the history of photography, it has been reported that red and infra-red radiation tends to reverse the effects of shorter wave-lengths on the photographic plate. The undoubted existence of other photochemical reactions in which there is an antagonistic action of radiation of different wavelengths, tends to support this by analogy. Draper and Herschel reported it for the daguerreotype, Waterhouse for the wet collodion plate[1] and it is important to note that Waterhouse found that the reversing effect was greatly increased by staining the plates with "aniline blue" or "annatto," and that his photographs of the solar spectrum in the red and infra-red were taken with stained plates. Abney[2] supported Waterhouse in his theory that red light has a specific reversing effect, but this theory is denied by two of the highest authorities on photography: Lüppo-Cramer[3], and Eder[4]. Neither of them was able to confirm the results of Waterhouse when unstained plates were used, and Bancroft[5] concluded that the effect is simply solarization.

Nevertheless, the existence of a specific reversing action of long wavelength radiation on *silver bromide-gelatine* emulsions has been assumed by recent investigators in spectrum photography. Furthermore, experimental evidence on spectral sensitivity for solarization is very limited. Assuming long wave-length radiation to be the most effective in producing reversal, this might indicate either the existence of a specific reversing action as mentioned above, or that the maximum sensitivity for solarization lay in the red or infrared. All authorities agree that fast, coarse-grained emulsions are most readily reversed; tests were therefore made with four of the fastest obtainable, namely: Eastman Speedway (Seed Graflex), Cramer Hi-Speed, Eastman Super-Speed Portrait Film, and Lumière Sigma. For spectographic tests, a Hilger E3 spectrograph, with quartz lenses and prism, was used. The slit width, unless otherwise stated, was 0.04 mm.; the source of light a 100 watt gas-filled tungsten lamp; the filament of which was focussed on the slit by a quartz lens of 40 mm aperture and 90 mm focal length.

Under these conditions, a strong spectral image extending from 0.35 to 0.55 μ was produced on all the emulsions by an exposure of one second; while longer exposures gave a range from 0.31 to 0.7 μ. Using backed plates, the four

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[1] Waterhouse: Proc. Roy. Soc. **29**, 186 (1875).

[2] Phot. J. **32**, 318 (1908).

[3] Lüppo-Cramer: Phot. Corresp. **39**, 134 (1902); **46**, 344 (1909).

[4] Eder: Beiträge zur Photochemie und Spektralanalyse, **2**, 172 (1904).

[5] Bancroft: J. Phys. Chem. **14**, 303 (1910).

emulsions noted above were each exposed 1, 10, 100 and 1000 seconds and developed with metol-hydroquinone nearly to γ_∞; the longest exposures on two of these emulsions are shown in Fig. 1. With all four, solarization in the region 0.39 to 0.48μ, was distinctly evident on the longest exposure. This is the region of maximum sensitivity for the direct image. There was no evidence of reversal in the red. Separate experiments showed that exposures of 10 to 30 seconds at one meter from a 200 watt gas-filled tungsten lamp were in the solarization region of the characteristic curves of all four emulsions, but still much short of the second negative, which had not appeared in three minutes. Having thus carried the exposure of the entire plate into the initial stages of solarization, each of the emulsions was exposed in the spectrograph for one hour to the entire spectrum, and for one to two hours to wave-lengths above 0.6μ, using a Jena red glass of known transmission as filter. In all cases, strong reversal was produced between 0.40 and 0.48μ or even wider limits; but in no case was there visible reversal at wave-lengths above 0.6μ.

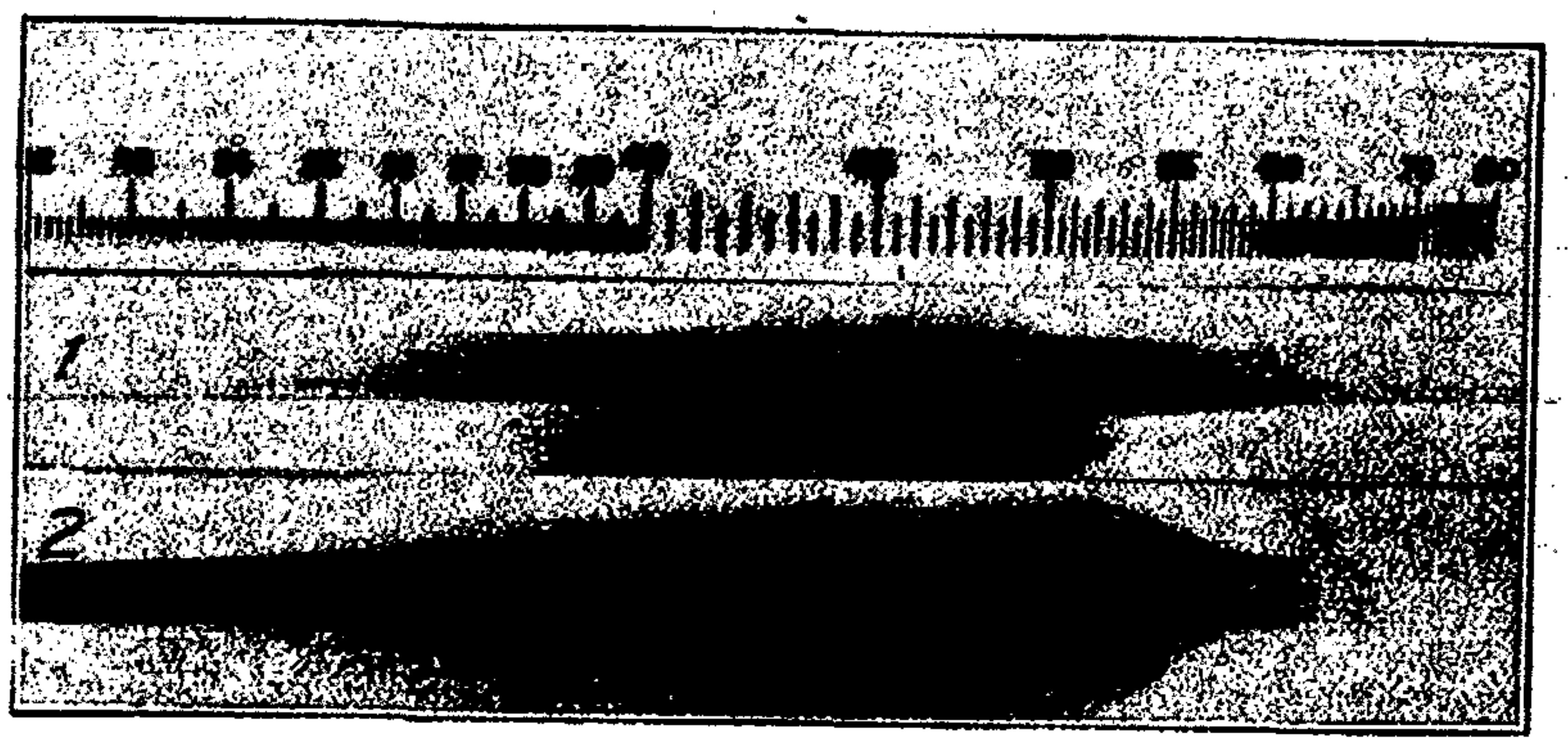

Fig. 1

Spectrograph exposures, showing solarized (light) region from 0.39 to 0.47 u.
1. Lumière Sigma.
2. Eastman Super-speed Portrait Film.

In dealing with processes as complex at photography, it is difficult to deny the existence of any phenomena which have been reported, but there seems to be no adequate evidence for believing that exposure of the unsensitized silver bromide-gelatine emulsion to radiation of 0.6μ and longer wave-lengths produces any effects differing in kind from those due to radiation of 0.25 to 0.6μ; the difference is apparently one of rate only.

The case of emulsions which have been treated with appropriate dye solutions is, however, entirely different. The experiments of Lüppo-Cramer on desensitizers, as reported in "Kolloidchemie and Photographie," pp. 82 et. seq., (1921), throw the first real light on this. In the course of experiments on the sensitization and desensitization of the different silver halides, he partially converted a transparency plate to iodide, bathed it in phenosafranine solution, and exposed it behind an Eder-Hecht scale[1]. On physical development with acid metol-silver nitrate intensifier the plate showed a negative image up to 32 on the scale. From 32 to 80 there was a faint *reversed* (positive) image on the darker ground due to storage fog. Further experiments proved that when latent image on the plate had been produced by light it could be destroyed in the same way as that due to storage. It was at first difficult to obtain the effect with alkaline development; but, if the dye bath is followed by 1-2% potassium bromide solution, the reversal on silver bromide with alkaline development is much enhanced. Lüppo-Cramer was unable to secure reversal on fast plates. A large number of desensitizing dyes were effective, and even some sensitizers such as Rhodamine B and erythrosin, when used on silver iodide with physical development; certain of the dyes which produced satisfactory reversal under these conditions were not effective when used on silver bromide with alkaline development. A high relative sensitivity to yellow light was noted.

It accordingly becomes evident that dyes which desensitize the photographic plate strongly, restraining the formation of latent image under moderate illumination, are capable of destroying or deactivating that already existing, when sufficient exposure is given.

With this in mind, we may consider photography of infra-red spectra by the reversal method. This was first attempted by Millochau[2]. Using pre-exposed Lumière Sigma plates which had been bathed with a saturated alcoholic solution of malachite green, he was able to obtain a reversed image of the solar spectrum to 9325 A.U. Terenin[3] has recently improved the method by reducing the concentration of the dye to around 1:20,000 (amounts similar to those used in sensitization with cyanine dyes). He was successful with a number of basic dyes of the azine and triphenylmethane groups. In spectrographic exposures, a direct image was produced by light of wave-length below a definite limit which depends on the dye, and reversal above this. Terenin recognized that the difference between dyes is chemical as well as optical. He reported securing a faint image of the mercury line at 11280 A.U. on prolonged exposure, but it has been impossible to confirm this.

It is evident that the results obtained by Millochau and Terenin depend on a reversal of the same type observed by Lüppo-Cramer, since the dyes used are known desensitizers. The spectral characteristics should depend on the dye in a manner similar to sensitization in the ordinary sense; as would be expected, Terenin's best results were obtained with green dyes which have an absorption band, with maximum between 0.6 and 0.7μ, and extending into the infra-red with diminishing intensity. Although solarization takes place most readily with rapid, coarse-grained emulsions (leading Millochau and Terenin

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[1] The Eder-Hecht "sensitometer" is a neutral wedge, of density gradient (Kehlkonstante) 0.4014 per cm, on which there is a millimeter scale; it is also provided with strips of tricolor and yellow (correction) filters. It is accurately made, and valuable for preliminary measurements.

[2] Millochau: Compt. rend. 143 108 (1906); 144, 723 (1907).

[3] Terenin: Physik. Ber. 4, 1478 (1923).

to use these), it appears that the opposite type should be most sensitive to reversal when dyed with a desensitizer. In the first place, the amount of dye taken up is much larger, due to the larger specific surface of the grains. For this reason, fine-grained plates show much better relative color sensitivity[1] when bathed with ordinary sensitizing dyes, and the same may be expected of the reversal process. In the second place, the natural sensitivity of the emulsion, while greatly diminished by a desensitizer, is not totally destroyed, and fast plates are relatively less reduced in sensitivity; so that the reversal is opposed by much less residual sensitivity in the case of the fine-grained plate. My first experiments established conclusively that, using pre-exposed plates bathed with desensitizing dyes, with or without bromide, the reversed image was formed on the finest-grained plates with the least exposure. When Speedway and Process plates were pre-exposed, bathed with Desensitol and KBr, and then exposed for the same length of time behind the Eder-Hecht scale, the reversed images extended to 32 and 90 respectively. The corresponding ratio of the light intensities necessary to produce an image on the two plates is approximately 175:1.

As the original motive of these experiments was to extend the range of photographic sensitivity further into the infra-red, attention was concentrated on dyes and inorganic compounds which seemed likely to have absorption in the proper region. Desensitizing dyes are largely basic, and confined to the azine and triphenylmethane groups; from the great number available, choice was made according to the absorption spectra and desensitizing properties, as far as known or predicted.

After preliminary experiments to determine the optimum pre-exposure, the dye tests were carried out as follows. Seed 23 plates were pre-exposed 10-12 seconds to 1.4 candle-meters (unscreened tungsten); process plates 15-20 seconds to the same intensity. They were then bathed 5-10 minutes at room temperature in the dye solution, at a concentration of 1:20,000 unless otherwise stated; rinsed and dried rapidly in a current of air; again bathed for ten minutes, this time in a 1% solution of potassium bromide, again rinsed and dried. Using the spectrograph and light source previously described, one exposure was given without filter, and one with a Jena red glass transmitting practically no radiation below 0.6μ. Exposure times varied from one to five minutes, and slit width from 0.04 to 0.20 mm. on the first tests.

The results with dyes are summarized in Table I. Dyes are listed by name, and by number and class in the 1924 Colour Index of the Society of Dyers and Colourists. "Desensitol" and "Pinakryptol Green" are the products of Ilford, Ltd., and Meister, Lucius and Brüning, respectively. The former is undoubtedly a safranine. Bindschedler's Green was synthesized for the purpose in this laboratory. The other dyes were commercial samples in possession of the dye laboratory of the Bureau of Standards.

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[1] Walters and Davis: Bureau of Standards Science Paper, No. 422.

TABLE I

Spectral Absorption and Photographic Reversal of Various Dyes

Name	No.	Absorption maxima	Plate	Region of Reversal	Maximum	
Malachite Green[1]	657	0.61	23	0-61-82	0.63	
Brilliant Green[1]	662	0.623	Speedway	0-70-0.90	—	
			process	0-33-.80	0.65	
" "	662		Speedway	0.52-.72	0.65	
Iodine Green[2]	686	—	23	0.7-0.8 ?	Doubtful	
Pararosaniline[2]	676	0.544, 0.487	Process	0.36-.65	0.60	
Rosaniline[2]	677	0.547, 0.489	Process	0.38-.67	0.60	
Erythrosin[3]	773	0.526, 0.491	23	None		
Bindschedler's Green[4]	819	0.7	23	doubtful		
" + auramine			23	0.68-0.90	Very faint	
Neutral red[5]	825	—	23	0.70-0.87	0.75	
Safranine[6]	841	0.539	23	0.60-0.80	0.61	
Methylene violet[6]	842	0.555, 0.517	23	0.49-0.87	0.62	
Safranine 6B[6]	843	0.555, 0.517	23	0.52-0.83	0.60	
Rosolane B[6]	845	0.550	23	0.51-0.83	0.58	
Aniline violet[6]	846	—	23	0.67-0.85	0.75 (?)	
Diphen blue B[6]	851	0.549	23	0.49-0.85.	—	
Desensitol[7]	?	0.50	Process	0.38-0.67	0.57	
			23	0.50-0.95 long exposure	0.57	
Spirit Nigrosine P1[7]	860	0.544	23	None		Fog
Gallo violet D[8]	881	0.642, 0.549	23	0.50-0.60	Doubtful	
Brilliant Cresol Blue[8]	877	0.632, 0.578 and 0.40	23	0.45-0.60	0.50	
Methylene blue[9]	922	0.668, 0.609	23	None		Fog
New Methylene blue N[9]	927	0.636, 0.588	23	None		Fog
Pinakryptol green[10]	?	0.570, 0.4	Process	0.32-0.80	0.40-0.60	
Wool green	737	0.634	23	None		

[1] Diamino triphenyl methane
[2] Triamino triphenyl methane
[3] Xanthene
[4] Azine (indamine)
[5] Azine (eurhodine)
[6] Azine (safranine)
[7] Azine (nigrosine)
[8] Azine (oxazine)
[9] Azine (thiazine)
[10] ?

Tests were made on mixed solutions of auramine with Brilliant Green and Bindschedler's Green because of the recent report from the Pathe laboratories[1] that the auramine tends to reduce the considerable fog caused by the other dyes. There was no improvement in the reversal.

A number of experiments were made with salts of copper and other metals. Ferric chloride, potassium ferricyanide and potassium dichromate in 0.05% solution, potassium permanganate in 0.02%, and nickel nitrate in 0.05%, caused no reversal. Cupric salts appeared to be particularly promising, as they have an absorption band in the red and short infra-red with maximum at about 0.8μ, are photochemically sensitive, acting as oxidizing agents, and are strong photographic desensitizers. In the first experiments, pre-exposed plates were bathed in 0.1% cupric chloride or bromide, followed by or mixed with 1% potassium bromide. The latent image was totally destroyed without exposure; the plates after developing and fixing were glass clear. Sensitivity was greatly diminished, but not destroyed, as a direct image was obtainable on such plates in the region of sensitivity of the untreated plate. An attempt to reduce the copper ion concentration by using an ammoniacal solution produced only fog, but when 0.04% cupric tartrate or 0.1% cupric acetate was used, reversal appeared between 0.67 and 0.88μ. The tendency to destroy the latent image in the dark was still strong, and was greatly increased by bathing with potassium bromide after the copper salt. The pH of the copper tartrate solution was lowered to 2.5 by addition of tartaric acid, without noticeable effect; addition of ammonia caused fog. In all cases, the latent image faded rapidly after bathing with the copper salts. When their concentration was sufficiently low, their activity in the dark was correspondingly reduced, so that the effects of the reversing exposure became evident, but no salt or combination of salts was found which combined stability of the bathed plate in the dark with reversal over the entire absorption band of copper in the light. The photochemistry of copper salts should have further study as possible sensitive materials for infra-red photography. Further experiments with ferric salts were successful to the extent of securing a faint reversal around 0.6μ on a process plate bathed with ferric oxalate. Bathing with 0.1% mercuric chloride caused complete destruction of latent image in the dark and apparently complete desensitization.

Lüppo-Cramer made considerable use of conversion of the silver salt to iodide, and physical development. It seemed advisable to avoid the difficulties of the latter in tests of spectral sensitivity, but some experiments were made on iodide for comparison. Seeds 23 or process plates were converted to iodide with the iodide-sulphite-thiosulphate mixture recommended by Renwick[2] for reversal. They were developed in alkaline amidol (1 gm. amidol, 5 gm. each sodium sulphite and carbonate per 100 cc) and fixed in cyanide and sulphite solution. When a pre-exposed plate was converted to iodide and then exposed in the spectrograph, the maximum in sensitivity at 0.40-0.45μ was marked, as

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[1] Brit. J. Phot. No. V, 21 (1924).

[2] Renwick: J. Soc. Chem. Ind., 39, 15 (1920).

reported by Renwick, but a faint reversed image of the entire visible spectrum was readily obtained with one to five minutes exposure. The iodized plates were intensely stained by dyes, but the spectral sensitivity appeared to be little different, if any, from that obtained with the other procedure; the total sensitivity was about the same. No reversal was secured with cupric salts as sensitizers.

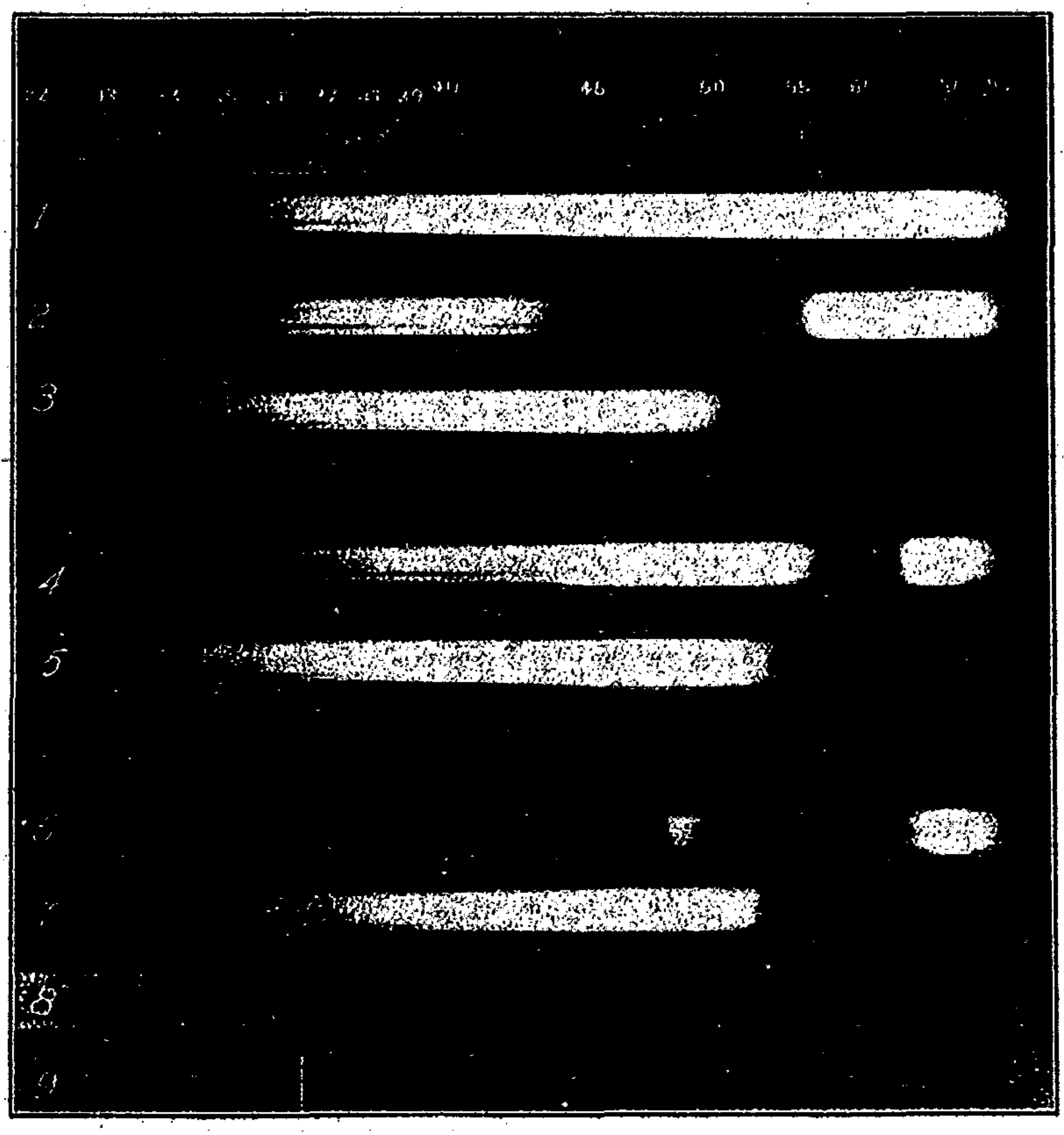

FIG. 2

Absorption spectra of desensitizing dyes, and reversed images on plates bathed with them.

1. Spectrum of continuous light source used.
2. Absorption spectrum of Desensitol.
3. Spectrograph exposure to continuous spectrum, of Seeds 23, pre-exposed and bathed with Desensitol.
4. Absorption spectrum of Brilliant Green.
5. Spectrograph exposure to continuous spectrum, of Seeds 23, pre-exposed and bathed with Brilliant Green.
6. Absorption spectrum of Pinakryptol Green.
7. Spectrograph exposure to continuous spectrum, of Seeds 23, pre-exposed and bathed with Pinakryptol Green.
8. Same as (7), except for use of process plate instead of Seeds 23.
9. Spectrograph exposure to mercury arc, of pre-exposed process plate bathed with Pinakryptol Green.

The relation between the regions of absorption by the dye, and of reversal, is clearly indicated in Fig. 2, which shows the absorption spectra of Desensitol, Pinakryptol Green and Brilliant Green in the concentrations used for bathing, and the reversal on plates treated with these dyes. The absorption spectra are for a thickness of one centimeter; they were photographed in the same spectrograph, using Seed 23 plates sensitized with a mixture of Pinachrome and Dicyanine. Regions of absorption and reversal both are dark in the print. In general, the latter are equivalent to the former displaced toward the longer wave lengths by as much as .05μ, a value of the same order as that usually obtained in direct sensitization. The explanation applied to the latter case is equally reasonable here; the adsorption of the dye causes a great increase in concentration. The results on plates treated with Pinakryptol Green are particularly interesting. Visual spectrophotometric examination of the solution shows a rather broad band with maximum at 0.57μ, and another band with maximum at less than 0.40μ. With the Seed 23 plate, the residual sensitivity of the plate in the region of the latter band is greater than the tendency to reversal, and a direct image is obtained. On the process plate, the residual sensitivity is less, and more dye has been absorbed, so that the entire spectrum is reversed. On prolonged or intense exposure, the reversed image is followed by the appearance of the normal image, beginning with the region of natural sensitivity. This is particularly clear in the photograph of the mercury spectrum; the lines at 4358, 4047, and 3655 A.U. show a direct image while the halation area around them is still reversed.

It is difficult to compare the sensitivity of materials giving respectively positive and negative images with one another, and no attempt was made to secure an absolute measure of the sensitivity of the reversal process. At its best, distinct spectrum images could be obtained with one to three hundred times the exposure necessary for a rapid emulsion such as the Speedway. With a given combination of emulsion and dye, the composition of the light obviously determined whether a positive or negative image was obtained. Thus, a process plate stained with Pinakryptol Green gives a positive image in white light, while a fast plate treated with Brilliant Green is reversed only by a fairly pure red, and in white appears only to be reduced in ordinary sensitivity. Attempts to measure the characteristic curve of the reversal process were attended with unexpected difficulty; it is apparently affected considerably by the intensity of the light, and measurements on time and intensity scale are not concordant. Measurements on the intensity scale were made by means of a neutral wedge; of density gradient 0.48 per centimeter (photographically determined), and density range of over four. The plates were exposed behind it to white light, bathed with the dye and bromide, backed, and again exposed with the wedge turned 90° from its former position. This secures a wide range of combinations of pre-exposure and reversing exposure, but the reversal is measurable only over a comparatively small portion of the plate. The time-scale measurements were made simply by suitable uniform pre-exposure of the plate, followed by treatment, and successive exposures of small patches for varying times to a constant light source (incandescent light with voltmeter).

All plates were developed nearly to γ_∞ under conditions known to give reasonable uniformity.

As is evident from Figs. 3 and 4, loss of density appears to be approximately proportional to log I, and more nearly proportional to T than to log T. Determinations suitable for formulating any general law will require more time than can be given to the subject at present.

The use of a fine-grained plate and of potassium bromide, gives a very much higher sensitivity than when the directions of Terenin are followed. Seed process plates and Desensitol or Brilliant Green are recommended for anyone interested in photography of the infra-red by this method; Pinakryptol Green is better for reversal effects by white light.

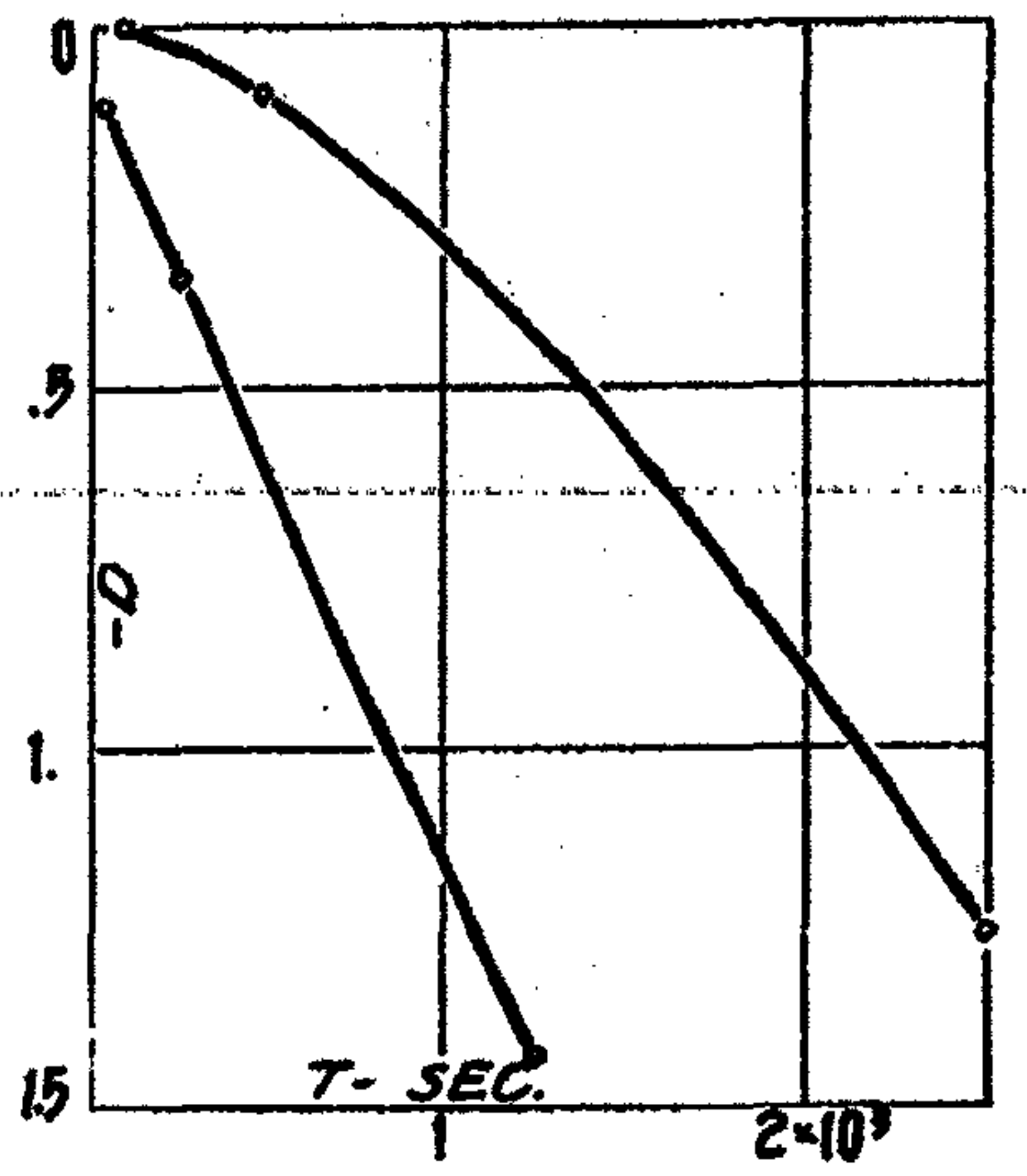

FIG. 3

Decrease in density with time of second exposure on pre-exposed process plates. Right curve for plates bathed with Desensitol and KBr; left curve for plates bathed with Pinakryptol Green.

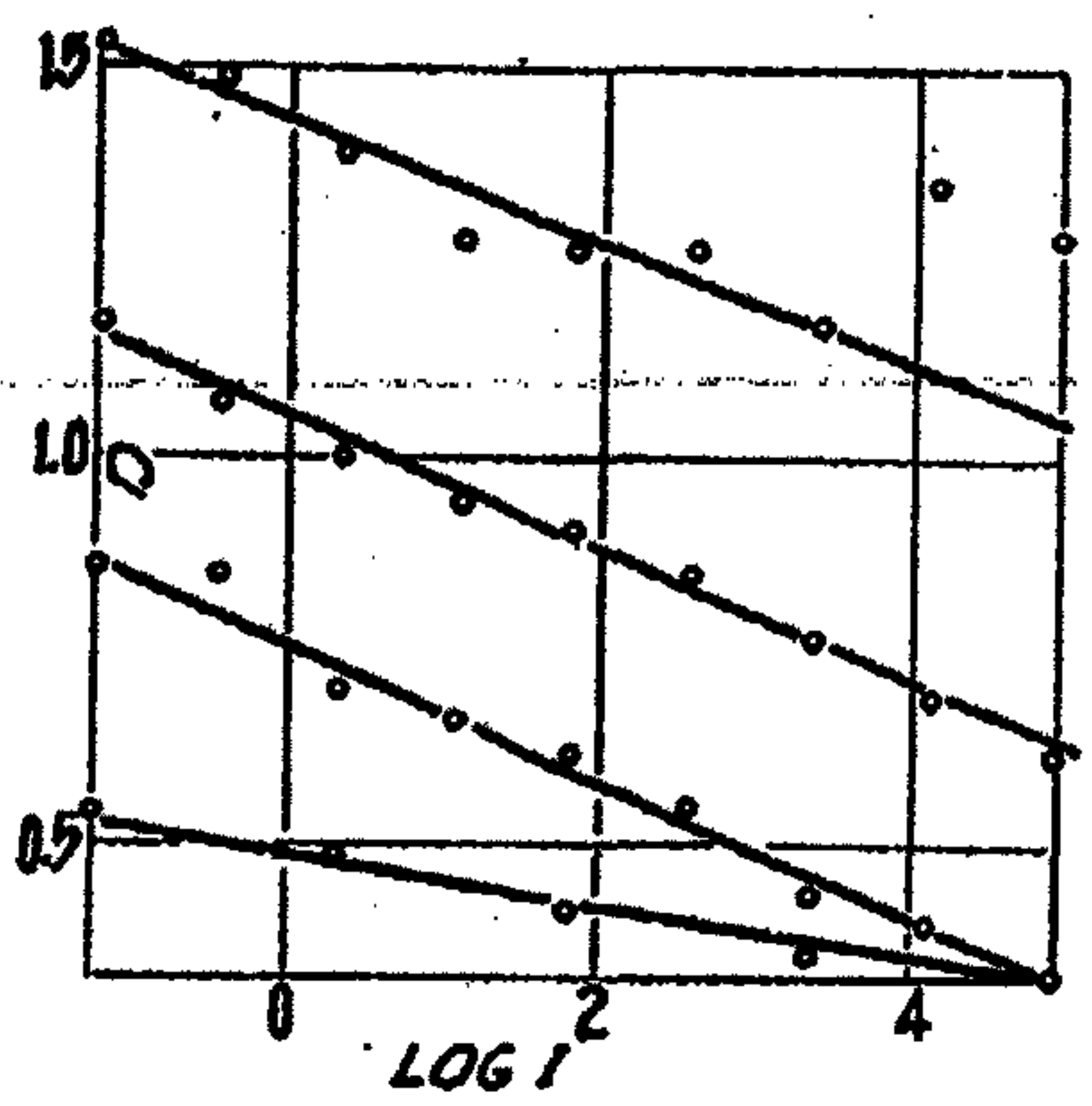

FIG. 4

Cross wedge exposures on process plate bathed with Desensitol and KBr after first wedge exposure. Ordinates, density. Abscissae, logarithms of relative intensity of second (reversing) exposure.

The loss of density on keeping, with active desensitizers and fine-grained plates, is very considerable. Two process plates were given identical exposures behind a wedge; one was untreated, the other bathed with 1:100 Desensitol solution and 1% potassium bromide solution. After two days they were developed together. The densities at corresponding points along the scale are given in the following table:

Untreated:	0.24	.26	.27	.27	.29	.80	2.54	4.5	4.5
Treated	.29	.32	.32	.30	.30	.31	.38	.56	.79

With process plates and Pinakryptol Green, it is advisable to omit the bromide treatment because of the resulting loss of density. This effect is, of course, so small as to be entirely negligible in the ordinary use of desensitizers when plates are developed immediately after desensitization.

In a recent contribution from the Eastman Kodak Research Laboratory on desensitization[1] it was stated that there is a fundamental distinction between the oxidizing densitizers such as chromic acid, on the one hand, and the dye desensitizers and heavy metal salts, on the other hand. This distinction is based on the statement that the second class of desensitizers are unable to destroy latent image already formed, their activity being confined to a "catalytic" action under illumination. As indicated by the above results, this is incorrect; the dye desensitizers and salts of copper, mercury and iron are able to destroy (or de-activate) latent image, even in the dark, although the rapidity of their action is in general, far below that of chromic acid.

The matter was further tested as follows:

Process plates were given a uniform exposure, then cut in half, and one of the halves bathed for ten minutes in the desensitizing solution. Both halves were then washed for one hour in running water, dried and left for twenty-four to forty hours. They were then developed together and the densities measured with a Martens photometer. The plates were in total darkness during and after desensitizing. Table II gives the resulting densities:

TABLE II

Densities on Normal and Desensitized Plates

	1% $CuSO_4$ 40 hours	1:5000 Pinakryptol Green, 40 hrs.	0.1% $CuCl_2$ 24 hours
Untreated half	2.60	2.49	>4
Desensitized half	0.03	1.68	0.36

The tendency of all classes of desensitizers to destroy latent image already formed is established by the experiments described in this paper, and there appears to be no reason for believing in the fundamental distinction as stated by Ross.

Discussion

Solarization has been ascribed both to oxidation, and to continued reduction past the condition of the latent image into an undevelopable stage. The weight of opinion is at present in favor of the latter view, and the evidence in this article that the spectral sensitivity remains the same into the solarization stage appears to be in agreement with it. Reversal by the combined action of light and dye may be either an oxidation or a reduction. Lüppo-Cramer believes desensitization to be an oxidation process; his argument is based largely on the readiness with which all desensitizers are reduced. A point which has not been brought up in this connection is that certain desensitizers are known to be catalysts for the photochemical oxidation of their own leuco bases, and may very well act by an intermediate compound mechanism which would serve equally well for other reactions. The argument that, since the formation of the latent image is essentially a reduction, a positive image must result from

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[1] F. E. Ross: Brit. J. Phot., Jan. 2, (1925).

oxidation, is not conclusive; as Renwick has pointed out, the latent image is essentially a catalyst for the reduction of the rest of the grain, and may be deactivated without being destroyed. The tendency of many desensitizers to cause fog might be used as an argument for a reduction theory of reversal. This would make it appear that they were reducing agents, which are so activated by light as to carry reduction of the silver salt on into the solarized state. This is, however, impossible. On prolonged exposure, first a reversed and then a direct image is obtained, and this last is not the second negative, because the exposure is insufficient, and there is no visible blackening. A compound capable of producing the solarized state by reduction, on a given exposure, might be expected to produce intermediate states on lesser exposure and thus be a very effective sensitizer. If it carries the silver salt directly to the non-reducible (solarized) state, it would be impossible to return from this, by continued exposure, to a normal latent image.

On the oxidation theory of desensitization and reversal, the explanation is much more logical. The dyes, in the dark or in feeble illumination, have an oxidation potential sufficient to prevent formation of new latent image. On activation by light of their characteristic frequency, their potential is raised sufficient to cause destruction of the latent image already existing. Prolonged exposure exhausts the dye, presumably by reduction, so that formation of latent image is free to begin again. The effects of the same desensitizer on plates of different sensitivity are readily accounted for by this idea of two opposing reactions. The reversal of cupric salts must necessarily be due to oxidation, since these are never reducing agents. As far as experiments in this laboratory go, no material has been found which causes under the same conditions fog, desensitization and reversal on further exposure. Dyes such as methylene blue when applied to bromide emulsions cause fog and desensitization, but no reversal, and the active desensitizers tend to destroy the latent image in the dark, rather than produce it. As usual in photography, we are probably dealing with a complex mechanism. It seems logical that any material which is as firmly adsorbed by the grains of the emulsion as are the sensitizing and desensitizing dyes must tend to affect the sensitivity. In general, it might be more likely to reduce it, by disturbing sensitive nuclei or retarding adsorption of developer. Among the numerous materials so adsorbed there may be all gradations between those which produce latent image in the dark—as methylene blue; those which produce it when activated by light—the typical sensitizers; those which destroy it when activated by light—the typical desensitizers; and those which destroy it in the dark—desensitizers such as cupric chloride: and any or all of these may reduce sensitivity or developability simply by adsorption at existing nuclei. In as complex a molecule as that of most dyes, there may be groups with more than one of these properties. This classification may appear unjustified, but there are good reasons for believing that color sensitization of silver bromide grains by adsorbed dyes is a mutual phenomenon, and in the same class with sensitization to reversal. Renwick has pointed out that (quinoline) sensitizing dyes are bleached by light much more rapidly when adsorbed on silver bromide than when pure. The whole phenomenon of a change in the condition of the silver salt by radiation absorbed by the dye indicates that the sensitivity is a property of the adsorption complex of dye and silver salt, and not of the latter alone. This applies with particular force to the reversal process, where the natural sensitivity of the silver compound opposes that acquired by treatment with the dye. To phrase it differently, the silver bromide grain of an emulsion, either unexposed or with latent image, is a system of great sensitivity to all manner of influences—light, heat, electrical discharges, pressure and chemical reagents. It can therefore serve as a detector for a photochemical change in an adsorbed dye which is too minute to be detected in any other way.

In connection with the work on dyes, it seems advisable to point out a rather discouraging fact. Further extension of the sensitivity of the silver bromide-gelatine emulsion into the infra-red depends on the discovery of a sensitizer with absorption in that region. Sensitizers have so far been restricted to organic dye stuffs, and, omitting from consideration bands at 2μ and longer wave lengths, there is no dyestuff of any type positively known to have an absorption maximum at a wave-length greater than 0.72μ, and little reason for predicting the existence of such. Sensitivity at about 1μ, the present limit either for direct or reversed images, is due to the edges of bands centering in the visible. Examination of Bindschedler's Green up to 0.70μ indicates that the maximum absorption is at a longer wave-length, but this material is useless. In the opinion of the writer, any marked extension of photography into the infra-red will be due to introduction of new sensitive materials. We have further to face the effect of the decreasing quantum of radiant energy as we progress into the infra-red. The analogy between frequency in photochemistry and potential in electrochemistry has much justification, and we are attempting to deal with radiation of decreasing frequency.

Summary

1. Further evidence has been provided that there is no specific reversing action of long wave-length radiation on the photographic plate (Herschel effect). The maximum of sensitivity for solarization is found to be the same as for the normal image.

2. Twenty-one dyes and a number of inorganic salts have been studied spectrographically as to their tendency to cause reversed images in pre-exposed plates, on a second exposure. The long wave length limit of this process is found to be approximately the same as for plates sensitized with Dicyanine.

3. It has been shown that the evidence from this study strongly supports the oxidation theory of desensitization.

THE PREPARATION OF CONDUCTIVITY WATER

BY ISAAC BENCOWITZ[1] AND HENRY T. HOTCHKISS, JR.

Introduction

In order to obtain accurate conductance data, water of a high degree of purity must be used in the experimental determinations. It has been shown that the successful application of the fundamental principles relating to the conductivity of dilute aqueous solutions is largely dependent on this factor; and from the extent of the discussion of the question it is evident that the preparation of pure water is a most important and difficult problem.

The most reliable method of determining the degree of ionization (α), of a univalent electrolyte at the concentration C is by means of the relationship $\alpha = \frac{\Lambda_{\prime}}{\Lambda_{\infty}}$ where $\Lambda_{\prime}$ is the true equivalent conductance of the electrolyte at the concentration C, and Λ_{∞} is the true equivalent conductance at infinite dilution[2]. Also the mobilities of the ions are accurately obtained by the application of Kohlrausch's law, given by the expression $\Lambda_{\infty} = \Lambda_a + \Lambda_c$ from which the mobility of the anion (U_a), and that of the cation (U_c), are obtained by dividing the respective ionic conductance Λ_a or Λ_c by one faraday. It is then obvious that it is of prime importance to determine the value of the true conductance at infinite dilution with great precision. The accuracy with which this is known will affect to a large degree the error involved in the calculation of the degree of dissociation, and of the mobilities.

Numerous empirical functions[3] were applied in the evaluation of Λ_{∞}. All of these expressions however, contain empirical constants which have no scientific foundation, and none were found to hold outside certain definite ranges of concentration. It was Washburn[4] who suggested a very logical way of obtaining true values for the conductivity at infinite dilution. The method consists in plotting K, the constant of the mass action equation against the concentration, using trial values of Λ_{∞}, and rejecting all those values where the coordinates cause the point, in the range of dilute solutions, to fall outside the path of a smooth curve. Obviously this method makes use of the assumption that at sufficient dilution all electrolytes must obey the mass action law. This assumption is a thermodynamic necessity. His procedure can only be followed when the correct values for the conductivity of very dilute solutions (0.00005 N. or lower) are known.

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[1] National Research Fellow in Chemistry.

[2] Washburn: J. Am. Chem. Soc. 40, 106 (1918). A more accurate relationship was discovered by MacInnes. Washburn: "Principles of Physical Chemistry", 261 (1921).

[3] Kohlrausch: Ges. Abh. 2, 1127, 1131, 1132; Noyes and Falk: J. Am. Chem. Soc. 34, 462 (1912); Kendall: J. Chem. Soc. 101, 1275 (1912); Kraus and Bray: J. Am. Chem. Soc. 35, 1315 (1913); Bates: 35, 527 (1913); Kendall: 36, 1069 (1914); Kraus: "The Properties of Electrically Conducting Systems," p 67 (1922).

[4] J. Am. Chem. Soc., 40, 122 (1918).

"Water Correction"

Two methods can be used for obtaining reliable data on the conductivity of dilute aqueous solutions. One requires the use of highly purified water under such conditions that no contamination takes place during the measurement of conductivity the other involves the determination of the nature and the amount of the impurities present in the conductivity water which is in equilibrium with the atmosphere, and then the application of the metathesis correction obtained from the mass action relation. This "water correction" has been discussed by many investigators[1]. As a result of a thorough treatment of the problem Kendall suggests the use of the latter method, which is the only logical procedure where the solutions are in contact with the atmosphere and the measurements are made in soda-glass conductivity cells. The use of glass cells was shown to influence the results to a somewhat greater extent than the impurities present in ordinary conductivity water[2]. However it was definitely established[3] that "equilibrium water" (water saturated with carbon dioxide under atmospheric conditions) has a variable conductivity depending upon local conditions, and the methods of experimentation. The study of this condition showed[4] that not only the normal atmospheric conditions, but even the presence of a person or a lighted gas burner in the laboratory affects the conductance of the water solution under investigation. "Equilibrium water," according to the accepted values has a conductivity of $1.0-0.8 \times 10^{-6}$ ohms^{-1}. However, in laboratories where other investigations are being carried on, the best water of this description which can be obtained has a conductivity of $3.0-2.0 \times 10^{-6}$. But even with water of 1.0×10^{-6}, the "water correction" for a 0.00001 N. solution of potassium chloride is 44 per cent, for a 0.0001 N. it is 8 per cent. The correction is even higher for lithium chloride[5]. In order to bring the accuracy of conductance data on dilute solutions to within a hundredth of one per cent it is necessary, therefore, to use "ultra pure conductivity water" (a term introduced by Kendall); to carry on all experimental operations in an atmosphere free from conducting impurities; and to employ quartz cells. This technique is now the accepted procedure for precision measurements. It was followed by Weiland[6], Kraus and Parker[7], Parker[8], and is being used in this laboratory.

To maintain "ultra pure conductivity water" at its original degree of purity is comparatively simple. The preparation of such water however, is attended with a great deal of difficulty. The lowest conductivity recorded for pure

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[1] Kendall: J. Am. Chem. Soc. 38, 1480, 2460 (1916); Washburn: 38, 2431 (1916), Kendall: 39, 9, (1917).

[2] Kraus and Parker: J. Am. Chem. Soc. 44, 2429 (1922).

[3] Washburn: J. Am. Chem. Soc. 40, 106 (1918).

[4] Kohlrausch: Ges. Abh. 2, 871; Kendall: J. Am. Chem. Soc. 38, 2464 (1916); Washburn: 40, 112 (1918).

[5] Washburn: J. Am. Chem. Soc. 40, 109 (1918).

[6] J. Am. Chem. Soc. 40, 131 (1918).

[7] J. Am. Chem. Soc. 44, 2429 (1922).

[8] J. Am. Chem. Soc. 45, 2017 (1923).

water is 0.043×10^{-6}, at 18°C.[1] This value was reached after forty-two back and forth distillations *in vacuo* at a low temperature. The glass conductivity cell in which the measurement was made had been standing for ten years. It was kept filled with conductivity water to remove traces of soluble matter from the glass. Only very small quantities of this water were obtained and attempts to duplicate the experiment have failed[2]. However, such purity is not necessary since water whose conductivity is 0.06×10^{-6} may be considered to be sufficiently pure for most measurements[3]. Several methods for the preparation of this kind of water have been suggested by various authors.

Previous Work

Kendall[4] reported that he obtained water having a conductivity as low as 0.9×10^{-6} by a single distillation of ordinary tap water. Bourdillon[5], and later Weiland[6] prepared pure water by bubbling air, free from gaseous impurities, (carbon dioxide, ammonia, etc.) through distilled water; a method described by Kohlrausch and others who found that it was an effective way of purifying water. Bourdillon charged a 13 litre copper boiler with ordinary distilled water containing some sodium acid sulphate, and collected conductivity water (0.11×10^{-6}) half an hour after steam was generated. The condensed water was allowed to fall in a vertical tube against a stream of carbon dioxide-free air. Weiland used the same principle. Starting with distilled water (0.8—0.6×10^{-6}), he redistilled from potassium permanganate after having bubbled carbon dioxide-free air through it for twenty hours, while the temperature was kept just below the boiling point. For his still he employed a 13 litre quartz flask, and collected about 3 litres of water having a conductivity of 0.07—0.05×10^{-6}. More recently Kraus and Dexter[7] built a still whose effectiveness is dependent on the principle of purification by fractional condensation. Three fractions of unequal purity were obtained, and the middle fraction was found to have the lowest conductivity. This may be taken as additional evidence that carbon dioxide does not comprise the whole of the conducting impurity in conductivity water[8]. Operating in its final form, steam from a 90 litre boiler, containing alkaline permanganate, was led through a trap which removed a small amount of condensed steam and any entrained moisture. Then twenty per cent of the vapor was condensed and collected in the conductivity cell, and the remaining steam separated and liquefied in a subsequent stage of the process.

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[1] Kohlrausch: Ann. Physik, Ergänzungsband, **8**, 1 (1878); Kohlrausch and Heydweiller: Ann. Physik, **53**, 209 (1894); Kohlrausch: Z. physik. Chem. **42**, 193 (1903).

[2] Taylor: "Treatise on Physical Chemistry," p. 521 (1924).

[3] Washburn: J. Am. Chem. Soc. **40**, 130 (1918).

[4] J. Am. Chem. Soc. **38**, 2465 (1916).

[5] J. Chem. Soc. **103**, 791 (1913).

[6] J. Am. Chem. Soc. **40**, 131 (1918).

[7] J. Am. Chem. Soc. **44**, 2468 (1922).

[8] Kendall: J. Am. Chem. Soc. **39**, 13 (1917); Washburn: **40**, 122 (1918).

We have experimented with stills similar in type to those discussed. As our work required large quantities of pure water, we found it necessary to design a new still, incorporating some effective changes in design with the features of these stills which our preliminary work showed to be desirable. The efficiency of a stream of carbon dioxide-free air as an agent for removing the absorbed gases from water cannot be questioned. Bourdillon records the lowest conductance of water obtained from his still as being 0.086×10^{-6}. The conductivity value at times was considerably higher. This may be attributed to the method used in treating the condensed vapor with air which had been scrubbed free of carbon dioxide. Weiland charged his still with pure distilled water having a conductivity of 0.8×10^{-6}, and since the range of conductivity water distilled and stored in an ordinary laboratory is $3.0—2.0 \times 10^{-6}$ we could not obtain good conductivity water by a single distillation using a similar still.

Kraus and Dexter installed a large 90 litre boiler because they found that a smaller still did not yield the proper water. In our experimental work we could not get good water when a 20 litre boiler was used,—which is in agreement with their results. We did not want to make use of a large boiler for several reasons. Aside from the fact that a bulky apparatus was undesirable, we wished to make the operation of our still practically continuous, that is, we wished to design our still so that it would produce good conductivity water in sufficient quantity for our work whenever required. The fact that this could not be accomplished with a still having a large boiler which required preheating for a much longer period of time was for us an important consideration. Moreover, when we take cognizance of the fact that Kraus and Dexter discarded the first 20 litres of the water they distilled over, it is apparent that the yield of conductivity water would of necessity be more or less spasmodic. Our work, however, demonstrated to us the value of their observation that fractional condensation is a very good method of purification, and we have applied the idea in the final stage of our process. The unit which we have built therefore embodies the principles used by Kraus and Dexter as well as by Weiland. It will yield, in an ordinary laboratory, conductivity water suitable for the investigation of dilute solutions. Our method is briefly this:—ordinary tap water is boiled with alkaline permanganate, and the steam generated is condensed to supply a second boiler with freshly distilled water. Air, freed from carbon dioxide, is then utilized to sweep out gaseous impurities, and the water so purified is subjected to a fractional condensation upon distillation.

Description of the Improved Still

Referring to Fig. 1, boiler I is charged with about 20 litres of tap water, and small amounts of potassium permanganate and sodium hydroxide are added. The water is heated to just below its boiling point. After it has digested for some time with the alkaline permanganate the temperature is raised and the water distilled over into boiler II. On account of the form of the apparatus, little or no water is carried over mechanically. The first litre of distillate is discarded. The second copper boiler is fitted with a tube H, connected with the source of the carbon dioxide-free air. This air is prepared by drawing air from outside the building and forcing it through an absorption train consisting of suitable containers holding sodium hydroxide and sulphuric acid[1]. Both the delivery tube (A) and the air supply pipe project almost down to the bottom of the boiler. Thus the steam cannot force its way back through condenser 1 to the first boiler, and the air which bubbles up constantly through the water in the second boiler stirs the water and remains in contact with it for the maximum period of time. This air, which is forced in by a pump of the Sprengel type, eventually passes up a long vertical tube, fitted with condenser 2, and escapes through a trap (B). Any water that condenses in 2 is returned to the boiler. When the water in the second still is boiling vigorously, steam rises and is condensed in 2 forming a column of water which seals the vertical tube so that the steam begins to flow through the connecting tube C. However, a very small amount of water vapor and air is allowed to pass to the trap B. One end of the connecting tube (C) is so attached that the water cannot drain into it from 2, while the steam jet at the other end is directed down into the air condenser 3 which is drained by the trap D. The diameter of this air condenser is quite large so that the mean velocity of the steam is decreased, allowing any drops of water which are entrained in the steam to be precipitated out. Practically dry steam therefore enters the long condenser 4, the temperature of which is so regulated that it condenses about eighty per cent of the entering water vapor. The condensed water is separated by gravity at E from the steam and air which continues to flow around a gentle curve and is con-

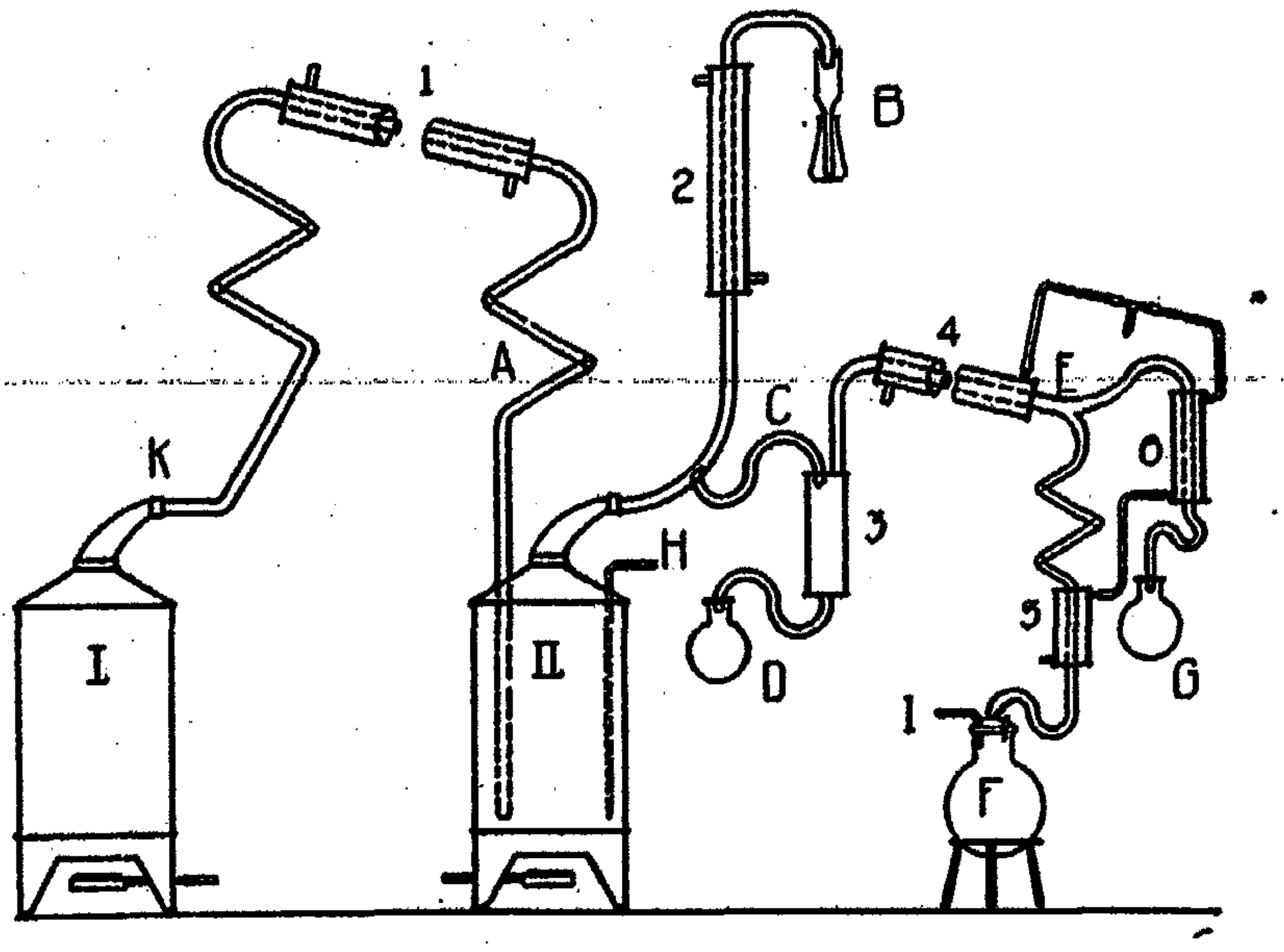

Fig. 1

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[1] Weiland: J. Am. Chem. Soc. 40, 134 (1918).

densed at 6. No part of the steam or air is sucked down the tube from E. This tube delivers the water to the quartz conductivity cell when flow is occasioned by displacement. There is a water seal due to the bend in the delivery tube below the cooling jacket 5. In order that the pure water collected in the conductivity cell may not be contaminated by contact with the atmosphere, a constant stream of carbon dioxide-free air, issuing from tube 1 prevents the water from meeting the impure air of the laboratory. Throughout the system the water seals, made by proper bends in the pipes, prevent air from the room being drawn into the apparatus if a momentary partial vacuum is created by the condensation of the steam.

It has been found in actual practice that it is convenient to disconnect boiler I at the coupling K while the conductivity water is being prepared in the succeeding stages of the apparatus. Boiler I is then filled and the water preheated. When the water in the second boiler becomes low some steam passes back through the delivery tube A and the first condenser, and exhausts into the air at K. By this time the digestion in the first boiler is complete, and it is again coupled with the rest of the system. The heat under boiler I is increased and the flame under boiler II lowered. The distillation from I to II is then allowed to take place over night. A minimum of time is thus expended in refilling the second boiler with fresh distilled water, which is maintained just below its boiling point while air freed from carbon dioxide is bubbled throuhg it. The following morning more heat is supplied beneath the second boiler and the still is flushed with live steam for half an hour to remove impurities which have been absorbed from any air which has entered the apparatus. We have found it necessary to do this when the distillation is discontinued even temporarily. The wet interior surfaces seem to adsorb the impurities which enter with the air which the water seals cannot keep out against the back pressure caused by the complete condensation and halting of the steam flow. After the still has been flushed with steam, the temperature of the water in condenser 4 is regulated and the conductivity water collected. For each litre of water collected in the cell, 200 cc. are removed from the system at B and D, and 200 cc. are collected in the receiver G. In building this apparatus standard sizes of block tin tubing were used in conjunction with the two copper boilers. All joints were soldered with tin, and the entire apparatus can be assembled by a tinsmith.

Conclusion

Kraus and Dexter found that the middle fraction in their condensation had the lowest conductivity. However, no explanation was offered. Assuming that carbon dioxide is the chief impurity causing the rise in the conductance of the condensed water, we may formulate an explanation of this phenomenon on the basis of certain physical laws governing gas-liquid systems. During the process of distillation, and after the water has been scrubbed for a considerable period of time, it is found that the water still contains an appreciable amount of carbon dioxide. Vigorous boiling, in conjunction with the turbulence caused by the entering stream of carbon dioxide-free air will produce in the saturated steam, a mist of minute droplets of water, part of which are carried in the steam flow. The heavier droplets will be removed in the first fraction, while many of the very fine droplets will be carried over into the condenser (4) where they serve as nuclei for further condensation. These minute particles, be they mechanically carried over or formed by condensation may be shown to consist of "ultra pure water."

The rate of absorption of a gas by a liquid is practically always limited by the rate of the diffusion through the medium.[1] This diffusion will take place at the liquid-gas junction through two films; one consisting of a layer of liquid in which mixing caused by convection currents is slight as compared with motion in the main body of the liquid, the other being a layer of gas next to the interface in which similar conditions obtain[2]. The rate of diffusion through the liquid film is proportional to the difference between the concentration of the solute in the liquid at the interface, and its concentration in the main body of the liquid[3]. In the case under consideration the gas (carbon dioxide) is very insoluble at the temperature employed. Therefore the gas film resistance to absorption may be considered to be negligible since the liquid at the interface is substantially saturated with solute at the existing pressure. Where the diameter of the droplet, constituting the liquid phase, is exceedingly small the liquid film will constitute the greater portion of its volume. Bohr[4] found the coefficients of absorption and escape were practically identical for carbon dioxide. It follows from this and the "two film theory" that the contamination of the water depends almost wholly on the slow diffusion of carbon dioxide into the liquid phase. The formation of small droplets at temperatures below the boiling point facilitates the removal of slightly soluble gases from the liquid phase into the gas phase. Furthermore, since the vapor pressure is inversely proportional to the radius of curvature of the surface, we can easily conceive that the solubility of gases in minute particles is smaller than in the bulk of the liquid. In the still which we have designed, a fine mist is created by the ebullition of the water in the second boiler, the minute droplets of which enter the condenser as condensation nuclei, while the air passing through the system sweeps out any gaseous impurities and any excess steam. This excess steam is condensed and forms the third fraction. We have attempted to show that the minute particles of water carried over into the condenser have a strong tendency to give up any dissolved gases and do not reabsorb gas readily. It stands to reason that these particles which act as nuclei of condensation consist of "ultra pure water," and that the second fraction, which is made up of steam condensed around these particles, should be the purest fraction, especially under conditions where the gaseous phase is removed continually.

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[1] Adeney and Becker: Proc. Roy. Soc. Dublin, **15**, 385, 609 (1918); **16**, 133, 143 (1920).

[2] Lewis and Whitman: Ind. Eng. Chem. **16**, 1215 (1924).

[3] Whitman: Chem. Met. Eng. **29**, 146 (1923).

[4] Wied. Ann. **68**, 500 (1890).

Summary

1. An improved type of still for the production of water for use in the investigation of dilute aqueous solutions has been described. Water, of a conductivity as low as $0.06—0.07 \times 10^{-6}$ can be readily obtained. The advantages of this still are,—that its operation is practically continuous, and that it can be operated successfully in any ordinary laboratory.

2. An attempt was made to explain the advantages of fractional condensation as a method of obtaining water of low conductivity.

We wish to express our thanks to Dr. R. R. Renshaw who has aided in this investigation.

Havemeyer Chemical Laboratory,
New York University,
January 29, 1926.

STUDIES IN THE EXPERIMENTAL TECHNIQUE OF PHOTOCHEMISTRY

II. THE DETERMINATION OF THE ENERGY DISTRIBUTION AND THE TOTAL ENERGY IN THE RADIATION FROM QUARTZ MERCURY VAPOUR LAMPS

BY R. G. FRANKLIN, R. E. W. MADDISON AND L. REEVE

In the first paper of this series[1] it was pointed out that, for the complete investigation of a photochemical reaction, it was necessary to determine the so-called "energy characteristics" of the light source employed; i.e., the total energy in the beam of light from it (expressed as ergs per sq. cm. per second) together with the distribution of this energy amongst the various wave lengths comprising the lamp's radiation. A brief account was also given of the methods employed for determining these energy characteristics. It is proposed, in the following paper, to describe these methods more fully, with particular reference to the light source most commonly employed by photochemists, viz: the quartz mercury vapour lamp. The determination of the energy distribution will be considered first.

Determination of Energy Distribution

A. *Apparatus employed.*

As mentioned in the last paper, the method employed in this laboratory for determining energy distribution is the direct one, using a spectrometer, spectro-thermopile and galvanometer. The disposition of the complete apparatus is shown in Fig. 1, a detailed description of which will now be given, under the following headings:—

The Spectrometer and Linear Thermopile.

The spectrometer F is a Hilger monochromatic illuminator for the ultra violet and is fitted with quartz telescope and collimator lenses, a quartz prism and a metallic mirror. The collimator and telescope slits are fitted with micrometer adjustments each division on which corresponds to 0.001 inches (0.025 mms.). To the eyepiece end of the telescope tube is fitted a brass block, in a receptacle in which is a Hilger linear thermopile L of resistance about 10 ohms. This block was found to be an insufficient protection against draughts, which set up thermoelectric potentials greater than those given by many of the lines in the mercury spectrum. The block and thermopile have therefore been enclosed in a wooden box, painted dull black inside, covered outside with aluminium foil and packed with cotton wool. Through a small hole in one side pass the galvanometer leads.

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[1] J. Phys. Chem. 29, 39 (1925).

Another similar wooden box, but without cotton wool, is fitted over the prism table of the instrument. Both boxes are shown dotted in Fig. 1. The whole front of the instrument is protected from the heating effect of the lamps used, by means of a hollow, water-cooled, copper screen M, about 25 cms. square. A rectangular aperture about 3 cms. by 1.5 cms. is cut through this, exactly in front of the collimator slit. This aperture is normally covered by a smaller, hollow, water-cooled screen, about 10 cms. square, which the operator can raise by pulling a suitably arranged cord.

The Galvanometer G.

This is a moving magnet instrument of the Paschen type, the suspended system of which is extremely light. The internal resistance of its four coils, arranged in series parallel, is 11.77 ohms. Its sensitivity can be varied from about 80 to 400 mms. per microvolt at 1 metre by means of an external controlling magnet, whilst its period, when shielded, varies from 2 to 6 seconds according to the sensitivity. Deflection and current are proportional. The instrument is protected against external magnetic fluctuations by means of two massive dome shaped shields of a special steel. The thermopile leads are connected directly to the galvanometer, as it was found that switches introduced varying thermoelectric and contact E. M. F. s. The unavoidable junctions at the terminals are heavily lagged with cotton wool and, to avoid draughts, the whole inside of the galvanometer, wherever possible, is protected in the same manner. The galvanometer is used in a laboratory in the basement of the building and stands on a stoutly built wooden table resting on a concrete bed sunk into the floor.

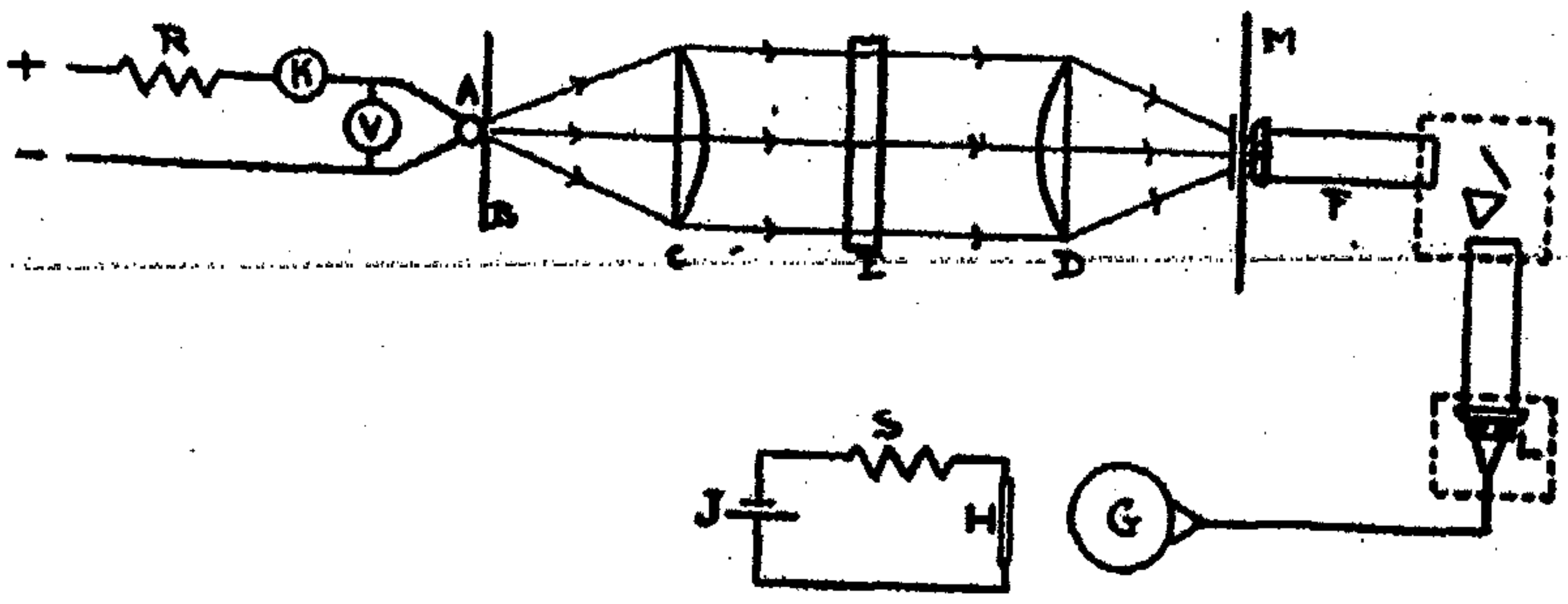

Fig. 1

Despite all these precautions, no greater steadiness of zero than 3 mms. on maximum sensitivity can be attained under average conditions. The biggest disturbing factor is the too close proximity of electrical machinery, particularly of electric tramways about 100 yards away. Some of the more spasmodic deflections have been traced to the opening and closing of the laboratory door: others, however, are still inexplicable. Apart from these spasmodic deflections, trouble is experienced through a steady creep of the zero across the scale. This is probably due to a steady heating up of one side of the thermopile. It has to be constantly corrected by an appropriate movement of the controlling magnet. Unfortunately this alters the sensitivity of the instrument, which, therefore, has to be redetermined each time the zero is brought back.

The Standardising Coil H.

This is done by passing a known current of about 0.1 ampere through the standardising coil H, a method due to Coblentz[1]. The coil is about 15 cms. in diameter and consists of an appropriate number of turns of wire mounted on the galvanometer table a few inches in front of the outer shield of the instrument and in a plane parallel to its coils. It is standardised by first connecting the galvanometer directly to the output leads of a potentiometer which, when its input leads are connected to an accumulator cell, gives a P. D. of just over 1 microvolt. The deflection per microvolt is thus determined. The standardising coil circuit is then closed and the deflection given by the galvanometer observed. By variation of a resistance S in series with the coil, the current through it is controlled until the deflection obtained is equal to that given by the microvolt P. D. applied directly at the terminals of the instrument. The sensitivity of any subsequent occasion can be determined by passing the same current through the standardising coil; and, since the coil circuit is entirely external to the galvanometer, errors which would be introduced by change-over switches in the thermopile circuit are entirely avoided.

In recording galvanometer deflections, readings are generally reduced to a standard sensitivity of 250 mms. per microvolt.

The Mounting of the Lamps.

The mercury lamps used are mounted on brass frameworks on wooden stands screwed to the steel slides of an optical bench. Immediately in front of the lamp A and extending over its whole width is fixed an aluminium framework carrying an aluminium diaphragm B pierced with a suitable-sized circular aperture. Three interchangeable diaphragms are used with apertures 1.0, 1.2 and 1.4 cms. in diameter respectively. These diaphragms are arranged to lie in the focal plane of a quartz condenser lens C, of 7.6 cms. available aperture and 10.5 cms. focal length. The approximately parallel beam of light thus produced, after passing through a 1 cm. deep water-cell with quartz sides E and any other necessary light filters, is used in all the quantitative photochemical work for which the lamp is required. For energy distribution determinations another quartz lens D is utilized, arranged to refocus the parallel beam onto the collimator slit of the spectrometer when the shutter covering it is raised.

B. *Method of taking Observations.*

The wave-length drum of the spectrometer is set to its lowest reading, and collimator and telescope lenses are adjusted to be in focus for this wave length. The shutter covering the collimator slit is then raised and the galvanometer deflection observed. This procedure is carried out till the whole of the spectrum has been worked through.

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[1] Bull. Bur. Standards 9, 33 (1911).

Mention has already been made of the unsteadiness of the Paschen galvanometer. Hence, in order to obtain an accurate value for the deflection at any point the following method has been finally adopted. One observer takes a series of readings for the deflection produced by a spectral line and for the sensitivity as given by the standardising coil. Any readings which show a sudden change in the rate of swing as the spot passes across the scale are rejected. In this way between five and twenty fairly concordant readings are obtained. Another observer does likewise. If both sets of readings give the same mean value, this is taken as a trustworthy result. If not, the whole operation is repeated. It follows that each galvanometer deflection recorded represents the mean of from ten to forty separate observations.

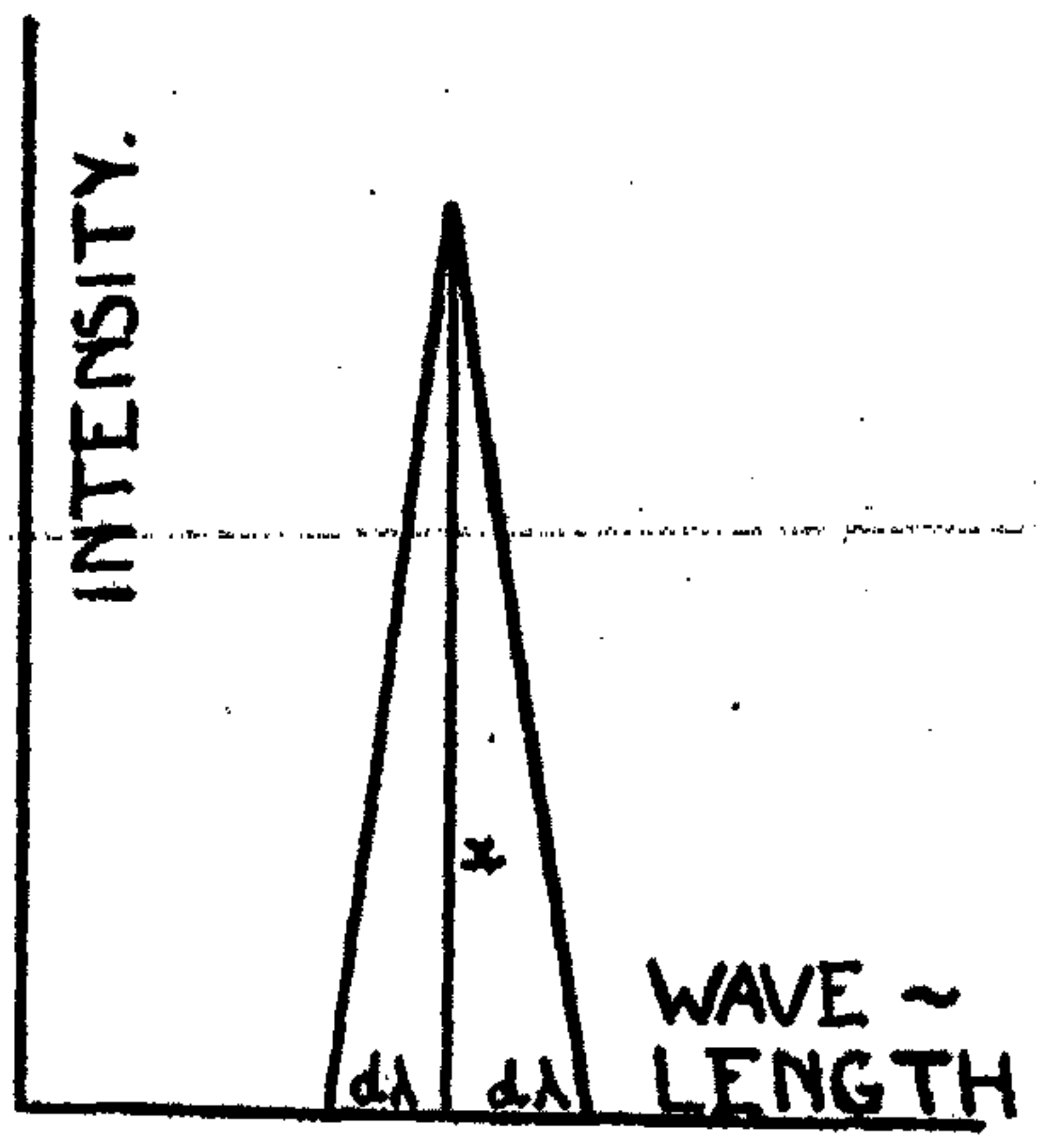

FIG. 2a

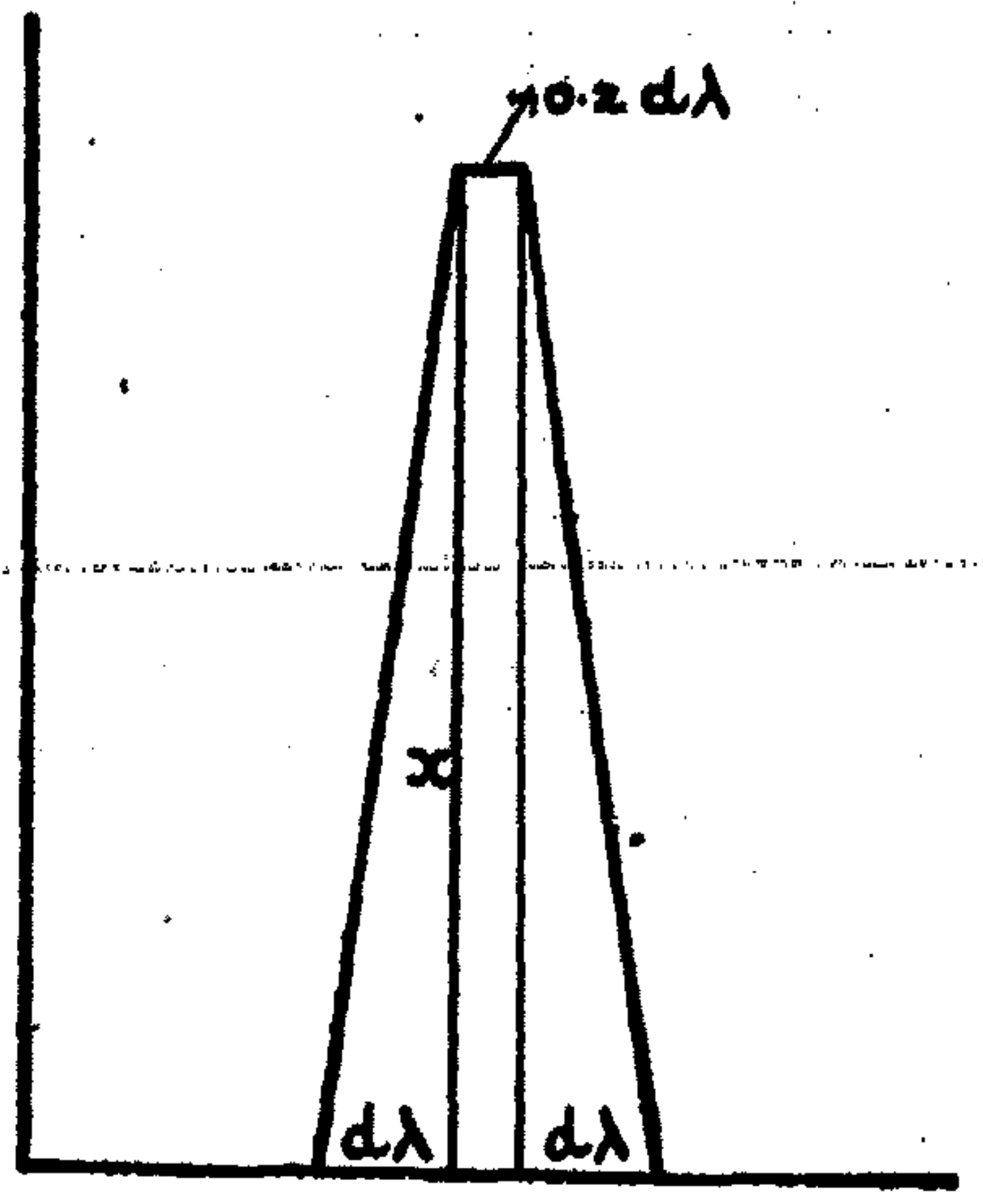

FIG. 2b

C. *The Representation of the Results.*

The results obtained for a given lamp are represented graphically by plotting the galvanometer deflections (reduced to a standard sensitivity) against the wave length. Such a curve was shown in Fig. 1 of the first paper in this series[1].

It was shown in that paper that the true energy distribution between the spectral lines, whether they be simple or compound, could be obtained from the areas of the triangular diagrams which they give, if these are divided by the corresponding values of dλ, the wave length range embraced by the telescope slit at that part of the spectrum. A more detailed discussion of this matter, particularly of the relation between the nature of the line and the shape of the triangular diagram it gives, was also promised. It is proposed to give this here.

It will be remembered that a pure spectral line is nothing but an image in monochromatic light of the collimator slit and, owing to the symmetry of the optical system of the spectrometer, of exactly the same size. If a line is com-

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[1] Reeve: J. Phys. Chem. 29, 40 (1925).

pound it will give a number of images, each the size of the collimator slit, which images may or may not overlap, according to the wave length difference $\partial\lambda$ between the components. In every case, however, the base of the triangular diagram, expressed as a wave length range, is equal to the sum of the wave length ranges embraced by the width of the telescope slit and the width of the spectral line respectively. Remembering these points, let us now go on to consider the possible values of the width of this base, and the possible shapes of the graph figures.

Case I. *Pure Lines.*

(*a*) *Collimator and Telescope Slits of Same Width.*
(say 10 divisions).

The graph figure will be a practically isosceles triangle of base $2d\lambda$ and height x (the maximum galvanometer deflection). See Fig. 2a. $d\lambda$ is the wave length range embraced by a telescope slit of 10 divisions.

Area of Fig. 2a = $x.d\lambda$; divide by $d\lambda$; = result = x.

It is obvious that, if all the lines were pure, the relative energy distribution between them would be given by the respective values of x. Some of the lines are compound, however, and this introduces complications which will be dealt with in due course. Meanwhile the above procedure should be noted.

(*b*) *Telescope Slit wider than Collimator Slit.*
(say collimator slit of 10 and telescope slit of 12 divisions.)

The effect of this inequality is to continue the maximum deflection x through a wave length range equal to the difference between the two slit widths. See Fig. 2b.

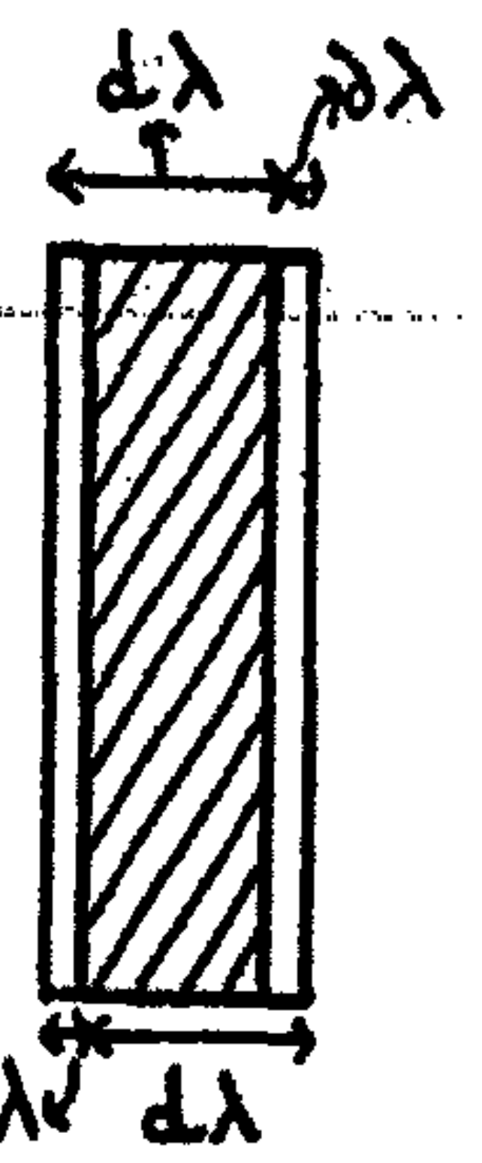

Fig. 2c

Area of figure = $(1.2x)d\lambda$; divide by $d\lambda$; result = 1.2x.

It is again obvious that if all the lines were pure their relative energy would be given by the values of x.

Case II. *Compound Lines.*

It will now be shown that the diagram given by a compound line is due to the sum of the diagrams given by the separate components, and hence its energy is still obtainable by dividing the area by the mean $d\lambda$ for the line.

Assume for the sake of simplicity that we are dealing with a compound line made up of two components λ and λ' of equal intensity, *each of which alone would have given a maximum galvanometer deflection of x.* Let $\lambda - \lambda' = \partial\lambda$.

Then, as we have already mentioned, the spectral line will consist of two images, each in monochromatic light, of the collimator slit, which may or may not overlap, depending upon the relative values of $\partial\lambda$ and $d\lambda$.

(*a*) *Slits of Equal Width.*

Again, let us first consider the case of equal slits, say again 10 divisions.

Case 1. $\partial\lambda < d\lambda$

The images of the two components will overlap as shown in Fig. 2c. The total width of the line is $d\lambda + \partial\lambda$.

The line is made up of three portions:—

(1) A central portion, width $d\lambda - \partial\lambda$; i.e., less than the width of the telescope slit by $\partial\lambda$. This portion by itself, when fully embraced by the telescope slit would, therefore, give a deflection of $\frac{d\lambda - \partial\lambda}{d\lambda}\, 2x$

(2) Portions on each side of this of width $\partial\lambda$, each of which alone, would be responsible for a maximum deflection of $\frac{\partial\lambda}{d\lambda}x$. Hence, as the compound line moves across the slit, it will be responsible for galvanometer deflections expressing themselves in a diagram of the type shown in Fig. 2d. This can be seen more clearly by considering Fig. 2e, in which the dotted lines represent the two spectral images of the components, and the full line represents the telescope slit. Assuming a movement of the lines across the slit from left to right, the figure shows the relative position of the two images and the slit for the six limiting galvanometer deflections marked 1 to 6 in Fig. 2d; e.g., at the position of the lines and slit shown by 2, Fig. 2e, the deflection obtained is given by the ordinate at the point 2 of the graph diagram Fig. 2d: at position 3 of Fig. 2e the deflection is given by the ordinate at point 3 of Fig. 2d and so on; whilst at intermediate positions we have intermediate deflections.

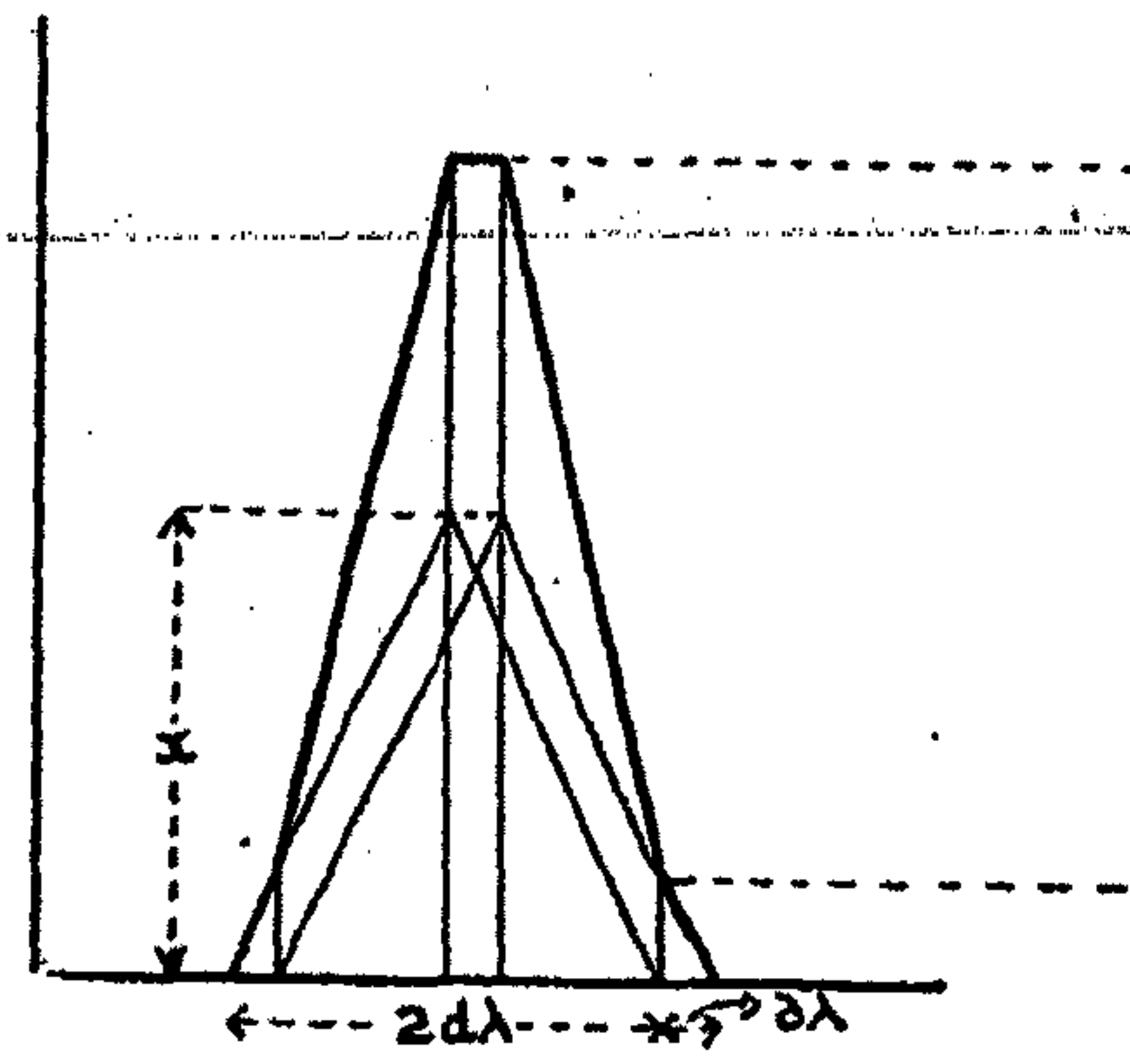

FIG. 2f

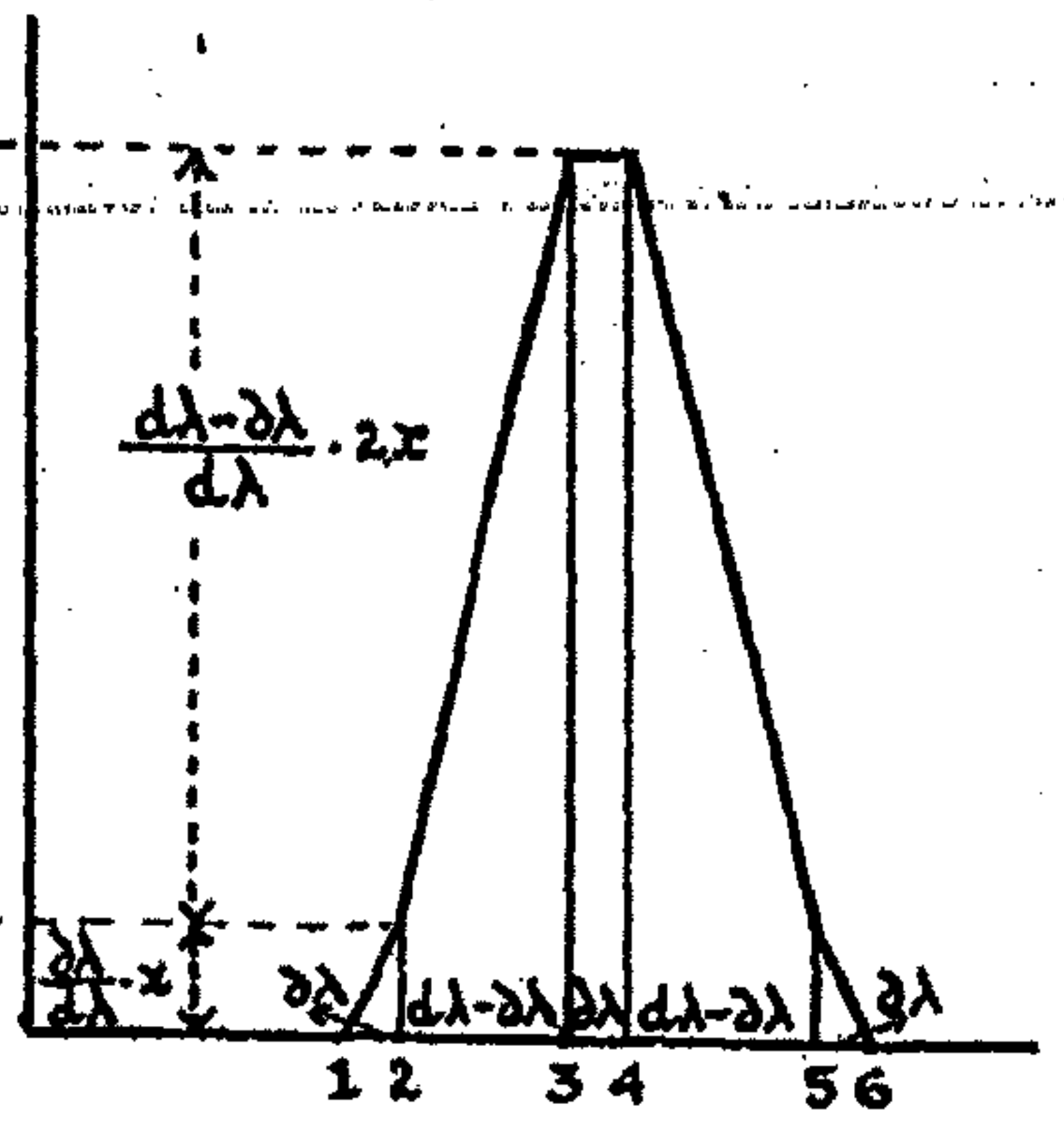

FIG. 2d

The total width of the base of the graph diagram Fig. 2d is $2d\lambda + \partial\lambda$; the excess above that given by a pure line is therefore $\partial\lambda$ which is equal to the wave length difference between the components. See the first paper of this series[1].

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[1] Reeve: J. Phys. Chem. 29, 41 (1925).

The area of the diagram can easily be shown[1] to be 2x.dλ. Divide by dλ. Result = 2x; i. e., the same result as would have been obtained had the two lines registered their effects separately. (Note however that the maximum deflection obtained is *less* than 2x.). This additive property of the diagram is of course also true graphically; add up two triangles each of base 2 dλ and height x, separated by a distance ∂λ less than dλ, as shown in Fig. 2f, and Fig. 2d will be obtained.

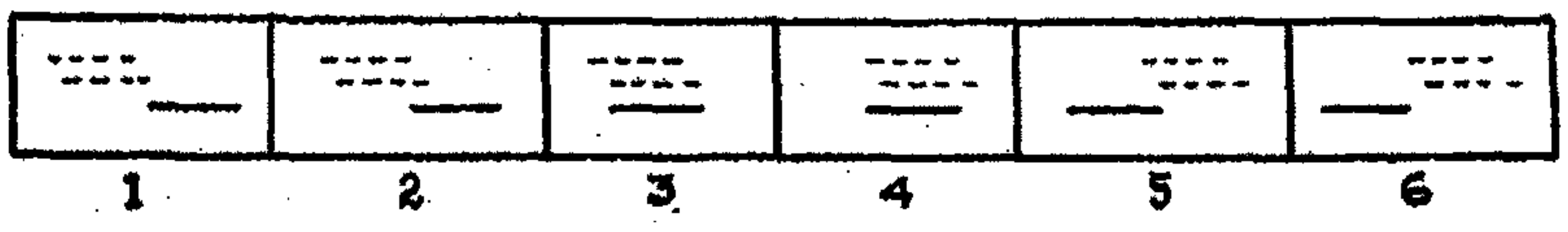

FIG. 2e

Case 2. ∂λ = dλ

For all values of ∂λ up to dλ similar diagrams as for Case 1 would be obtained. When ∂λ = dλ the images of the two components would just touch; see Fig. 3a. The result on the energy distribution diagram would therefore be as shown in Fig. 3b. Area of this is 2dλ.x; divide by dλ; result = 2x, the same result as would have been obtained had the two components registered their effects separately. Also, it is again true graphically; see Fig. 3c.

FIG. 3a

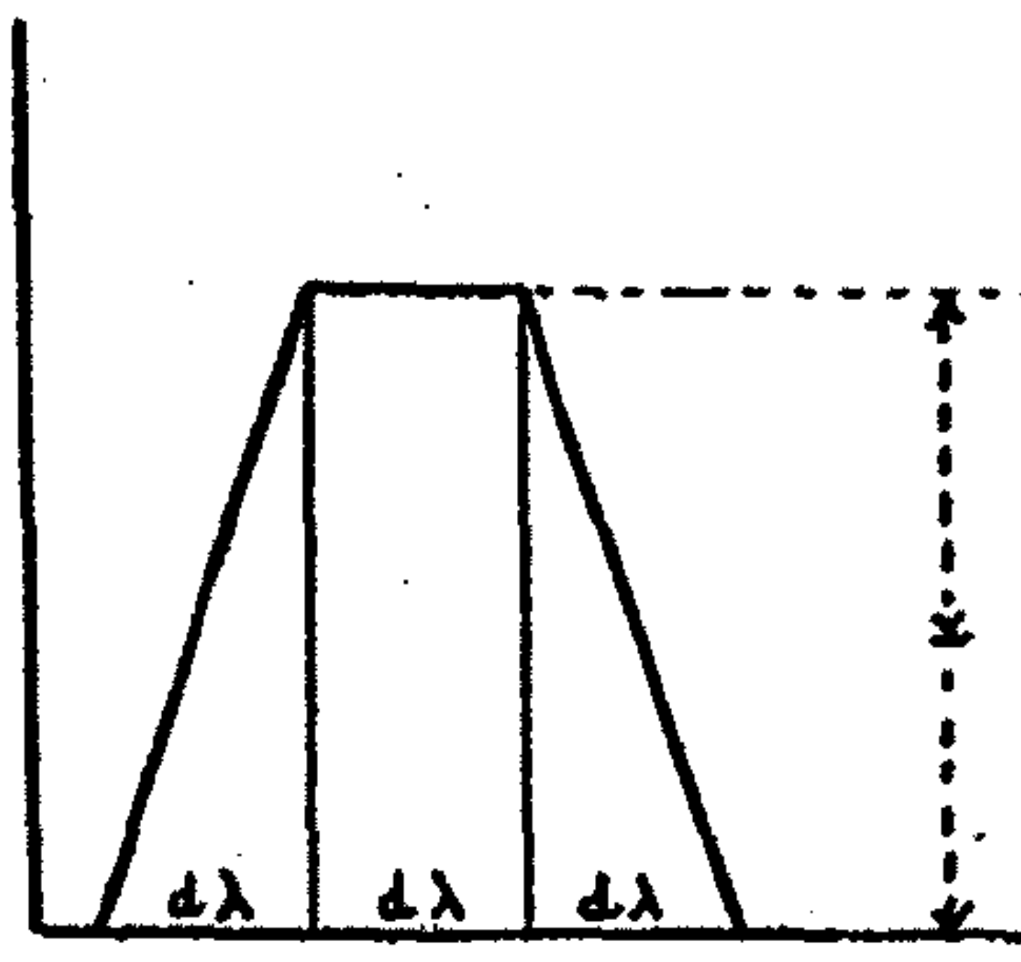

FIG. 3b

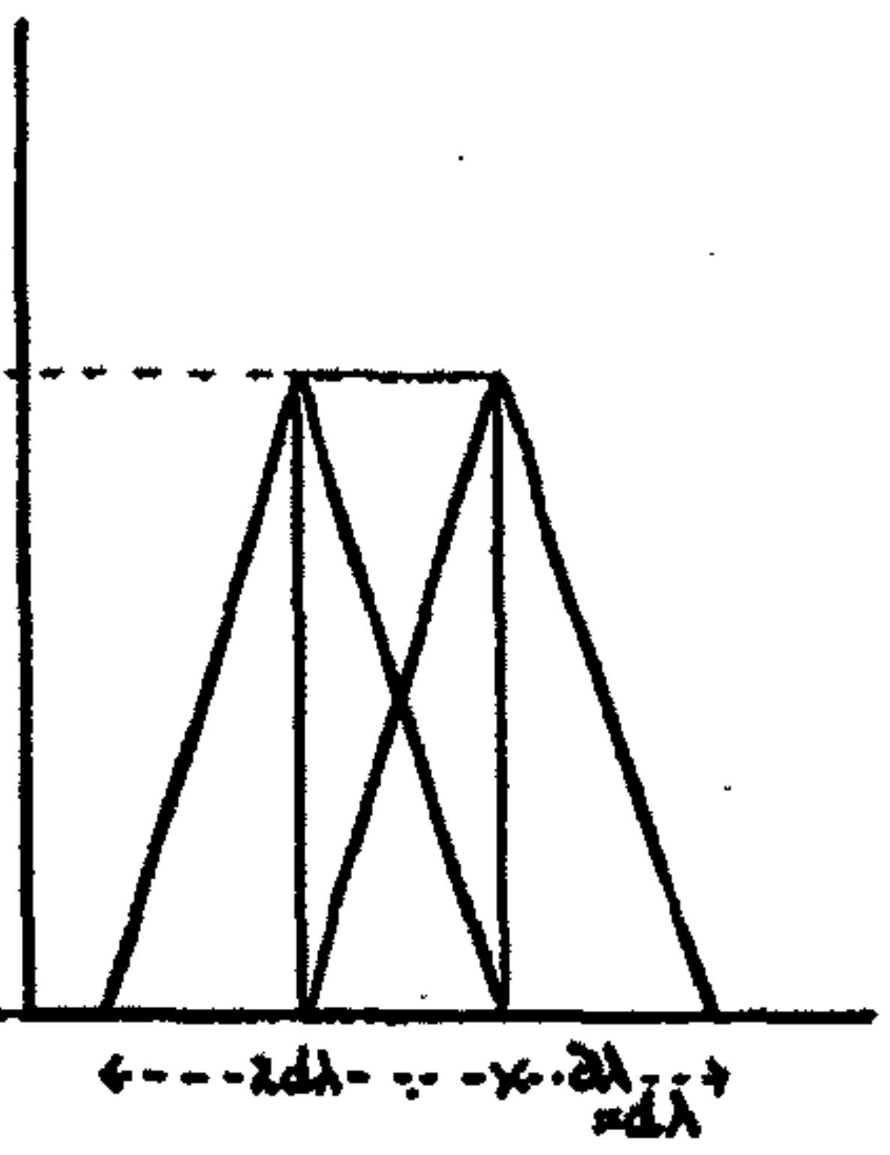

FIG. 3c

Case 3. ∂λ > dλ but < 2dλ

If now ∂λ becomes greater than dλ (but less than 2dλ) the images of the two components separate, the distance between them being ∂λ − dλ. The result on the energy distribution diagram is shown in Fig. 3d, where a = dλ, b = ∂λ − dλ, c = 2dλ − ∂λ, and, therefore, b + c = dλ.

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[1] Area of portions 1.2 and 5.6 (see Fig 2d) = $2\left(\frac{\partial\lambda}{d\lambda}\ x.\ \frac{\partial\lambda}{2}\right)$

Area of portions 2.3 + 4.5 = $2\left([d\lambda-\partial\lambda]\ \frac{\partial\lambda}{d\lambda}x + \frac{d\lambda-\partial\lambda}{2}\ \frac{d\lambda-\partial\lambda}{d\lambda}\ 2x\right)$

Area of portion 3.4 = $\partial\lambda\left(\frac{\partial\lambda}{d\lambda}x + \frac{d\lambda-\partial\lambda}{d\lambda}2x\right)$

The sum of all which = 2x. dλ

The limiting positions of the telescope slit and the spectral images are shown in Fig. 3e, using the same method of presentation as described under Case 1, Fig. 2e. The area of Fig. 3d can again be shown to be equal to 2dλ.x; divide by dλ and the result is 2x: again the same result as would have been given by the sum of the two separate components. An inspection of the diagram will show that this is also true graphically.

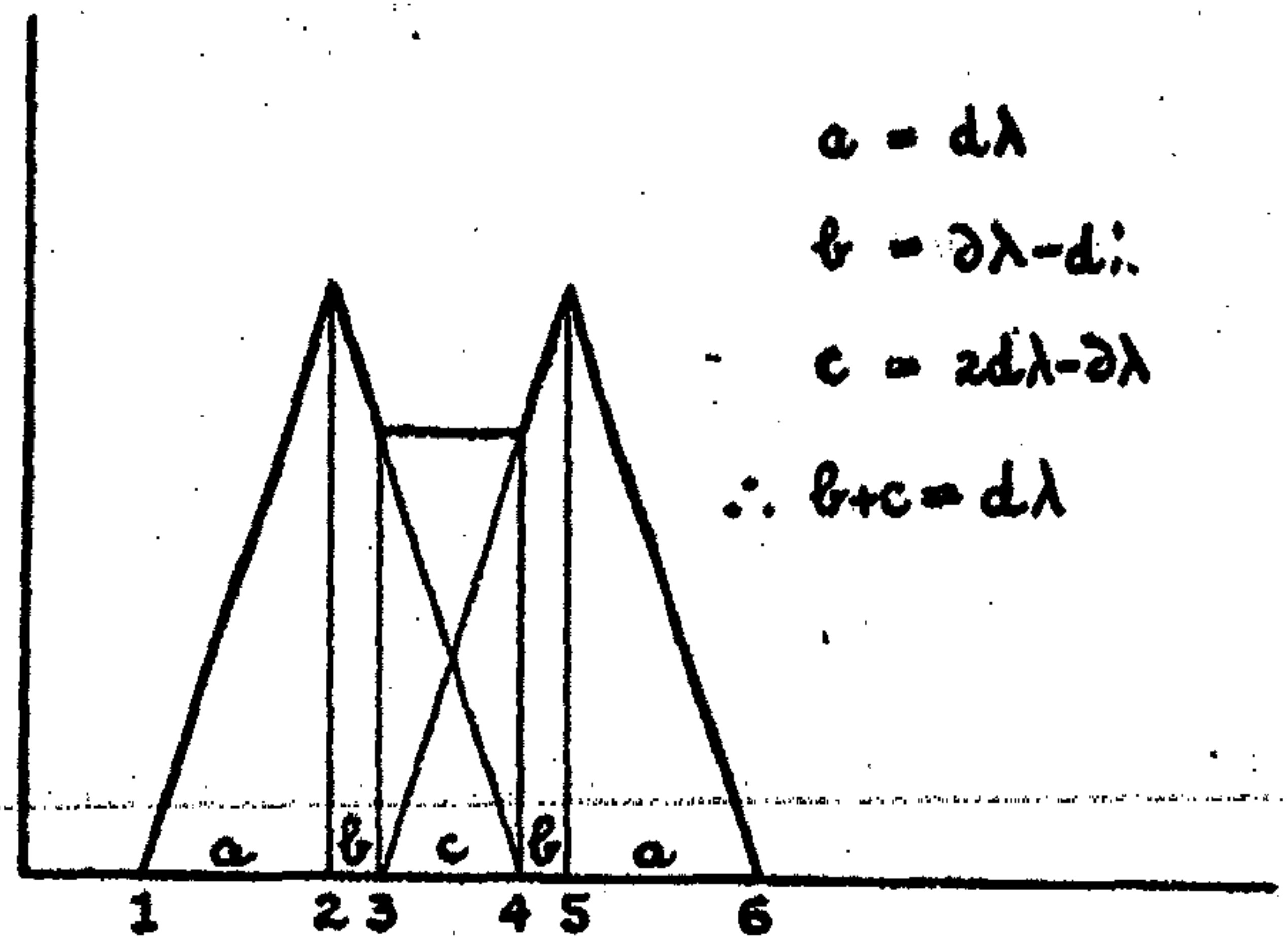

Fig. 3d

Case 4. ∂λ = 2dλ

The images are now separated by a distance equivalent to dλ. The result is that they are just resolved by the spectrometer; see Fig. 4a, the area of which is once again 2dλ.x. Divide by dλ and we get the usual result, 2x.

Case 5. ∂λ > 2dλ

The components are now two completely separable lines, as shown in Fig. 4b.

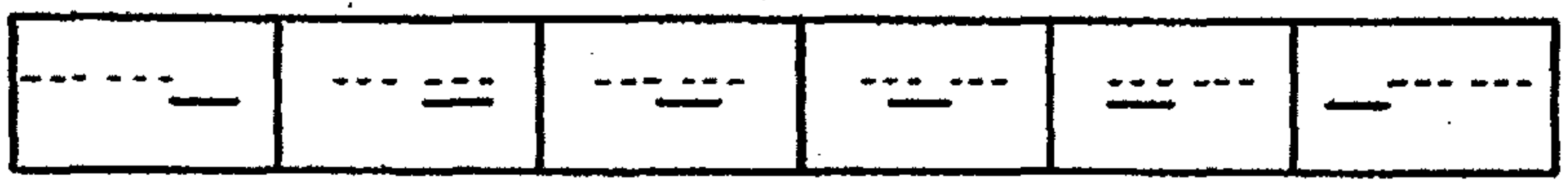

Fig. 3e

Effect of Inequality of Intensity of Components.

In the above discussion we have been assuming the components to be of equal intensity. The general effect of an inequality would be to make all the above symmetrical diagrams asymmetrical. Thus, any horizontal portions of the diagrams would now slope up or down, according to whether the left hand or the right hand component were the more intense. If the components separately were capable of giving maximum deflections of x and y respectively then, on dividing the area of the complex diagram by the mean dλ for the lines, the result would be x + y. For, as we have shown already for a number of cases, the compound energy distribution diagram is the sum of the simpler triangular diagrams due to the separate components. The areas of these, divided by their respective dλ's give the results x and y respectively; Hence, on doing this with the compound diagram, the result would be x + y.

(*b*) *Slits of Unequal Width.*

E. g. telescope slit of 12 divisions and collimator slit of 10. In the case of a simple line, it will be remembered, the effect of inequality in slits was to introduce a phase of constant deflection into the graph diagram, so that instead of a triangle we obtained a trapezium. On dividing the area of this figure by dλ we obtained the result 1.2x instead of x. This factor 1.2 would enter into all other pure lines; hence the relative energy of these would remain unaffected. Turning now to compound lines: the effect of a wider telescope slit on the diagram given by these would be to introduce extra phases into the energy distribution diagram. Thus with equal slits Case 1, where $\partial\lambda < d\lambda$, gave the diagram shown in Fig. 2d. With a wider telescope slit this would now appear as shown in Fig. 4c. the limiting positions of slit and lines for which, numbered in the usual manner, are given in Fig. 4d.

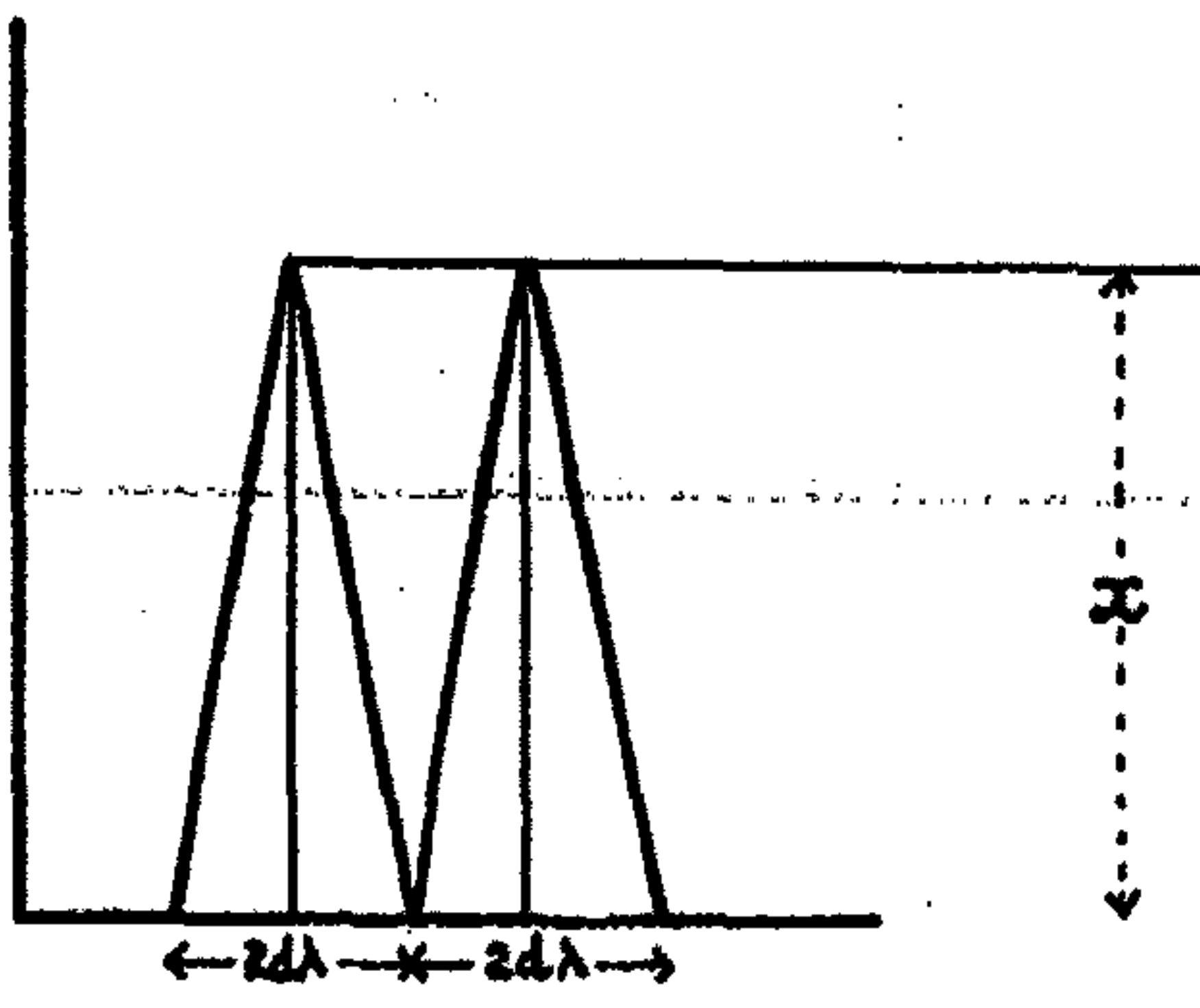

FIG. 4a

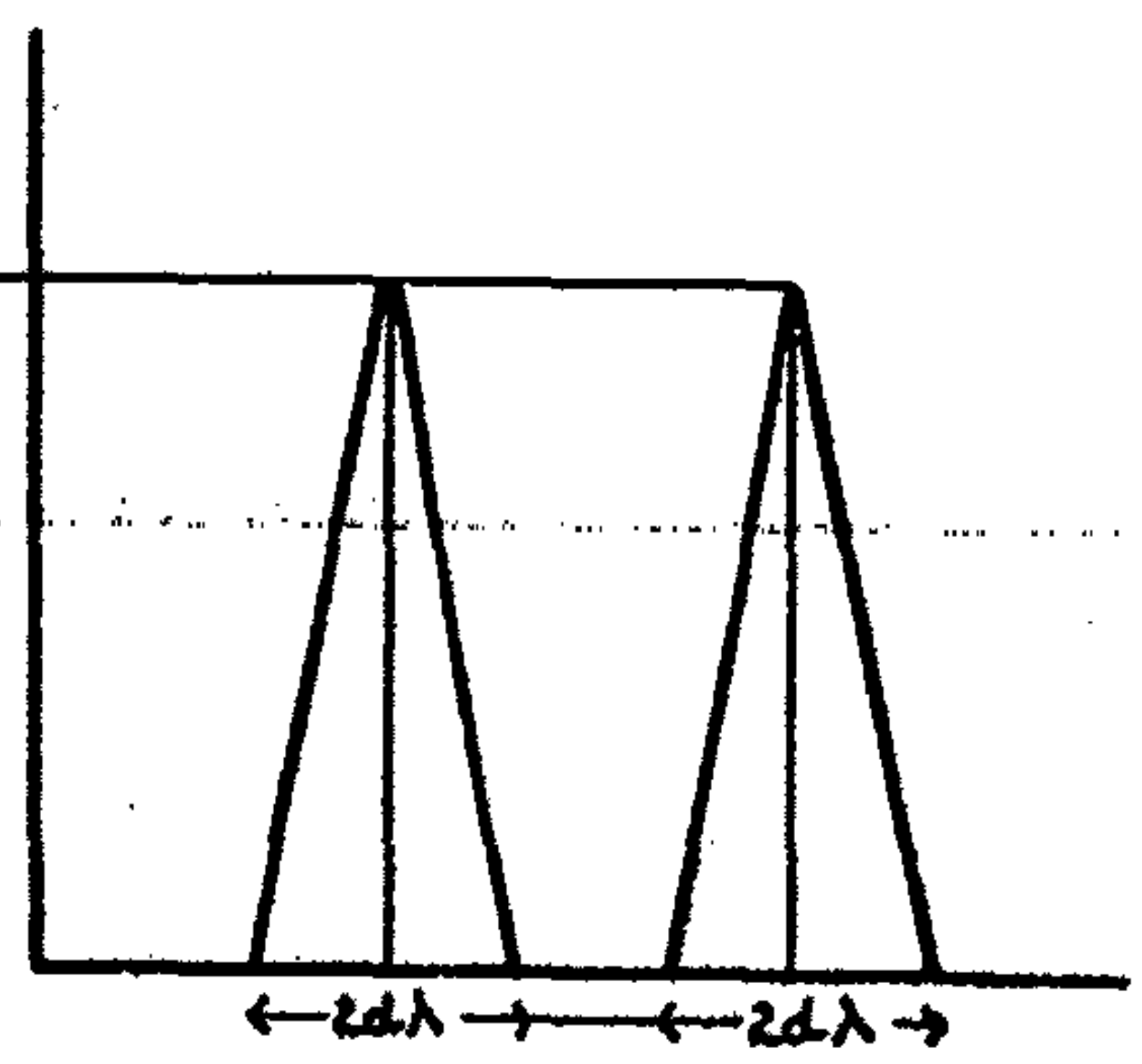

FIG. 4b

The slope of the side of a graph diagram may be taken as a measure of the rate of increase or decrease in intensity of the radiation falling upon the thermopile. Hence any sudden change of slope is due to a sudden change in this rate. Referring now to Fig. 4c, from 1 to 2 the rate of increase is due to an increasing amount of one component passing through the telescope slit. From 2 to 3 the rate is doubled since both components are now acting. From 3 to 4, although deflections are still increasing, they do so at the same rate as for the section 1 to 2; for the increasing deflection is due to the telescope slit embracing an increasing portion of one component only. From 4 to 5 the deflection remains constant, i. e., the rate of increase is zero. For, although the right hand edge of the right hand component is passing off the slit, exactly equivalent portions of the left hand component are taking its place. From 5 to 8 there occur a series of deflections symmetrical to those between 4 and 1.

The resulting diagram, though so complex, is again nothing but the sum of the two simpler diagrams due to the separate components; (see Fig. 4e).

Hence, to obtain the energy of the compound line, we must once again find the area of the compound diagram and divide by the mean dλ for the components. The result will be 2(1.2x).

We may now repeat the general result, already given in the first paper of this series, viz:—*Whatever the nature of a line may be, whether simple or compound, and in the latter case whether doublet, triplet, etc., and whatever the width of the slits employed, its relative energy is obtained by dividing the area of the energy distribution diagram it gives by the mean valne af dλ.*

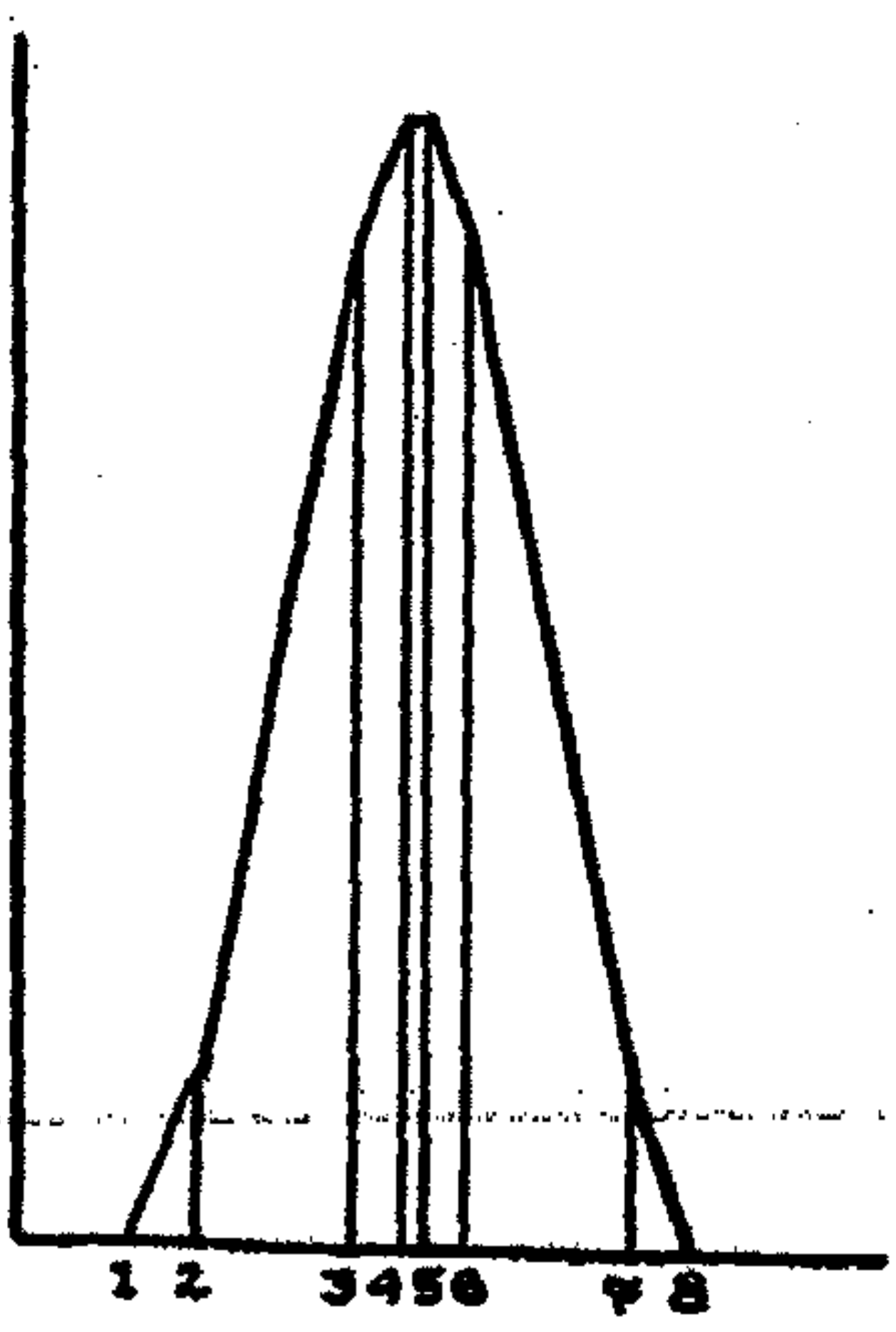

Fig. 4c

It is obvious, however, that the use of slits of equal width results in simpler diagrams. Since these can be determined with greater accuracy and are convenient from other points of view, their employment is strongly recommended.

Cases where there is no need to work out Areas.

In the case of some lines there is no need to work out the areas of their diagrams in order to obtain their relative energy. This is the case for pure monochromatic lines whose energy is given directly by the heights of their triangles. The purity of lines can be determined from (a) photographs, or (b) from the value of the base of the graph diagram. If, in the case of equal slits, this does not exceed 2dλ the line must be pure. Any excess ∂λ is due to a corresponding wave length difference between the extreme components of a compound line.

It follows from the above that the accurate determination of the true base of a diagram is as important as the measurement of the galvanometer deflections. In the case of the more intense lines this can be done fairly easily; but with the weaker lines it is more difficult, since the galvanometer deflections bounding the base are, necessarily, extremely small. In fact, in the case of very weak lines, it may be found that the base determined is less than 2dλ, which we know is impossible.

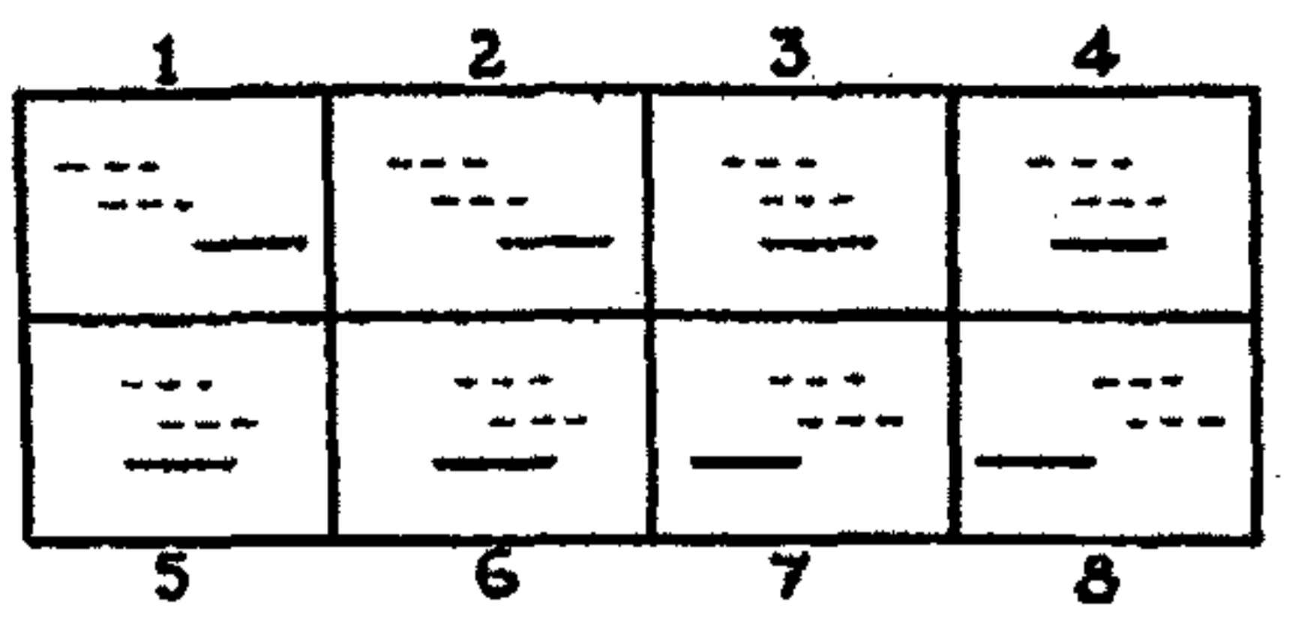

Fig. 4d

Fortunately most of these lines in the case of the mercury spectrum are simple, so their relative energy content is best determined directly from the heights of their triangular diagrams. Even when they are known to be compound it is likely that smaller errors would be involved in doing likewise, than in calculating their areas (which involve base values, of course).

Correction for Reflection of Mirror.

The relative energy distribution between the lines, calculated from their diagrams in the manner described, has to have one important correction applied to it before it can be used. This is due to the selective reflection of the metallic mirror which forms part of the optical system of the Hilger monochromator. It has been determined in this laboratory by one of us and a graphical representation of the results obtained is shown in Fig. 5. From it the necessary corrections can be applied.

The Determination of Absolute Energy

We must now turn to the second of the energy characteristics, viz; the total energy in the beam of light from the lamp used. Briefly, this is determined by comparing its energy with that from a Hefner lamp, the energy of which, under standard conditions, is known[1]. For this purpose a Moll surface thermopile (1 cm. in diameter) of internal resistance 10 ohms. is employed in conjunction with a sensitive Gambrell moving coil galvanometer of internal resistance 23.6 ohms. and a sensitivity of about 6 mms. per microvolt.

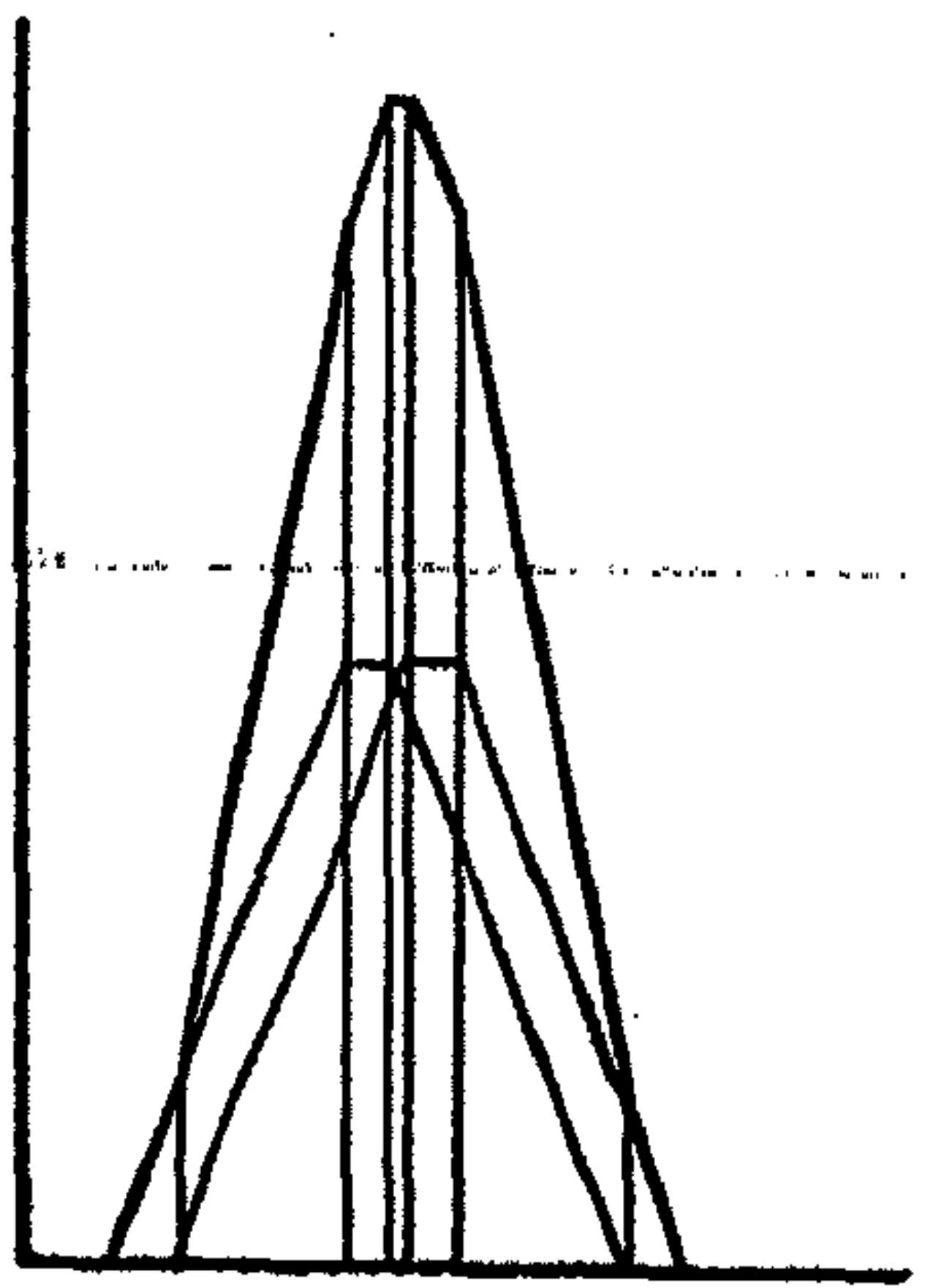

FIG. 4e

A. *Disposition of Apparatus for Measurement with Hefner Candle.*

The apparatus, the arrangement of which is shown in Fig. 6a, is mounted in a cupboard, free from draughts and blackened inside. A is a large slab of stone, blackened to a matt surface and placed behind the lamp. BC is the screen by means of which the radiation from the Hefner lamp D is cut off from or admitted to the thermopile E. BC is also blackened, and arrangements are made for using it from the outside of the cupboard. The object of the stone slab A is to act as a background for the Hefner lamp which shall be in the same state of thermal equilibrium as the side C of the screen BC nearer the thermopile. The height of the flame of the Hefner lamp is adjusted by means of a cathetometer, observation being made through a circle in the blackened glass window of the front of the cupboard (a converted fume-cupboard). The thermopile is similarly adjusted so that its centre corresponds to the centre of the flame. The distance DE is 1 metre. G is the galvanometer, mounted outside the cupboard. Its sensitivity is determined by applying a P. D. of about 15 microvolts at its terminals with the aid of a suitably arranged potentiometer.

The Hefner lamp arranged as described above and burning under the usual standard conditions gives a mean deflection of 4.95 cms. corresponding to a P. D. of 7.89 microvolts.

B. *Disposition of Apparatus for Measurement of Total Energy of Mercury Lamp Radiation.*

For determining the total energy, the lamp A (Fig. 6b) is mounted on an optical bench in the same way as described in connection with Fig. 1 and it is

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[1] Gerlach: Physik. Z. **14**, 577 (1913).

fitted with the usual diaphragm B. One condenser lens only (C) is employed, the water cell E is retained, and flush up against its back plate is placed the Moll thermopile D connected to the Gambrell galvanometer G. In order to obtain reasonable deflections when working with the intense beam from the mercury lamp, an additional series resistance R of about 200 ohms is introduced. The light field passing the water cell is then examined. In spite of the fact that the lens C is placed so as to give a parallel beam, the field obtained is only approximately uniform. It is therefore important for the determination of the total energy that the lamp should be in the very position in which it is to be used for the quantitative experiments and that the energy measured by the thermopile should be taken with the receivers of the latter in exactly the position occupied normally by the front surface of the reaction cell. Further, owing to the fact that the beam is not strictly uniform, it is necessary to explore the field to obtain a mean value for the total energy. The figure finally obtained for the latter is reduced to microvolts by determining the sensitivity of the galvanometer. Knowing the energy of the Hefner lamp in microvolts, it is now possible to express the energy of the beam of light from the mercury lamp under consideration in terms of Hefner candles; and, since a Hefner candle is equivalent to 9.42×10^2 ergs per sq. cm. per second at a distance of one metre, we can finally express the total energy in the beam of light from the lamp in absolute units. Finally, the energy distribution being known it is possible to state the quantity of radiant energy of any given wave length present in the beam falling upon the reaction vessel.

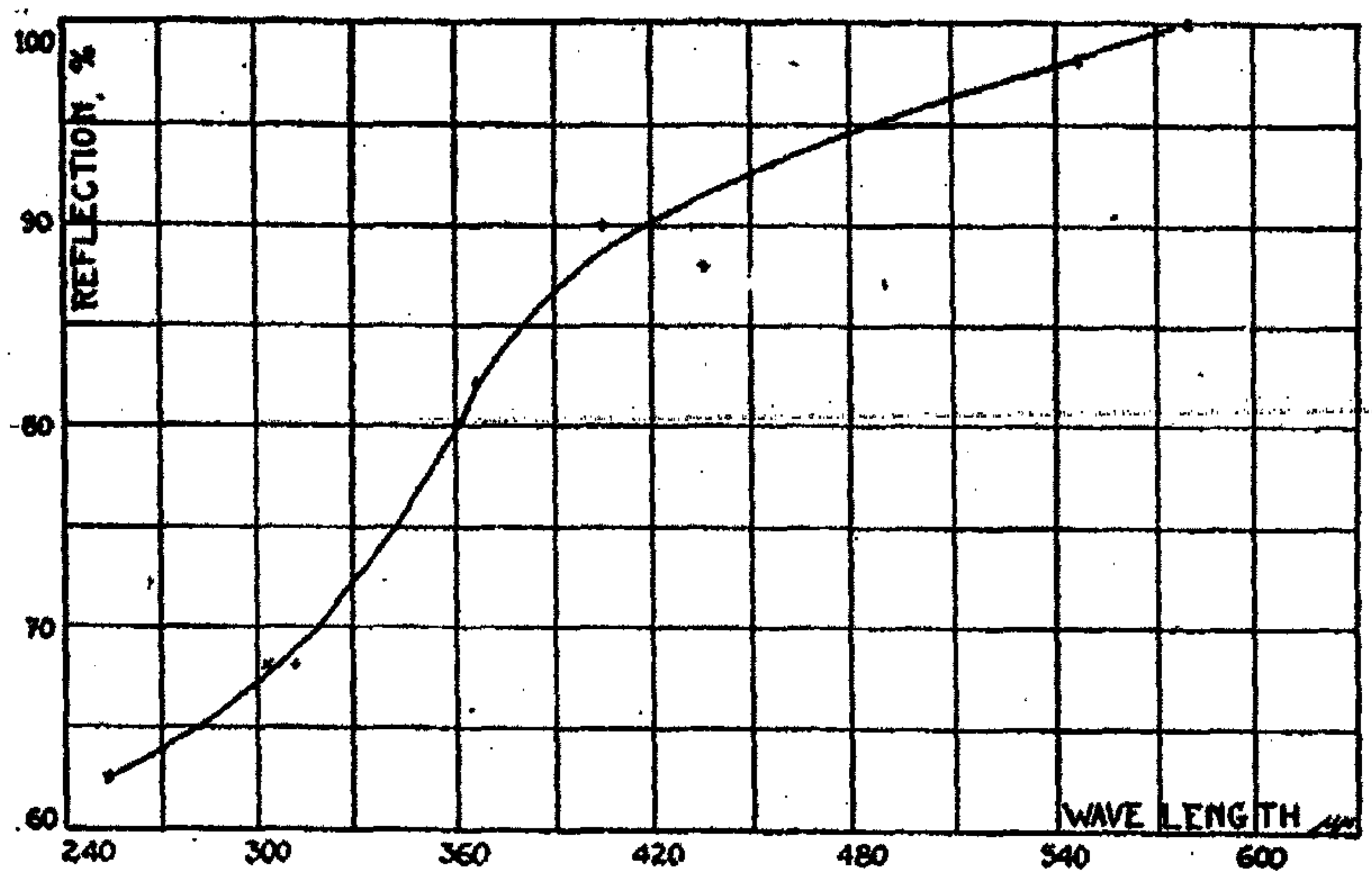

Fig. 5

Losses by Reflection

A certain amount of light is always lost by reflection at the surface of any medium, even if perfectly transparent to the incident radiation. This therefore will occur at the surface of the quartz plates and lenses normally used in photochemical work. The extent of the loss can be calculated from Ruben's figures for the refractive indices of quartz at various wave lengths, in conjunction with Fresnels equation:—

$$R = \left(\frac{n - 1}{n + 1}\right)^2$$

where R = reflection at wave length λ, for normal incidence and for a single surface, and n = the refractive index for that wave length. For example:—

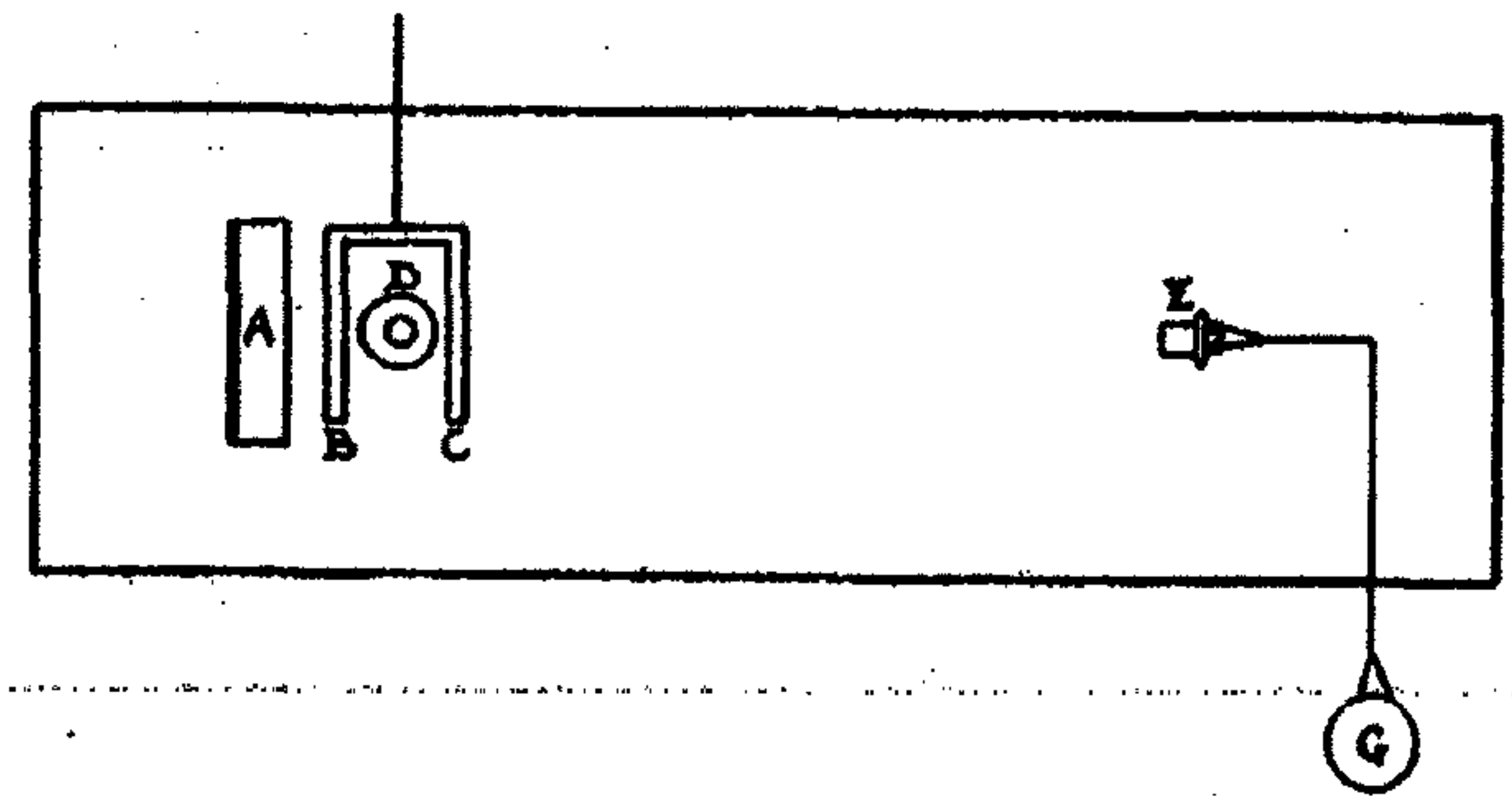

Fig. 6a

for λ 535 μμ, n = 1.54663 and therefore R = 4.5%; for λ 274 μμ, n = 1.58750 and therefore R = 5.2%.

Since the effect of wave length upon this reflection is not very large, there is no need to take into account its effect at the quartz surfaces inside the spectrometer when determining energy distributions. It has to be allowed for only when dealing with absolute energy data.

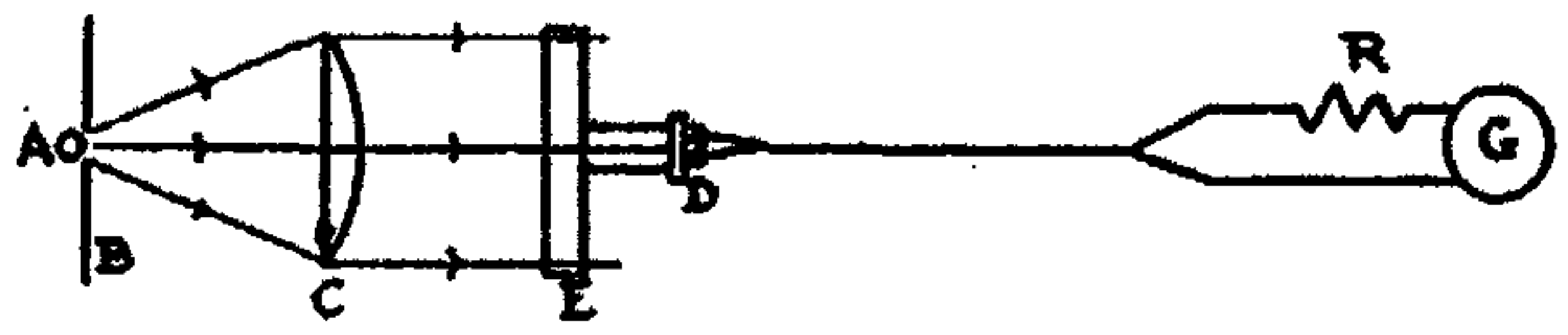

Fig. 6b

Correction for Infra Red Radiation passed by a 1 CM. Quartz Water Cell

According to Coblentz, Long and Kahler[1], the intensities of the lines of the mercury infra-red spectrum for wave lengths shorter than 1.4 μ (with which we are particularly concerned) are approximately as follows:—

line at 1.014 μ: intensity about same as 0.436 μ.
line at 1.128 μ: " " " " 0.406 μ.
3 lines at 1.2 μ: intensity of each about 2/3 of 0.406 μ.
2 lines at 1.37 μ: " " " " 2/3 " " μ.

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[1] Bur. Standards, Scientific Papers No. 330, p. 4.

A 1cm. quartz water cell, though absorbing entirely all infra-red radiation longer than 1.4 μ, will transmit, according to Aschkinass[1]:—

67.5% of 1.014 μ.
73.5% of 1.128 μ
31.5% of 1.2 μ.
14% of 1.37 μ.

The total energy figures have therefore been corrected on this basis. It is recognised that the method is approximate, but it must suffice until new determinations of the infra-red spectrum of the mercury lamp can be carried out.

Summary

(1) A complete account of the method of determining the energy distribution in the radiation from quartz mercury lamps, or any other light source, has been given.

(2) The interpretation of the results obtained has been discussed, and the connection between the width of the slits used in the spectrometer, the nature of the line and the shape of the diagram it gives on the energy distribution diagram has been fully considered.

(3) Finally, the method of determining the total energy in the beam of light employed has been discussed.

We wish to thank Professor Allmand for the suggestion of writing this paper and for the interest he has taken in it, and also the Department of Scientific and Industrial Research for grants to us whilst Students in Training.

The Chemistry Department,
Kings College,
London.
September, 1924.

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[1] Aschkinass: Ann. Physik. 55, 415 (1895).

SOME PHYSICAL-CHEMICAL PROPERTIES OF MIXTURES OF ETHYL AND ISO-PROPYL ALCOHOLS

BY GEORGE S. PARKS AND KENNETH K. KELLEY

In a recent study[1] of some physical-chemical properties of mixtures of ethyl and normal propyl alcohols, the system was found to approximate to the requirements of an ideal or "perfect" solution to a remarkable degree. Thus the process of forming the solutions was accompanied by a very small heat absorption, in no case more than five calories per mol of resulting mixture, and by a volume shrinkage averaging only .025%. Moreover, the partial pressures of each component as calculated from the experimental data at 25° C were but slightly higher than those called for on the basis of Raoult's law. Indeed, the data obtained were so striking that the question at once arose as to whether a study of other binary systems involving closely related alcohols would yield analogous results. Accordingly the two systems, ethyl and iso-propyl alcohols, and iso-propyl and n-propyl alcohols, were investigated in an essentially similar manner. The present paper presents the data obtained in the study of mixtures of the former pair of liquids.

In constitution iso-propyl alcohol differs from ethyl alcohol merely by the substitution of a methyl group for one of the hydrogen atoms in the carbinol group of the latter compound. Hence in several important physical-chemical properties the two alcohols are very similar, as the following table indicates.

TABLE I

	CH_3CH_2OH	$(CH_3)_2CHOH$
Dielectric Constant at 20° C	25.8[2]	26(±1)[3]
Capillary Constant at 31° C[4]	1.08	1.05
Association Factor at 31° C[4]	2.74	2.86
Relative Internal Pressures[5] at 20°C		
From surface tension $(\gamma \div V^{1/3})$	5.7	4.9
From critical data $5(10^5)(a \div V^2)$	3.5	2.6
From coefficients of expansion and compressibility $\left(\frac{\alpha}{\beta} T\right) 10^{-3}$	2.8	2.8

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[1] Parks and Schwenck: J. Phys. Chem. 28, 720 (1924)

[2] Abegg and Seitz: Z. physik. Chem. 29, 246 (1899).

[3] Löwe: Wied. Ann. 66, 398 (1898).

[4] Ramsay and Shields: Z. physik. Chem. 12, 468 (1893).

[5] These relative internal pressures were calculated by the methods described by Hildebrand: J. Am. Chem. Soc., 41, 1067 (1919). The necessary data were obtained from the Tabellen of Landolt-Börnstein-Roth (1912).

The equality in dielectric constants and the relatively small differences in the capillary constants and degrees of association indicate that we are dealing with two liquids of the same degree of polarity. A comparison of the values for the relative internal pressures is not quite so satisfactory, since the three different pairs of results obtained by the various methods of calculating internal pressures are not very concordant. On the average, the values for iso-propyl alcohol run about 14% lower than those for ethyl alcohol. This difference, altho appreciable, is hardly great enough to lead us to expect any large deviations from the laws of a perfect solution; since, as Hildebrand has remarked (loc.cit.) "a very decided difference in internal pressures is required to produce any considerable deviation from Raoult's law." On the other hand, the two preceding factors—chemical similarity and equal polarity—point definitely in the other direction and would lead us to suspect that this pair of liquids might form a series of solutions which would be almost "perfect."

Experimental

Purification of Substances. A good grade of 95% ethyl alcohol was dehydrated by a preliminary distillation over lime in the ordinary manner, followed by a second distillation over a small quantity of calcium metal. The resulting product was carefully fractionated and the middle portion, about 60% of the total, was selected for use in the present investigation $D_{4^\circ}^{25^\circ}$ 0.78516, which corresponds to 99.97% ethyl alcohol according to the U. S. Bureau of Standards tables[1].

The iso-propyl alcohol was prepared in exactly the same way. After the fractionation process the final product had a density of 0.78086 25°/4°, which corresponds to 99.99% alcohol on the basis of Brunel's value[2] of 0.78084 for 100%, and the variation per 1% of water of 0.00230 obtained by Lebo[3]. Hence it is safe to conclude that our purified materials had much less than .1% water at the start of the following series of measurements.

Formation of the alcohol mixtures. The alcohols thus prepared were used in making two series of five mixtures each, which varied systematically in steps of approximately 16% of each component. Thus the first mixture in series A contained by weight 15.95% of iso-propyl alcohol and 84.05% of the ethyl alcohol; the second mixture, 33.26% iso-propyl and 66.74% ethyl, etc. About 100 cc of each mixture was made up.

In the course of the preparation of these solutions the heat of mixing was determined. In this measurement the apparatus and procedure used in the determination of the heats of mixing of ethyl and n-propyl alcohol were again employed. For the details concerning these the reader is referred to the earlier article[4].

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[1] U. S. Bureau of Standards: Scientific Paper, No. 197 (1913).

[2] Brunel: J. Am. Chem. Soc. 45, 1336 (1923).

[3] Lebo: J. Am. Chem. Soc. 43, 1006 (1921)

[4] Parks and Schwenck: loc. cit.

The data obtained in the present investigation appear in columns four and five of the following table. In contrast with the results found for the ethyl-n. propyl alcohol system, the process of forming the various solutions in this instance took place with the evolution of heat. The numerical values of the heat effect, while not great, are about two and a half times those obtained in the earlier study—an indication that the solutions in the present case may not be as "perfect."

TABLE II

Heat of Formation of the Mixtures at 25°

Liquid	% C_2H_5OH by weight	Mol fraction of C_2H_5OH	Heat of mixing in calories per gram of mixture	Heat of mixing in calories per mol of mixture
1	100.00	1.000	——	——
2A	84.05	.873	+.152	+ 7.3
2B	83.19	.866	+.149	+ 7.2
3A	66.74	.724	+.204	+10.2
3B	67.05	.726	+.201	+10.0
4A	49.92	.565	+.242	+12.7
4B	49.83	.565	+.238	+12.4
5A	33.67	.398	+.212	+11.6
5B	33.49	.396	+.207	+11.3
6A	16.95	.210	+.175	+10.0
6B	17.72	.219	+.168	+ 9.5
7	0.00	.000	——	——

The numbers given in the first column to the various liquids are for convenience in reference in subsequent pages of this paper. Thus, when we mention "liquid No. 4A" for instance, we shall be referring to the solution containing 49.92% (by weight) of ethyl alcohol.

Densities and Total Pressures. The densities of the liquids were next determined in the usual manner, a double-walled, evacuated specific gravity bottle of 10 cc capacity being used for this purpose. All weighings were corrected for the buoyancy of the air, and the final values appear in the second column of Table III. For purposes of comparison determinations were also run on samples of the pure alcohols after they had been put thru the mixing apparatus; this was done because it seemed inevitable that the samples would absorb traces of moisture during such a procedure and we desired to have all our liquids in as comparable a condition as possible.

On the assumption that we are here dealing with perfect solutions, the densities of the mixtures were calculated by use of the relationship

$$\frac{1}{D} = \frac{P_1}{100\,d_1} + \frac{P_2}{100\,d_2}$$

where d_1 and d_2 are the densities of the components in the pure state, P_1 and P_2 are their corresponding weight percentages in the resulting solution and D is the density of the solution. The values, thus obtained, appear in column three of the following table: they average only .01% lower than the experimental results. In fact, we are practically justified in concluding that, within the limits of experimental error, the volume of the solution is the sum of the volumes of the two pure components—a characteristic relationship of the ideal solution.

TABLE III

(Temperature 25° C)

Liquid	Density Observed	Density Calculated	Vapor Pressure Observed	Vapor Pressure Ideal
1	0.7857	——	59.0 mm (assumed)	——
2A	0.7852	0.7851	57.2 "	57.2 mm
2B	0.7851	0.7851	57.2	57.0
3A	0.7845	0.7844	54.9	55.0
3B	0.7846	0.7844	55.3	55.0
4A	0.7839	0.7839	52.4	52.5
4B	0.7840	0.7839	52.6	52.6
5A	0.7833	0.7833	49.7	50.2
5B	0.7834	0.7832	49.5	50.2
6A	0.7829	0.7827	47.6	47.5
6B	0.7829	0.7827	47.5	47.6
7	0.7820	——	44.4	——

In column four are tabulated the vapor pressures of the various liquids, determined by the differential method described in the previous paper. These results have been obtained on the assumption of 59.0 mm. as the vapor pressure of pure ethyl alcohol and are probably reliable to ± 0.5 mm. For purposes of comparison the "ideal" vapor pressures have been calculated by Raoult's law. Throughout the entire range of concentrations the two sets of values, observed and ideal, agree within the limits of experimental error.

Refractive Indices. At this stage of the investigation the two series of solutions, A and B, were combined. The new series of liquids, thus produced, had the compositions indicated in Table IV.

The refractive indices of the various liquids were then determined with a Zeiss-Pulfrich refractometer. These measured values agree remarkably well with those calculated (column 5) on the basis of the assumption of a straight-line relationship between the index of refraction and the composition, by weight, of the solution. Thus this measurement provides an easy and rapid method of analyzing an unknown mixture of these alcohols. As the instrument used could be read with a percision of ± 1 minute and the refractive angles for the two pure alcohols differ by 168 minutes, the accuracy of the method is about 0.6%.

TABLE IV

(Temperature 25° C)

Liquid	% C_2H_5OH by weight	Mol fraction of C_2H_5OH	Refractive Index Observed	Refractive Index Calculated
1	100.00%	1.000	1.3595	———
2	83.61	.869	1.3622	1.3620
3	66.89	.725	1.3646	1.3646
4	49.87	.565	1.3673	1.3673
5	33.60	.393	1.3697	1.3698
6	17.23	.214	1.3721	1.3723
7	0.00	.000	1.3750	———

Vapor Composition at 25° C. The composition of the vapor phase in equilibrium with the solutions at 25° C. was next determined. This was accomplished by passing air (freed from water and carbon dioxide) thru a series of three bubblers, each containing about 20 cc of the mixture under consideration. The air thus saturated with the vapor of a mixture was then passed thru a condensing tube immersed in liquid air; the alcohol separated out as a solid glass on the walls of this tube and, when about 1 cc of distillate had been collected, was analyzed by measurement of its refractive index. Two separate determinations were made on each mixture; the results appear in Table V.

TABLE V

Ethyl Alcohol in the Vapor of the Liquids at 25° C

Liquid	% by weight	Mol Fraction (mean value)
1	100	1.000
2	87.5 and 87.5	.901
3	72.9 " 74.6	.785
4	59.5 " 59.0	.654
5	41.8 " 40.6	.479
6	20.4 " 22.5	.263
7	0	.000

Viscosities. We also determined the viscosities of the various liquids, using an Oswald viscosimeter in a 25° C thermostat, regulated to .01°. The value 0.00893 dynes per sq. cm., as obtained by Hosking[1], was assumed for the water which was used in standardizing the instrument. The time, measured by a stop-watch, averaged around 100 seconds and thus limited the accuracy of these results to ±.00003 dynes per sq. cm.

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[1] Hosking: Proc. Roy. Soc. N. S. Wales, 43, 37 (1909).

TABLE VI

Viscosities at 25° C (in dynes per sq. cm.)

Liquid	Observed values	Calculated (Kendall's equation)	Calculated (Logarithmic equation)
1	.01080	———	———
2	.01182	.01184	.01174
3	.01299	.01306	.01288
4	.01445	.01450	.01426
5	.01607	.01614	.01588
6	.01796	.01806	.01786
7	.02048	———	———

Comparison of the experimental results with the data calculated by Kendall's cube-root equation[1] ($\eta^{1/3} = x_1\eta_1^{1/3} + x_2\eta^{1/3}_2$, where η_1 and η_2 are the viscosities of the pure components and X_1 and X_2 are their respective mol fractions) show the latter to be too high by an average value of 0.4%. On the other hand the logarithmic relationship, $\log \eta = X_1 \log \eta_1 + X_2 \log \eta_2$, gives results which are on the average 0.9% low. Evidently Kendall's equation, while not entirely satisfactory, is the better approximation for ideal solutions of this type.

Summary

Reviewing the results of the various measurements, we find that

(1) A small heat evolution (in all cases less than 13 calories per mol of resulting mixture) takes place on formation of the several solutions.

(2) An extremely small volume shrinkage, on the average only .01%, accompanies the process.

(3) The measured vapor pressures of the resulting liquids agree within the limits of experimental error with the "ideal" values calculated by means of Raoult's law.

(4) The refractive indices of the solutions are practically a straight line function of their weight compositions.

(5) The observed viscosities for the various solutions exhibit on the average a negative deviation of 0.4% from Kendall's cube-root equation.

The only appreciable deviation from the laws of the perfect solution is found in the heat effect on formation of the mixtures and even in this case the departure from the ideal is relatively small. Judging the data as a whole, we are led to the conclusion that the system under discussion is almost "perfect." Furthermore, in view of the fact that a similar situation was found to exist in the case of mixtures of ethyl and n-propyl alcohol, it seems probable that this conclusion will be found valid for all systems involving closely related alcohols.

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October 28, 1924.

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[1] Kendall: J. Am. Chem. Soc. 42, 1776 (1920).

THE THERMAL DECOMPOSITION OF SILVER CARBONATE*

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In the course of our study of the thermal decomposition of carbonates[1], we investigated the *kinetics* of their reactions. We have come to the conclusion that these reactions, which, according to Ostwald[2], are classified as second order heterogeneous reactions, are usually monomolecular with temperature coefficients for ten degrees of about 2. Like the decomposition of silver oxide, observed by G. N. Lewis[3], an *induction period* was observed in several cases. We sought to explain this phenomenon by postulating the formation of an intermediate phase. This hypothesis explained the decrease of velocity of carbonate decomposition when the formulas of successive radioactive decomposition were applied.

The subject matter of this paper deals with a peculiar type of decomposition shown by *amorphous silver carbonate.*

First it should be mentioned that *crystalline* silver carbonate shows a *normal* behaviour on heating. This carbonate is obtained by slow crystallization from a solution of silver bicarbonate which in turn was prepared by passing carbon dioxide through an aqueous suspension of amorphous silver carbonate. Crystalline silver carbonate decomposes above 218°C. directly into silver oxide and carbon dioxide. This decomposition may be formulated exactly by means of the *unimolecular* reaction velocity equation, namely,

$$I = I_0 e^{-kt}$$

where I is the velocity of decomposition at time t, I_0, the *initial* velocity, and k is the velocity *constant.* The ten degree temperature coefficient in the range observed (220°-250° C.) has the value 2.14, a magnitude shown by reactions the velocities of which are independent of diffusion.

Amorphous silver carbonate showed an entirely different behaviour. It was prepared by precipitation, with stirring, of a solution containing 34 g. of silver nitrate in 500 cc. of water with a solution of 20 g. of potassium bicarbonate in liter of water, and drying the thoroughly washed precipitate at 50-60°C.. This substance decomposes far more slowly on heating than does the crystalline modification, and the progress of its decomposition does *not* follow the simple unimolecular equation.

For illustration we quote, from a number of experiments, the data obtained at 245°C. in Table 1. The volumes of carbon dioxide evolved at different time intervals were measured. A large scale curve was constructed from these data, from which the volumes of carbon dioxide evolved at equal time intervals,

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* Contribution from the laboratory of physical chemistry of the University of Latvia.

[1] Acta Universitatis Latviensis **10**, 495, 524; **11**, 271, 289 (1924); **12** in press; Z. physik. Chem. **111**, 79; **114**, 237 (1924).

[2] W. Ostwald: Lehrb. allgem. Chemie, 2 II, 291 (1896-1902).

[3] G. N. Lewis: Z. physik. Chem. **52**, 310 (1905).

were obtained. These latter values are given in column 2. Column 3 contains the specific velocities of decomposition, i.e., cubic centimeters of carbon dioxide evolved per minute from one initial gram of silver carbonate. The fourth column contains the logarithms of the velocities. The data of Table 1 are *mean values* of two concordant determinations.

Figure 1 presents the specific velocity (I) curves taken from the data of Table 1. From this it may be seen that the velocity of decomposition of amorphous silver carbonate rapidly *decreases* at first, then remains constant for a period of approximately forty minutes, and finally decreases in a regular manner asymptotically approaching the zero value. It is evident that the curve of Fig. 1 is analogous to the curves obtained by Curie and Danne for the rate of decay of radiation intensity of plates *exposed for a short period of time* to radium emanation[1]. Consequently, we have assumed that amorphous silver carbonate decomposes with the formation of an *intermediate product*, an oxycarbonate. For the occurrence of such a product, evidence can be found in the literature[2].

TABLE I

Decomposition of *amorphous* Ag_2CO_3 at 245°C.. Weight of $Ag_2CO_3 = 0.8020$ g. Barometric pressure = 760.1 mm. Room temperature = 20°C.

Time in minutes	Volume of CO_2 evolved	Specific Velocity (I)	Log (I. 10^2)
5	5.06	1.194	2.077
10	10.01	1.128	2.052
20	16.38	0.629	1.799
30	20.79	0.509	1.707
40	24.70	0.492	1.692
50	28.67	0.492	1.692
60	32.64	0.492	1.692
70	36.55	0.469	1.671
80	40.32	0.448	1.651
90	43.87	0.397	1.599
100	47.02	0.329	1.517
120	52.07	0.236	1.373
140	55.87	0.179	1.253
160	58.51	0.122	1.086
180	60.38	0.092	0.964
200	61.86	0.076	0.881
220	62.87	0.061	0.785
∞	69.9	—	—

The *first* stage of the decomposition takes place relatively fast, with the reaction constant k_1, the value of which may be obtained from the *initial* slope of the *logarithmic* velocity curve of fig. 1.

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[1] P. Curie and J. Danne: Compt. rend. **136**, 364 (1903); **138**, 683 (1904).

[2] H. Rose: Pogg. Ann. **85**, 314 (1852).

$$k_1 = \frac{2.303\,(\log I_0 - \log I)}{t} = \frac{2.303\,(2.21 - 1.62)}{30} = 0.045\ (\text{min.})^{-1}.$$

The product of decomposition of silver carbonate, namely, the silver *oxycarbonate*, in turn decomposes at a slower rate. For a certain period of time, the reactions counterbalance one another and the rate of evolution of carbon dioxide remains seemingly constant. This behavior is exactly analogous to the temporary radio-active equilibria of the Curie-Danne experiments.

After the lapse of 90 minutes from the beginning of the reaction, the silver carbonate is practically entirely decomposed. The further course of the reaction consists in the decomposition of the silver oxycarbonate into silver oxide and carbon dioxide, which may be formulated by the equation for a unimolecular reaction.

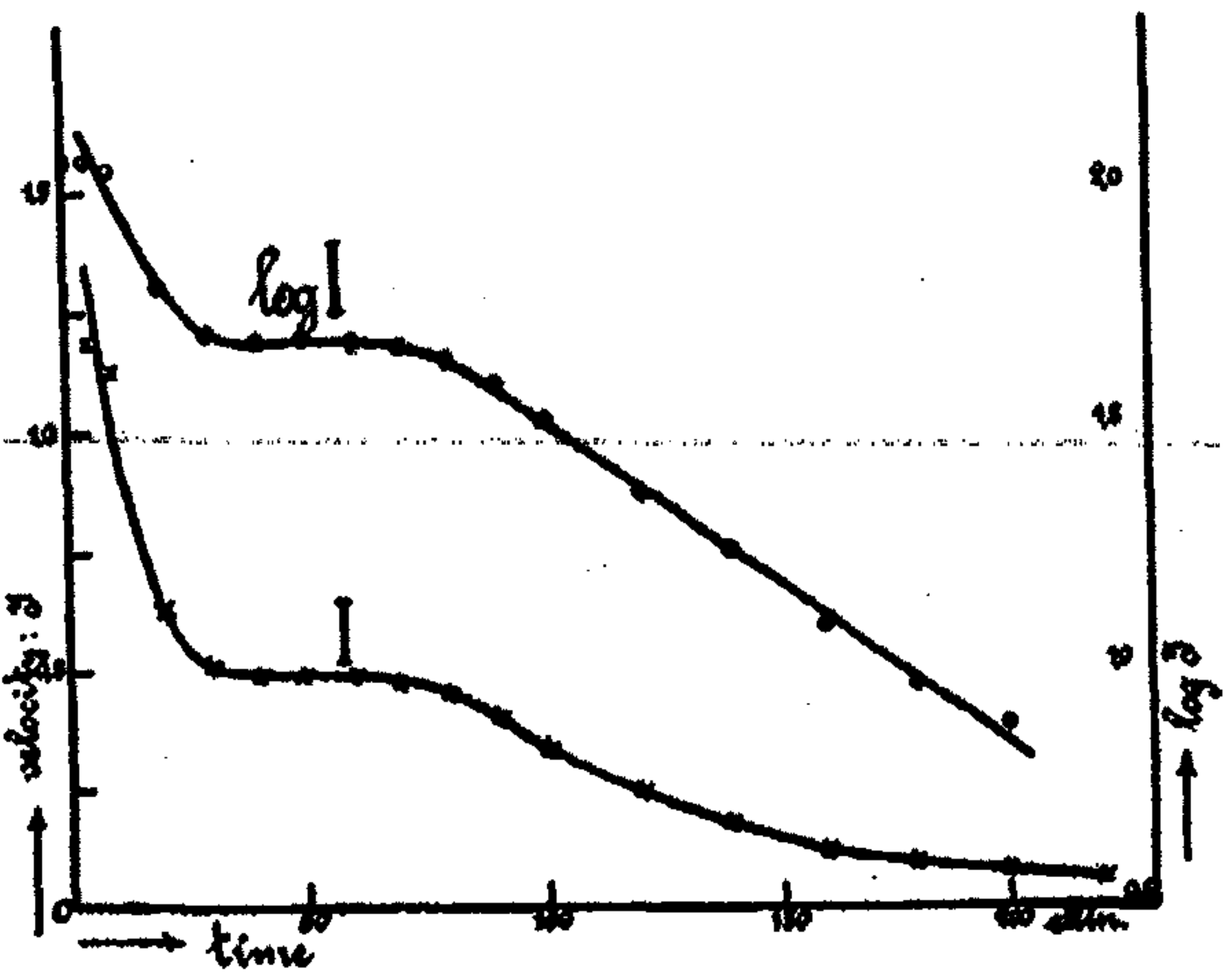

FIG. 1

Decrease of velocity of decomposition of *amorphous* silver carbonate with time.

$$I_t = I_0\, e^{-k_2 t}.$$

This stage of the reaction is characterized by the *linear course* of the logarithmic velocity curve. (Fig. 1) The value of the velocity constant k_2 may likewise be calculated from the slope of this curve.

$$k_2 = \frac{2.303\,(\log I_1 - \log I_2)}{t_2 - t_1} = \frac{2.303\,(1.52 - 0.84)}{100} = 0.016\ (\text{min})^{-1}.$$

We further considered the rate of decomposition of the *half-decomposed* silver carbonate. This was prepared by heating, at constant temperature, amorphous silver carbonate until half of its carbon dioxide had been evolved. The preparation was then cooled and allowed to stand over night. We expected to find that the ultimate decomposition would follow the normal course of a unimolecular reaction, since the silver carbonate had been entirely converted into silver oxycarbonate and silver oxide.

We performed several such experiments at different temperatures. Contrary to our expectation, the course of the decomposition of the latter preparation was analogous to the decomposition of the freshly prepared amorphous silver carbonate. A rapid decrease of the velocity in the beginning was followed by a period of apparent constancy and finally by a slow decrease. The only difference was manifested in a more rapid initial decrease of velocity. This behavior of the *half-decomposed silver carbonate* forces us to conclude that the intermediate product, i.e. silver oxycarbonate, is *unstable*, and decomposes into silver carbonate and silver oxide when the reaction is interrupted. The slight difference in the curves of the freshly prepared and the half decomposed preparations is caused by the incomplete decomposition of the intermediate product.

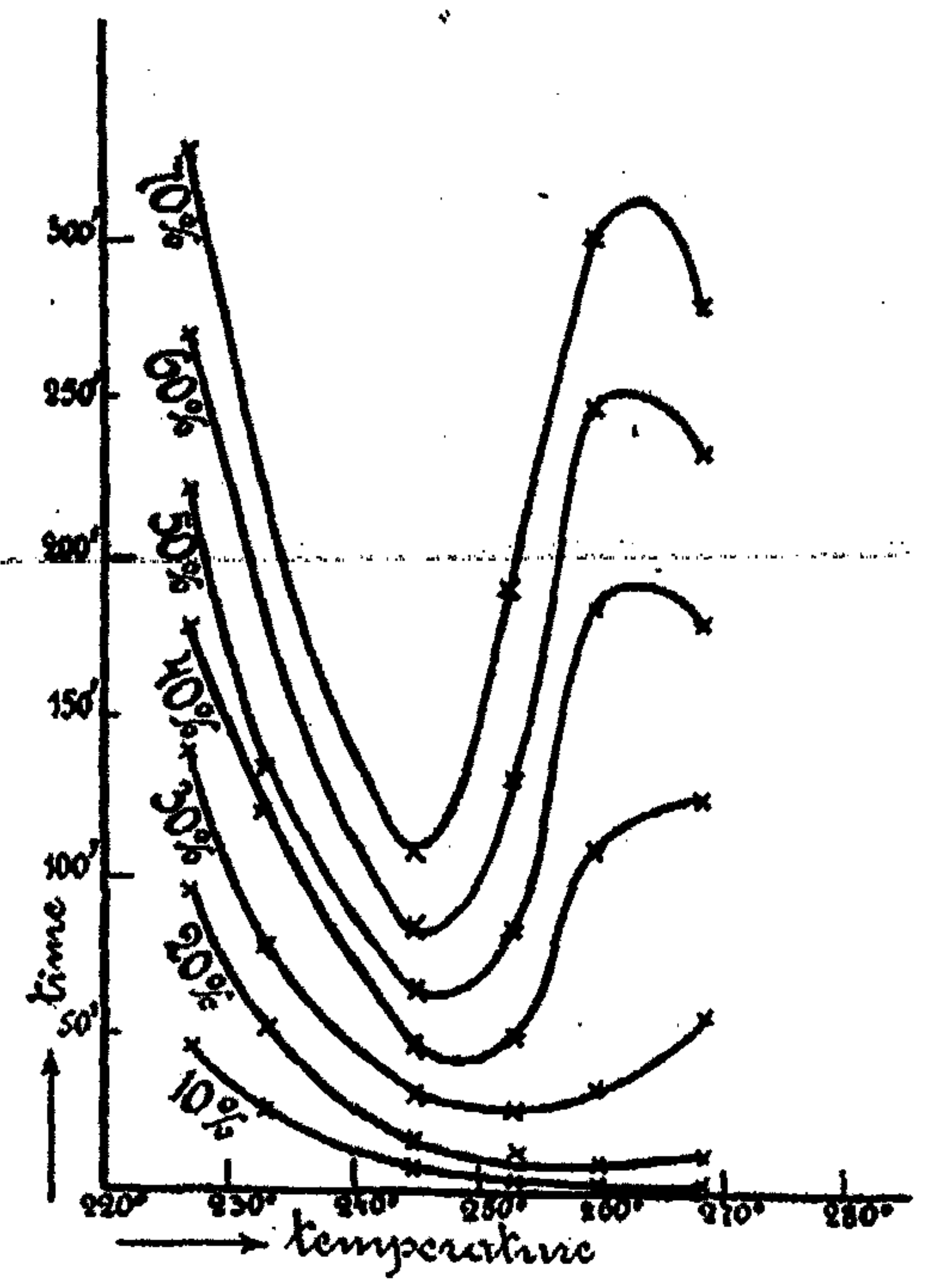

Fig. 2
Graphic presentation of the data of Table II

Interesting results were obtained when we compared the decomposition of amorphous silver carbonate at *different temperatures*. For this purpose, we plotted the *percentage decomposition* against time for different temperatures as recommended by *Zawidzki*[1]. However, it was found that these curves intersected one another. From these curves we read the *intervals of time* necessary for the *same percentage decomposition* at different temperatures; and we plotted the results as *time - temperature* curves. These data[2] are given in Table II and Fig. 2.

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[1] J. v. Zawidzki, Bull. de l'Académie des sciences de Cracovie, 1916A, 349; Roczniki chemii, 3, 18 (1923).

[2] For detailed data see Vol. 12, Acta Universitatis Latviensis (Riga).

Table II

Time required for the decomposition of equal fractions of amorphous silver carbonate at different temperatures.

Temperature	Percentage Decomposition						
	10%	20%	30%	40%	50%	60%	70%
227°C.	47 min.	94 min.	139	178	222	270	328
233	26	53	79	120	135	—	—
245	7	15	30	47	65	85	109
253	4	13	26	49	82	131	193
260	3	8	32	108	185	249	302
268.5	2	12	56	124	180	235	281

It is evident from the diagram that the time intervals required for the decomposition of equal fractions of amorphous silver carbonate *decrease* first with temperature and reach a minimum value of 245°C. In other words at 245°C. *the velocity* of decomposition *is at a maximum*. From 245 to 260°C. the velocity of decomposition decreases with the temperature. Such examples of *negative temperature coefficients* are seldom observed. At temperatures higher than 260°C., the velocity of decomposition increases again.

According to the hypothesis previously developed, the decomposition of amorphous silver carbonate takes place in *two successive stages*. In the first stage of the reaction, an intermediate oxycarbonate is formed, which, in turn, decomposes. This plays the role of a catalyst[1]. We have seen further that this intermediate product is unstable, and decomposes spontaneously into silver oxide and silver carbonate. It is quite probable that the formation of this intermediate product is restricted to certain temperature ranges. If the upper limit of the formation of the intermediate product is at 245°C. then, *above this temperature*, the silver carbonate must decompose *directly* into carbon dioxide and silver oxide. This *direct decomposition*, according to the experimental data, takes place *more slowly* than does the stagewise reaction, as has been observed in similar cases. Thus, it is possible to reconcile the negative temperature coefficient with the hypothesis of the formation of an intermediate compound.

Summary

In investigating the decomposition of amorphous silver carbonate, we found that;

1, at constant temperature, the velocity of decomposition decreases at first, then remains constant for a certain period, and finally decreases *exponentially* with time; and

2, in a certain interval of temperature (245° - 260°C.), the velocity of decomposition decreases with rise of temperature.

These facts are explained by means of the hypothesis of the formation of unstable silver oxycarbonate as an intermediate product.

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[1] Similar ideas for autocatalytic reactions have been deduced mathematically by J. v. Zawidzki: Roczniki chemii, 3, 18 (1923).

STUDIES IN EMULSIONS

BY WILLIAM SEIFRIZ

III. DOUBLE REVERSAL OF OIL EMULSIONS OCCASIONED BY THE SAME ELECTROLYTE

Introductory

Emulsions made from petroleum distillates form, when stabilized with casein, oil-in-water emulsions if the oil is of less than 0.828 specific gravity. If the oil is of a greater specific gravity than 0.857 the emulsions are of the water-in-oil type. If the oil is of intermediate specific gravity (between 0.828 0.857) it either cannot be emulsified at all, or it forms a coarse unstable emulsion.

The oil-in-water emulsions of light petroleum distillates are made more stable and the degree of the dispersion of the oil increased by the addition of NaOH, $Ba(OH)_2$, $Th(NO_3)_4$ and $Al_2(SO_4)_3$. The water-in-oil emulsions of the heavier oils are reversed into the opposite type by the same four electrolytes.

The effects of the above four electrolytes on emulsions of light and of heavy petroleum oils leads one to expect that these electrolytes will promote the emulsification of the unemulsifiable oils, which are of intermediate specific gravity (from 0.828 to 0.857), into oil-in-water systems. This is true in part.

Experimental

When either the hydroxide of Na or Ba is added to an unemulsifiable mixture of aqueous casein and an oil of intermediate specific gravity, the unstable system usually becomes first a water-in-oil emulsion, and then, on the addition of more of the *same* electrolyte, reverses into an oil-in-water emulsion. The following is a specific example of the production of a water-in-oil emulsion from an unemulsifiable petroleum oil, and the reversal of this emulsion into one of the opposite type on the further addition of the same hydroxide.

Double reversal of petroleum oil emulsions.—A mixture of 25 c.c. of a petroleum distillate of 0.834 specific gravity and 25 c.c. of an aqueous casein dispersion cannot be emulsified by repeated shaking. The two phases separate immediately. The addition of 0.03 c.c. of M/5 $Ba(OH)_2$ causes, after shaking, the production of a coarse but moderately stable water-in-oil emulsion, in the large water globules of which are a few scattered oil droplets. These latter are the forerunners of the future oil-in-water emulsions. (Photo. 1). One drop more of M/5 $Ba(OH)_2$ (0.66 c.c. of hydroxide in 50 c.c. of emulsion) leaves the coarse water-in-oil emulsion unchanged but increases the amount of dispersed oil in the water globules (Photo. 2). One c.c. of M/5 $Ba(OH)_2$ reverses the entire emulsion into a stable oil-in-water system. (Photo. 3).

While the above description is the usual effect of $Ba(OH)_2$ and of NaOH on the petroleum distillates which lie in the zone of instability (specific gravity

0.828 to 0.857), some surprising variations of this behavior often occur. Two samples of an unstable mixture of a hydrocarbon oil of 0.828 specific gravity, behaved quite differently, as follows. One sample practically duplicated in behavior the emulsion described above. It gradually became a fine stable water-in-oil system on the addition of 0.2 c.c. of M/5 NaOH. Further addition of NaOH coarsened the water-in-oil emulsion until at a concentration of 5 c.c. of M/5 NaOH the two phases separated. One more c.c. of hydroxide produced a fine stable oil-in-water emulsion. A second sample of this same originally unstable mixture became immediately a fine and stable oil-in-water

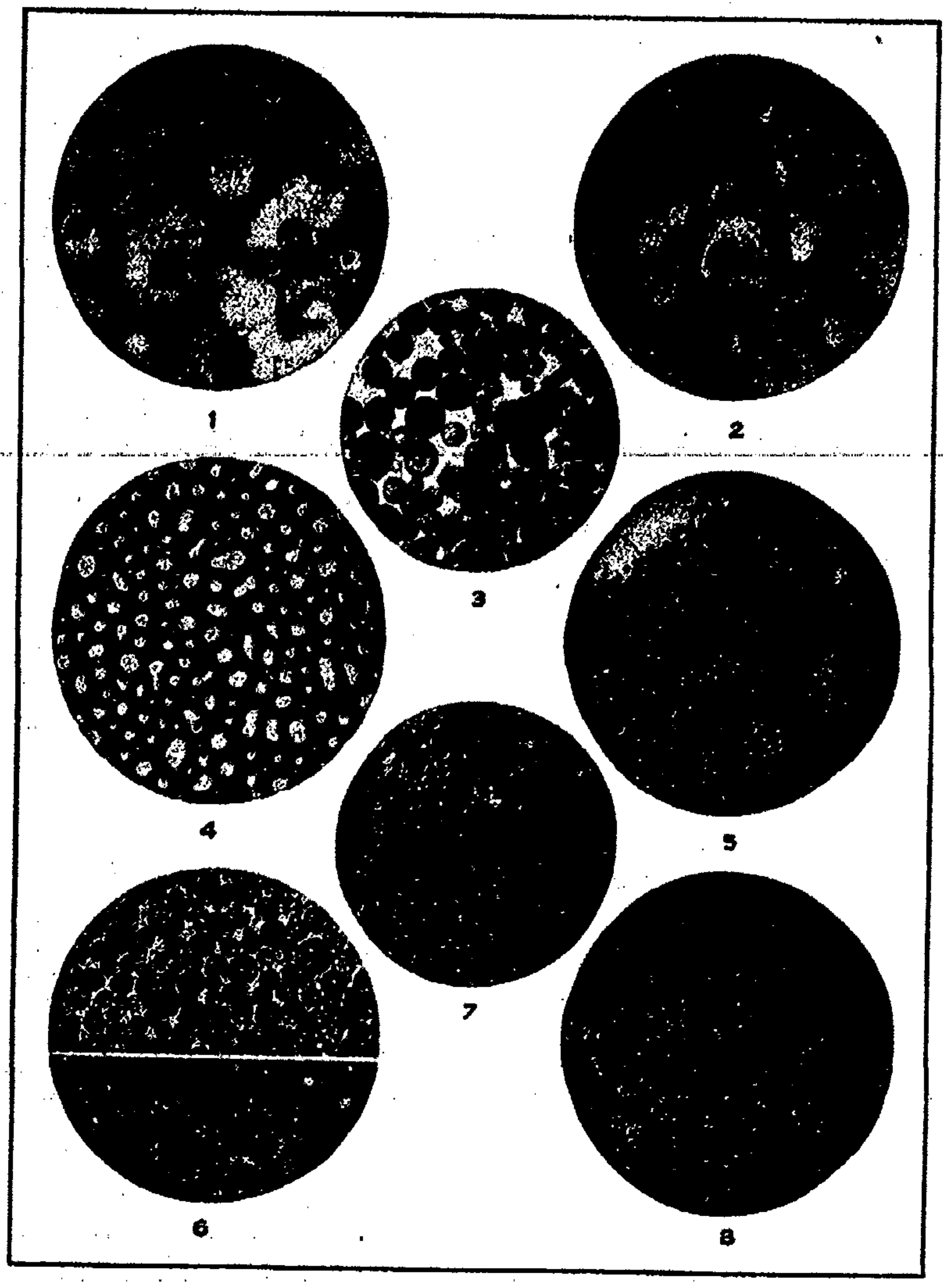

PLATE I

emulsion on the addition of $Ba(OH)_2$, thus omitting altogether the preliminary water-in-oil stage through which its sister sample went.

Still another unstable emulsion of a petroleum distillate of 0.852 specific gravity passed through the preliminary stages of establishing a water-in-oil emulsion but instead of this emulsion subsequently reversing into an oil-in-water one at a moderate concentration of hydroxide, it became so thoroughly established that at 25 c.c. of M/5 $Ba(OH)_2$ the system was still a fine water-in-oil one with no indication of reversal into the opposite type. (Photo. 4). Ten more c.c. (total 35 c.c.) of hydroxide reversed the system into a fine stable oil-in-water emulsion. The firm establishing of this water-in-oil emulsion is possibly in part accounted for by the fact that the oil (specific gravity 0.852), though within the unemulsifiable zone of instability, is very near the upper limit of the zone (specific gravity 0.857) at which point petroleum oils form stable water-in-oil emulsions without the addition of any electrolyte. The first oil discussed (specific gravity 0.834) which became at the outset a water-in-oil emulsion and later reversed with a low (1 c.c.) concentration of hydroxide, is near the other end of the unstable zone below which point (specific gravity (0.828) the petroleum distillations form stable oil-in-water emulsions without the addition of an electrolyte.

These double reversals of petroleum oil emulsions with the same electrolyte take place only on the addition of a hydroxide, and more frequently with $Ba(OH)_2$ than NaOH; and only with petroleum distillates which lie in the zone of instability.

Double reversal of olive oil emulsions.—Double reversal on the addition of the same electrolyte was first observed in the case of olive oil stabilized with gelatose[1]. Such an emulsion is originally a fine and very stable one of the oil-in-water type. It cannot be reversed with $BaCl_2$ or $CaCl_2$ both of which reverse numerous other oil-in-water emulsions, but is reversed by either the hydroxide of Ba or the hydroxide of Na. It is the only one of eleven kinds of olive oil emulsions studied, each stabilized with one of eleven different organic substances, which can be reversed in the same direction with a monovalent *or* a bivalent electrolyte, but the electrolyte must be a hydroxide. This is an exception for olive oil emulsions. In addition, there is the remarkable double reversal. The following is a brief account of the behavior of this emulsion.

On the addition of either Na or Ba hydroxide to a gelatose-stabilized, olive oil emulsion which is of the oil-in-water type, the system partially reverses into a water-in-oil emulsion which ramifies among the remaining original oil-in-water emulsion. Complete reversal into a water-in-oil emulsion cannot be obtained. The adding of more hydroxide, instead of reversing the remainder of the original oil-in-water emulsion, now again reverses that which has already been reversed. The water-in-oil part of the system is reversed back into the original oil-in-water type.

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[1] W. Seifriz: Am. J. Physiol. **66**, 124 (1923).

This behavior is illustrated by photographs 5 to 10. The history of this particular olive oil emulsion is as follows. The olive oil is emulsified with 10% gelatose and forms a very fine and stable oil-in-water emulsion. (Photo. 5). One half c.c. of M/5 $Ba(OH)_2$ increases the dispersity of the oil. There is no further change until 3 c.c. of the hydroxide is added, when the emulsion becomes more coarse and the larger oil globules have now become small water-in-oil systems. (Photo 6a and b). Four c.c. of hydroxide brings about the formation of an almost complete reversal into a fine stable water-in-oil emulsion, the dispersed water droplets of which harbor numerous small oil globules.

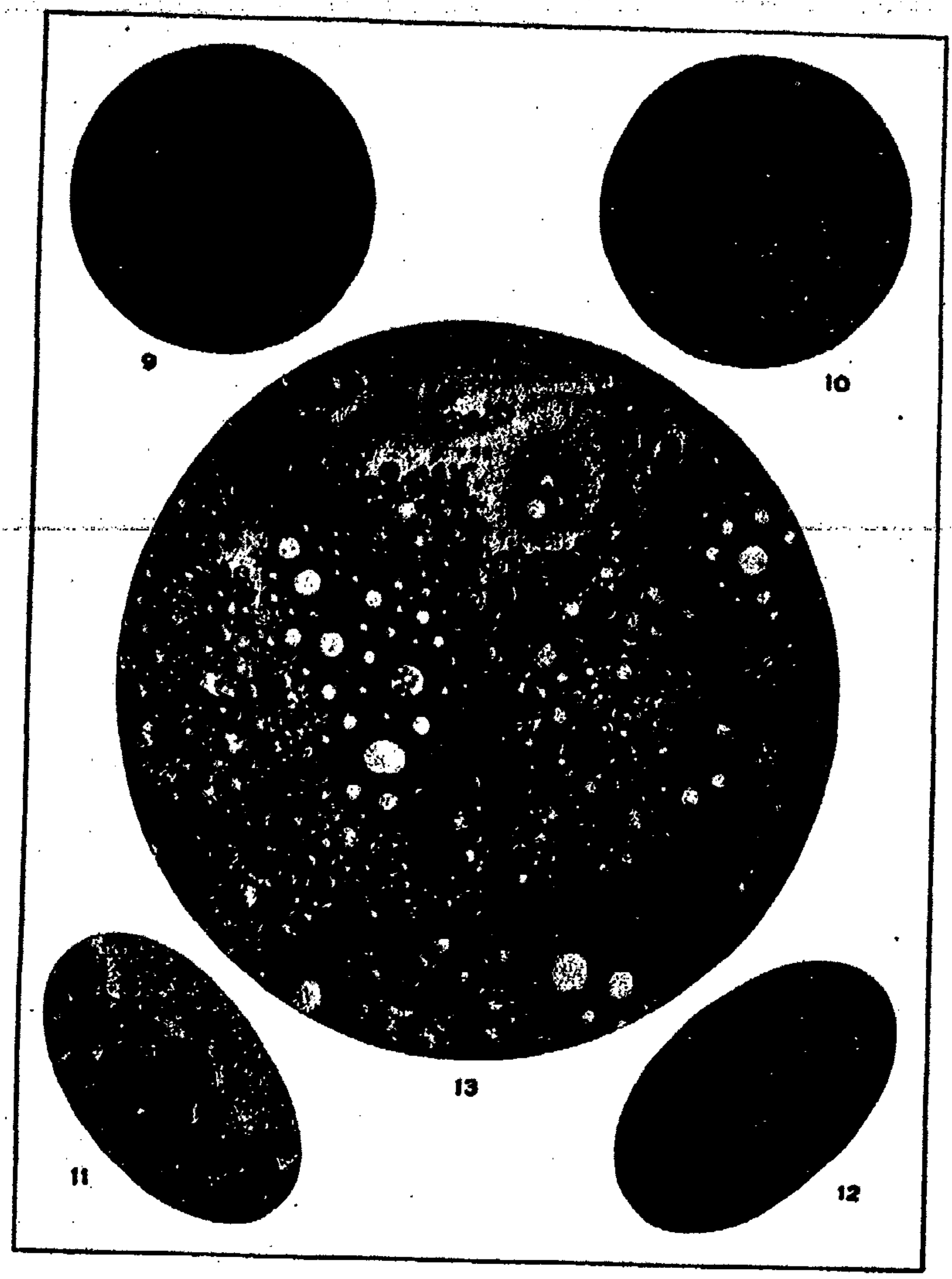

Plate II

(Photo. 7). The reversal is, however, not complete as some oil-in-water emulsion is still present, ramifying among the water-in-oil system. (Photo. 8). Nor does more hydroxide complete the reversal. Five c.c. of M/5 $Ba(OH)_2$ starts the reversal back to the original oil-in-water state. The system may now be as in photograph 9, where both types of emulsion ramify among each other, with the "oil" globules of the one containing dispersed water, and the "water" droplets of the other containing dispersed oil; or the system may consist of a conglomerate of large and small oil droplets scattered in the aqueous matrix, with most of the "oil" droplets being themselves smaller water-in-oil emulsions. (Photo. 10).

After 3 hours this double emulsion still exists as such. Neither time nor reshaking changes the dual nature of the system.

Two more c.c. of hydroxide, 7 in all, causes complete reversal of the system back into the original fine stable oil-in-water emulsion. (Photo. 5).

An interesting exception to the above behavior of a gelatose-stabilized olive oil emulsion to which an hydroxide has been added, is that illustrated in photograph 11 where the two types of emulsions in the same system are so firmly established that the system as a whole cannot be thrown one way or the other, even with so high a concentration as 50 c.c. of M/5 $Ba(OH)_2$ added to 50 c.c. of emulsion. The system consists of a moderately coarse but stable oil-in-water emulsion, the oil globules of which are tightly pressed against the oil matrix of a fine water-in-oil emulsion, without any fusion of the oil phases or the water phases of the two emulsions.

Agar agar as stabilizer.—Some few test experiments with ungelatinizable agar agar (5%, boiled 12 hours) as the stabilizing agent in olive oil emulsions, revealed the following differences from the behavior of gelatose-stabilized emulsions.

Agar-stabilized olive oil emulsions are fine stable oil-in-water systems which are readily reversed into fine water-in-oil emulsions by either NaOH or $Ba(OH)_2$. The inversion is complete, which is not true of gelatose-stabilized olive oil emulsions. These reversed agar-stabilized water-in-oil emulsions are readily brought back to their original type by NaOH, but not by $Ba(OH)_2$. Here again the agar-stabilized olive oil emulsions differ from the gelatose-stabilized ones, since the latter are re-reversed by the hydroxide of either Na or Ba.

Photograph 12 shows the condition of an agar-stabilized emulsion when just passing from the reversed water-in-oil state back to the original oil-in-water condition. The "oil" drops of the future fine oil-in-water emulsion, are still very coarse and are themselves water-in-oil systems. Some areas of the former water-in-oil emulsion are still present.

The stabilization membrane.—The writer wishes to call attention to the fact (which will be more fully discussed in Part V of these studies) that in these gelatose-stabilized, olive oil emulsions, and casein-stabilized, petroleum oil emulsions (oil of medium specific gravity), which exhibit double reversal with $Ba(OH)_2$, we are not always dealing with monomolecular surface tension interfacial films, but with actual morphological membranes, which are of the nature of precipitation membranes, although not irreversible coagula. That this is true will be quite evident when these stabilization membranes are discussed in detail, but the fact is also clear from several behavior phenomena already considered. The formation of large top-shaped drops of a casein solution falling through kerosene from a Traube stalagmometer (text fig. 2 Part II these studies) is one instance in point. Also, in photographs 1 and 2 it will be noticed that the large water drops are of irregular form, some containing small attached "buds," and others joined to one another by minute canals, a condition which could not be maintained were the interfaces purely surface tension films. When these emulsions, on the addition of more hydroxide, finally reverse to fine stable oil-in-water systems, the oil droplets are spherical, surrounded by optically invisible, labile, surface membranes, which are probably still not true tension films in the sense of being one or two molecules in thickness.

The stabilization membrane of emulsions is by no means always a monomolecular film.

Conclusion

In further emphasis of the conclusion stated in Part II of these studies, that the behavior of emulsions in the presence of electrolytes is dependent upon three prime factors, the oil, the stabilizer, and the electrolyte, and to alter any one of these may mean a change in the behavior of the emulsion, let it here be added that the very similar behavior (of double reversal) in the emulsions of olive oil and petroleum oils on the addition of NaOH or $Ba(OH)_2$, is restricted in the case of olive oil to emulsions stabilized with *gelatose*, while in the case of petroleum oils it takes place in emulsions stabilized with *casein*. *Olive oil* emulsions stabilized with *casein* do not show this phenomenon, but behave like other reversible olive oil emulsions, that is, they are reversed directly into oil-in-water emulsions by NaOH, and then, on the addition of $Ba(OH)_2$ or $BaCl_2$ back into water-in-oil emulsions.

Double reversal with the same electrolyte is the rule for olive oil emulsions stabilized with gelatose and treated with Na or Ba hydroxide. It is not occasioned on the addition of NaCl or $BaCl_2$. It is quite evident, therefore, that the hydroxyl ion must be primarily responsible.

Double reversal by the same electrolyte is also the usual thing in unstable petroleum oil emulsions from distillates of medium specific gravity which are in the zone of instability, and is here likewise occasioned by the hydroxides of Na and Ba but also by $Th(NO_3)_4$, though not by $BaCl_2$ or NaCl. The fact that $Th(NO_3)_4$ stabilizes an unstable mixture of petroleum oil and aqueous casein into a water-in-oil emulsion and then reverses it into an oil-in-water emulsion, as do NaOH and $Ba(OH)_2$, is in line with the similarity of the effects of these three electrolytes on petroleum emulsions in general. It also precludes ascribing to the hydroxyl ion alone the responsibility of double reversal in petroleum oil emulsions.

IV. MULTIPLE SYSTEMS

Readily reversible petroleum emulsions frequently consist of more than one type of system. Where two types are present in the same general emulsion the double nature may be of two main sorts: the two types of systems may exist side by side or one within the other. Both of these states are illustrated in photograph 13.

To the right and left in photograph 13 are large areas of oil-in-water emulsions. Between these (left center) is a water-in-oil emulsion with other scattered patches of the same at the right top and bottom. Such a double emulsion may be arbitrarily termed a dual system. It is again illustrated in photograph 27.

The matrixes of the two systems in these dual emulsions may be separated by an interfacial film as in photographs 8 and 9, or such a membrane may be apparently entirely lacking as in photographs 13 and 27.

Many of the "oil" drops of the oil-in-water emulsion shown in photograph 13 contain droplets of water, and are, therefore, themselves water-in-oil systems. So also do several of the "water" drops of the primary water-in-oil emulsion contain tiny oil globules, as is especially noticeable slightly to the left of the center of photograph 13. The large "water" drops are, therefore, themselves oil-in-water systems. This is best illustrated in photograph 16. Such types of double emulsions, where one emulsion is within the other, may be called bimultiple systems. The term is convenient since these multiple systems may be still more complex, becoming trimultiple, quatremultiple, and even quinquemultiple.

Other bimultiple emulsions of the oil-in-water in water-in-oil type are shown in photographs 2, 7 and 24, and of the opposite bimultiple type in photographs 6, 10 and 15.

An emulsion which has been reversed from the water-in-oil state to that of oil-in-water, frequently contains trimultiple systems, where the "oil" drops of the primary emulsion contain a single large water globule which in turn harbors one or more oil droplets (Photos. 3, 13, and 14). We have here, first, the preliminary oil-in-water emulsion; second, the secondary water-in-oil emulsion (with the single water globule having often but a thin membrane of oil as its matrix); and third, a tertiary oil-in-water emulsion. Not infrequently quatremultiple emulsion systems occur. The inner oil droplets of the trimultiple system are again water-in-oil emulsions, as is the case in the lower left center of photograph 15.

The most remarkable instance of multiple emulsions is that illustrated in photograph 17 where three oil and two water droplets alternate one within the other. The primary emulsion here is oil-in-water. One large oil globule of this emulsion contains an almost equally large water globule. This, in turn, contains a smaller oil drop, the core of which is a water globule which harbors the last of the series, a small oil droplet. The system contains five emulsions, —OW, WO, OW, WO, and OW. It is, therefore, a quinquemultiple emulsion system.

The most striking feature of these multiple emulsion systems is that they often persist indefinitely. Neither standing (for three hours) nor repeated reshaking robs them of their multiple nature.

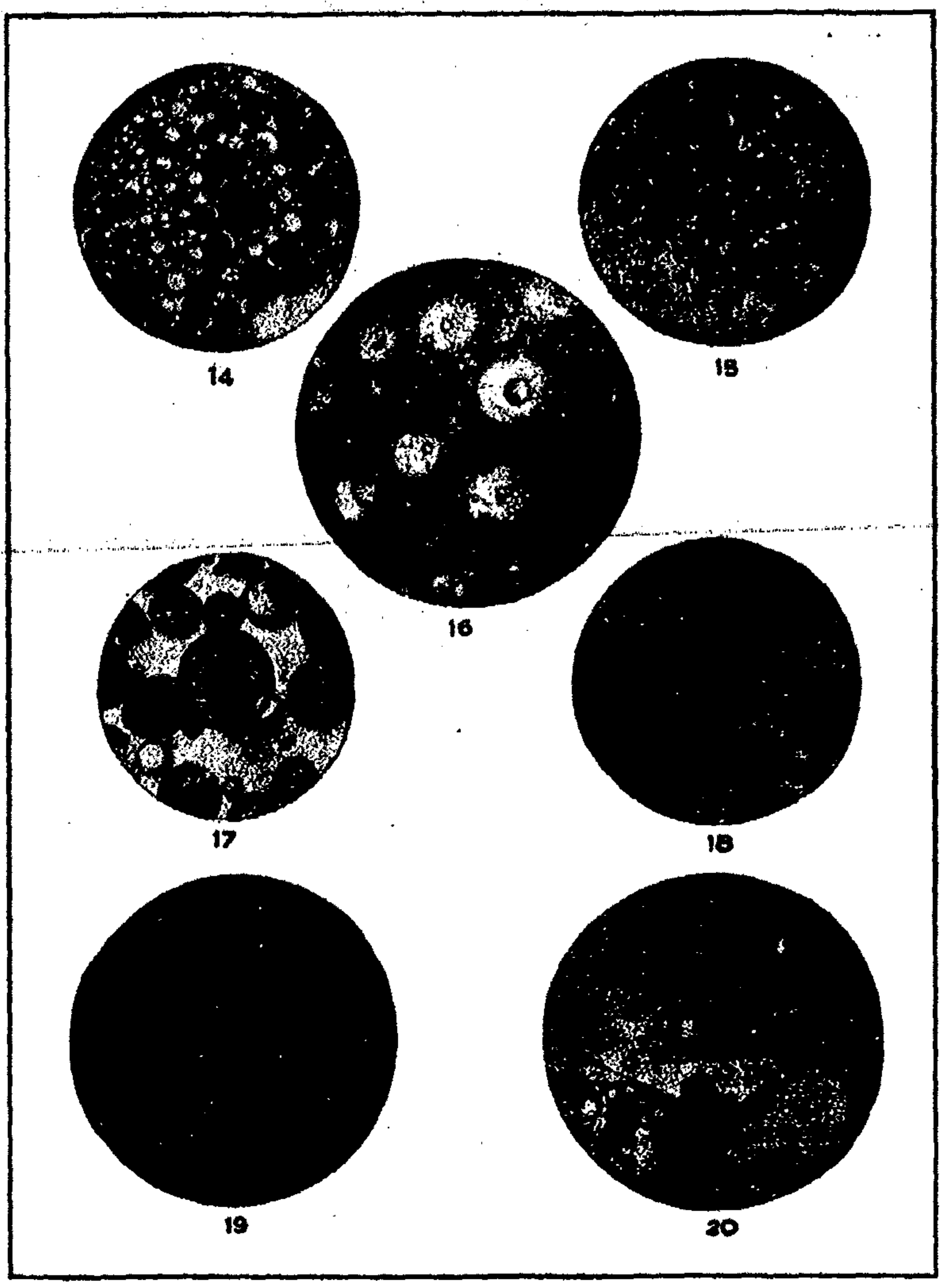

PLATE III

In the light of present day theories of emulsification one is forced to conclude, what research so far tends to support, that multiple emulsion systems of any stability are obtainable only when one or the other of the two liquids is chemically impure, or alternatively, when the stabilizer is not the same throughout the system. We are apparently forced to grant that the stabilizer is not the same substance when stabilizing water-in-oil as when stabilizing oil-in-water.

Brownian movement of emulsion particles.—The maximum size at which suspended particles will exhibit the characteristic perpetual zigzag motion known as Brownian movement, was early established by Wiener[1] as 3 to 5μ.

The minute oil droplets of a fine water-in-oil emulsion often exhibit active Brownian movement. In bi- or trimultiple systems the water globules of the primary (Photos. 13, 16) or of the secondary (Photo. 15) water-in-oil emulsions are themselves emulsions of the oil-in-water type. The smallest of the oil droplets harbored by these water globules are frequently in Brownian movement.

In a gelatose stabilized, olive oil emulsion the minimum sized oil particles of 1/2μ are in active Brownian movement. Particles of 3μ are of the maximum size at which Brownian movement takes place. The motion of the 3μ particles is very sluggish.

V. The Stabilization Membrane

Introductory

Emulsions of pure oil and water are unstable except where the oil phase is very dilute (1 : 1,000) and highly dispersed. In order to maintain a stable emulsion of oil and water in any thing like equal parts of each phase, a third stabilizing substance is necessary. This third substance acts as an emulsifying agent by establishing itself in the form of a membrane around each dispersed globule. The efficacy of emulsifying substances such as soap, gelatine, gums, casein, saponin, etc., and the types of emulsion which they form, has been extensively studied, but the manner in which the stabilizers function is still a matter of speculation. That emulsifiers form interfacial membranes is generally agreed, but the nature of the membrane is unknown. Hypotheses purporting to explain the mechanism of emulsion behavior have been based on the assumption that the stabilization membrane is, in thickness, of the order of magnitude of the thickness of surface tension membranes, namely, one to several molecules.

The interfacial film between dispersed phase and dispersion medium is believed by Bancroft[2]—who advanced the first definite theory of the relation between emulsion type and stabilization agent—to be a film of two surface tensions, one on the water side and one on the oil side. Such a membrane would of necessity be at least several molecules thick. Other workers[3] have also regarded the stabilization membrane as multimolecular in thickness. Langmuir[4], Hildebrand[5], and Harkins[6] have regarded the interfacial film of emulsions as a single layer of oriented wedge-shaped molecules.

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[1] Pogg. Ann. 118, 79 (1863).
[2] J. Phys. Chem. 7, 501 (1913).
[3] Freundlich: "Kapillarchemie," 419 (1922).
[4] Chem. and Met. Eng. 15, 468 (1916).
[5] J. Am. Chem. Soc. 45, 2780 (1923).
[6] Science, 39, 463 (1924).

It is possible that in many instances the stabilization membrane of emulsions is of the order of molecular dimensions. It is equally true, however, that in many, if not most oil emulsions to which an organic substance has been added as a stabilizing agent, the membranes surrounding the dispersed liquid particles are definite, morphological, at times microscopically visible, structures.

Ramsden[1] has demonstrated that an actual solid membrane forms around the globules of some persistent emulsions. He worked with pure neutral olive oil and saponin solutions.

Wilson[2] has observed the same irregular shape of oil droplets described by the writer and pictured in Fig. 2, Part II, which he (Wilson) believes to be due to "plastic solid films" which "are of colloidal rather than of molecular dimensions."

In fine, stable oil-in-water or water-in-oil emulsions of the kind above enumerated, the interfacial film is not at first visible as a distinct, morphological structure, but on the addition of sufficient hydroxide the film begins to stiffen and wrinkle, finally becoming plainly visible as a definite structure. The membranes are then seen as delicate but stiff veils, often, on the collapse of the dispersed globules which they enclose, separating off in great quantity, like so much crumpled tin-foil. Photographs 19 and 20 illustrate such entangled masses of these membranes left after the collapse of the oil drops or of the large oil masses which they surround. In photograph 18 is to be seen the empty remaining shell of a previously existing oil drop. Photograph 21 shows the long funnel-shaped membrane of a former large oil globule. Out of the funnel (at the left) the oil contents of the membranous bag is being discharged. Photograph 22 shows two large funnels discharging their contents and connected by a continuation of the membranes which surround each discharging mass.

These membranes may be formed by precipitation or coagulation, but the process is reversible, if it does not progress too far. The membranes are first liquid and labile, and optically indistinguishable. Later, on the addition of sufficient hydroxide, they stiffen somewhat, though still pliable: such a state exists in the membranes surrounding the water globules in the coarse water-in-oil emulsion pictured in photographs 1 and 2. The semi-solid, coherent nature of these membranes is evident from the irregular shape of the globules and from the small channels of communication which join some of the drops. The membrane is of the nature of a plastic jelly at this stage.

When an emulsion, such as is pictured in photographs 1 and 2, reverses into a fine oil-in-water system, the partially stiffened membranes surrounding the water drops disappear, and the small oil droplets of the subsequent oil-in-water emulsion become perfect spheres, indicating the presence of facile, liquid, membranes comparable to surface tension films. It is unlikely, however, that the membranes are monomolecular.

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[1] Proc. Roy. Soc. 72, 156 (1903).

[2] Am. Colloid Symposium Monographs, 1923.

The redissolving or reversal of the process of partial coagulation can be nicely observed when the concentration of hydroxide is just right and the process of precipitation or coagulation has not gone too far. A mid-point in the gradual redissolving of the empty membrane of a collapsed oil drop is shown in photograph 23 (center).

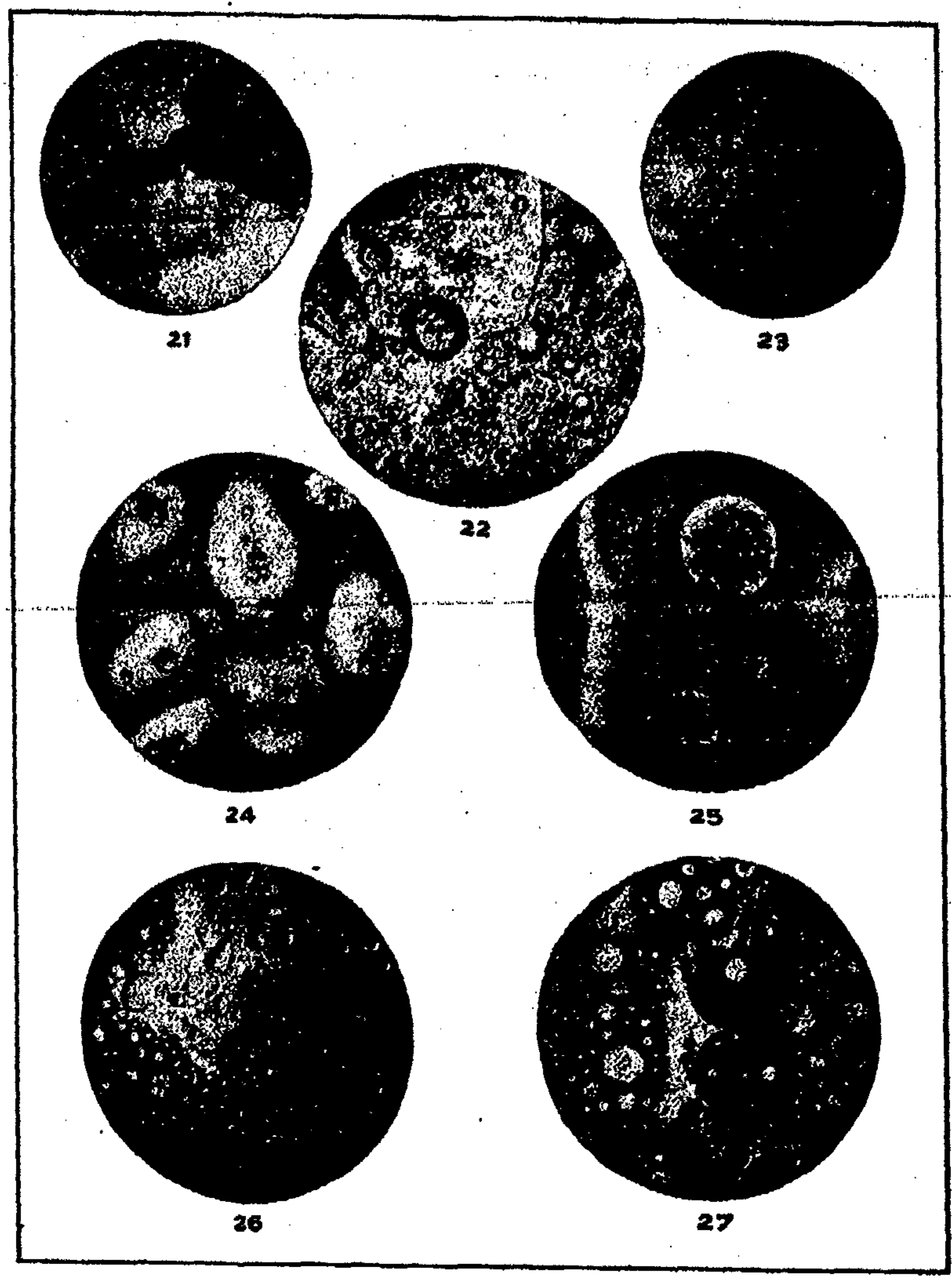

PLATE IV

The degree of visibility of the interfacial film between the two phases of an oil and water emulsion run the whole length of possibility, from the definite microscopically visible structure just described, through the usual surface tension membrane "visible" only because of refraction, to those interesting cases where the oil and water are apparently miscible.

When an emulsion is passing through the transition period in reversing from one type to the other, the interfacial tension is, as one would expect, reduced to a minimum. Theoretically there should be a point at which the surface tension between oil and water is zero. The beginning of the transition period of an emulsion which is passing from the water-in-oil to the oil-in-water state is shown in photograph 24, where the interfacial tension between the large water drops of the now very coarse water-in-oil emulsion is low: at one point the water shows no tendency to round up.

In photograph 25 the condition is still further advanced with little of the water-in-oil emulsion left and larger surfaces of contact where no evident tension exists between water and oil matrixes.

In photograph 26 the tension between oil and water is reduced to a very low point over a great area. This process is carried one step further in photograph 27 where, optically, there appears to be complete absence of any interfacial tension between oil and water. The oil matrix (dark in color) of the water-in-oil emulsion imperceptibly merges into the water matrix (while in color) of the oil-in-water emulsion. This is again illustrated in photograph 13.

450

TITANOUS CHLORIDE AND NITRIC ACID

BY M. COBLENS AND J. K. BERNSTEIN

Milligan[1] showed that, when the temperature is kept down, stannous chloride reduces nitric acid to hydroxylamine with over 90% of the theoretical yield. Ferrous sulphate, a weaker reducing agent, and titanous chloride, a stronger reducing agent, give nitric oxide only, showing that some disturbing reaction takes place. At the suggestion of Professor Bancroft, we have repeated and amplified a small portion of Milligan's work.

Stannous chloride was prepared and standardized at first by heating 35 cc concentrated hydrochloric acid with twenty grams of tin, and letting the mixture stand over night, the excess tin then being filtered off. The solution of stannous chloride was diluted and divided into two parts. To one portion an excess of iodine (15 grams) dissolved in potassium iodide was added. At first a red precipitate of stannous iodide forms but this soon disappears. The excess of iodine was then titrated with a sodium thiosulphate solution whose titer was known in terms of iodine. It is not necessary to add starch as an indicator as the solution becomes colorless at the end-point, except for a white precipitate, presumably stannic oxide. To the other portion nitric acid was added and, after the reaction was complete, the hydroxylamine was reduced to ammonia with titanous chloride. The excess titanous chloride was destroyed with copper sulphate, twenty grams of caustic soda were added and the ammonia was distilled into 25 cc of approximately normal sulphuric acid by the Kjeldahl process, using a Chamot tube and a spiral condenser. To be certain that no ammonia remained in the distilling flask, some sodium sulphide was added towards the end and the distillation continued for a while after that. The excess sulphuric acid was determined by back-titration with a standard caustic soda solution.

Making up small lots of stannous chloride was not very satisfactory, so we prepared a liter at a time, keeping it in an atmosphere of nitrogen. Under these conditions it remained standardized indefinitely. After we had become familiar with the manipulations we had no difficulty in getting 90-99% yields of hydroxylamine.

We next determined qualitatively the effect of adding a ferrous sulphate solution to the stannous chloride solution, varying the amount added from one drop up to an equal volume. Even the addition of one drop of the ferrous sulphate solution caused the evolution of nitric oxide, showing that the ferrous salt accelerates the decomposition of one of the intermediate reduction products into nitric oxide.

Though titanous chloride will reduce hydroxylamine quantitatively to ammonia, Milligan found, as has been stated, that it reduced nitric acid only to nitric oxide. The disturbing factor is not the oxidation product of titanous

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[1] J. Phys. Chem. 28, 744 (1924).

chloride. Milligan showed that if an excess of nitric acid is added to a titanous chloride solution and if the resulting solution is then allowed to react with a stannous chloride solution, the excess nitric acid is reduced to hydroxylamine by the stannous chloride. The disturbing factor is therefore the titanous chloride.

On the assumption that nitrous acid was the intermediate reduction product which gave rise to the nitric oxide, a sodium nitrite solution was added drop by drop to an acid solution of titanous chloride. Nitric oxide was given off at once and no ammonia was formed. In order to prove that the evolution of nitric oxide was due to the titanous chloride and not to a reaction between the sodium nitrite and the acid, a sodium nitrite solution was added drop by drop to an acid solution of stannous chloride. Reduction to hydroxylamine took place, as was proved by subsequent addition of titanous chloride and analysis for the resulting ammonia.

Nitric acid was next allowed to react with an excess of titanous chloride in a closed vessel, shaking continually so as to bring about intimate contact between the excess titanous chloride and the evolved nitric oxide. Reduction to ammonia occurred, showing that the reason we do not get ammonia with nitric acid and titanous chloride under ordinary conditions is that the gas escapes from the solution before it can be reduced.

It seemed desirable to find out whether the catalytic decomposition by titanous chloride was confined to the nitrous acid stage and whether titanous chloride would reduce hyponitrous acid to ammonia. Silver hyponitrite was prepared by the sodium amalgam method, which consists in treating sodium amalgam with potassium nitrate at low temperature and precipitation of the hyponitrite by means of silver nitrate. Our first attempt was a failure, the precipitate being black. We concluded that this was due to the oxidation of the hyponitrite by air. Working in a vacuum seemed to be rather a nuisance and we found that satisfactory results could be obtained by covering the solution with a layer of coal oil which was inert to sodium. This of course doe not keep out the air entirely; but it decreases enormously the rate at which air is taken up by the solution.

The following method of preparation was found satisfactory. About three grams of sodium were dissolved in 100–110 grams of mercury. The pasty amalgam was added a little at a time to 100 cc potassium nitrate solution, the molecular ratio of potassium to sodium being about one to four. The beaker was kept in an ice-bath. When the evolution of gas ceased, the solution was neutralized with acetic acid and silver nitrate was added in slight excess. After the precipitate had settled, the supernatant liquid was decanted, the precipitate dissolved in dilute nitric acid, and reprecipitated with sodium carbonate. The coal oil was then drawn off from the top and the mercury from the bottom. The solution was filtered and the precipitate was washed thoroughly with cold water. The precipitate was transferred to a watch-glass and dried in a vacuum desiccator over sulphuric acid. From the time the silver is introduced, the work is done in the dark. The precipitate thus obtained is a beautiful yellow and the process can be carried through to the drying stage in about two and a half hours.

When silver hyponitrite was added slowly to an acid titanous chloride solution, nitrous oxide was evolved. This is due to a specific action of titanous chloride, because we obtained ammonia when silver hyponitrite was added slowly to an acid stannous chloride solution and the resulting hydroxylamine was reduced with titanous chloride.

In order to determine whether titanous chloride will reduce nitrous oxide, we generated this gas by the interaction of sodium nitrite and hydroxylamine sulphate and shook it in a closed vessel with an excess of a titanous chloride solution. In these runs the yield of ammonia was 91.2, 86.6, and 84.2%. Titanous chloride therefore reduces nitrous oxide pretty completely to ammonia.

A few preliminary experiments showed that the reaction between nitric acid and an excess of sodium hydrosulphite gives ammonia as one of the reduction products; but the end of the term prevented our getting quantitative results.

The general results of this paper are:—

1. One drop of ferrous sulphate solution in a stannous chloride solution causes the evolution of nitric oxide when nitric acid is added.

2. Titanous chloride reduces nitric oxide and nitrous oxide to ammonia.

3. Nitric oxide is evolved and no ammonia is formed when a sodium nitrite solution is added drop by drop to an acid titanous chloride solution

4. Nitrous oxide is evolved and no ammonia is formed when silver hyponitrite is added slowly to an acid titanous chloride solution.

5. Titanous chloride has a specific decomposing effect on nitrous and hyponitrous acids. The gases escape before any appreciable reduction can take place.

6. Hydroxylamine is formed when a sodium nitrite solution is added drop by drop to an acid stannous chloride solution.

7. Hydroxylamine is formed when silver hyponitrite is added slowly to an acid stannous chloride solution.

8. Ammonia has been shown qualitatively to be one of the reduction products when nitric acid reacts with an excess of sodium hydrosulphite; but no quantitative measurements were made.

Cornell University
June, 1924.

NEW BOOKS

Chemical Dynamics of Life Phenomena. *By Otto Meyerhof. 21×14 cm; pp. 110. Philadelphia: J. B. Lippincott Company, 1924. Price: $3.00.* This volume is based on five lectures delivered at Cambridge University in 1922. "The title for the volume of lectures was chosen to express the deep gratitude which I owe to the late Dr. Jacques Loeb, who, by his book on "The Dynamics of Living Matter," gave the decisive stimulus for a new awakening of cellular physiology, from which resulted the most fertile connections of our science with physical chemistry."

The chapters are entitled: on the physicochemical mechanism of cell respiration; autoxidations in the cell; chemical relations between respiration and fermentation; the transformation of energy into muscle; the energetics of cell processes.

The effect of narcotics on respiration is unquestionably due to adsorption by the solid structural elements of the cells, p. 15; but there is no necessary connection with the lowering of the surface tension of water because the urethanes lower the surface tension of water considerably less than to the degree corresponding to their narcotic activity. It is the actual power of adsorption on boundary surfaces which counts.

Alcoholic fermentation is influenced by narcotics in the same way as oxygen respiration. Addition of narcotics also causes the precipitation of protein in the press juice of yeast. The degree of precipitation runs exactly parallel with the rate of inhibition of fermentation. Narcotic inhibitions can also be noticed with a solution of invertase free from protein. Meyerhof suggests as an interpretation for these inhibiting effects that "the more strongly adsorbed narcotics drive off the substrate from the colloidal enzyme surface but that the dispersion rate of the enzyme does not thereby undergo any change. This is obviously the case in any reversible narcosis," p. 16.

"Cyanide also inhibits respiration in a reversible manner even in a molecular concentration of 1/10,000. It is, therefore, considerably more effective than the strongest indifferent narcotics; but it is only slightly adsorbed, and its high activity must be explained in another way. The next assumption is a chemical combination of cyanide with some substance, present in a minute quantity, but yet essential for respiration, hence most likely with an oxidation catalyst of the cell. During the experiments with the cell-pulp of sea-urchin eggs our attention was drawn to the iron, which, as is well known, can easily enter into a complex compound with cyanide. The fact could be established that the oxidation of lecithin in presence of ferrous salt is the chief or initial process of respiration in the eggs. The chemical aspect of this process will be discussed in the next lecture. I will touch here only upon the following points concerning the bearing of iron on respiration. First, the sea-urchin eggs contain per gram of cell-substance, about 1/500,000 mol of iron in such a form that it yields a red color with hydrochloric acid and potassium thiocyanate. It therefore exists already in ionic form or is very easily split off as such. Second, an addition of iron salt, in quantities corresponding to those existing in the egg, increases the respiration considerably. Very much larger quantities do not produce any stronger effects. On the other hand, additions of the metal much smaller than the quantity present in the egg are ineffective. Third, the increase of oxidation caused by the addition of iron is inhibited in the same way as the normal respiration, by narcotics," p. 16.

"It is well known that amino-acids in aqueous solution are perfectly stable when exposed to the air. If, however animal charcoal is added to an amino-acid, the amino acid is burnt at the temperature of the body in presence of the oxygen of the air, without any other addition. It is burnt to the same end-products as in the body, e. g., cystine into carbon dioxide, sulphuric acid, and ammonia. Nitric acid is never formed as in the combustion in the Berthelot bomb. Thus, in chemical respects we have obviously before us a process of oxidation very similar to that in the cell. It takes place on the surface of the charcoal, and is inhibited by different narcotics in exactly the same way as the respiration in living cells," p. 18.

"The charcoal model imitates the inhibition by cyanides as perfectly as the inhibition by narcotics. The oxidation of the cystine is inhibited by n/10,000 to n/100,000 cyanide, though cyanide is very slightly adsorbed. Although, therefore, only a minimum part of the cystine is driven off from the charcoal, its oxidation is, nevertheless, completely stopped. Warburg suggests that the cyanide covers, not the whole surface, but exclusively those parts of the surface containing iron, and that the oxidation of the amino-acid takes place only on these. Indeed, the animal charcoal contains iron, about 5/1,000,000 mol per gram and the cystine oxidation is stopped by 10/1,000,000 mol of cyanide. Therefore both values correspond exactly. As a fact, the mechanism of cyanide effect and the way in which iron is active in charcoal, was recently explained still more clearly," p. 20.

"The more closely we study the machinery of life in the isolated cell, the clearer it becomes that the chemical and physiochemical processes predominate in it. Physiology in its classical period was studied chiefly by physicists, at least in Germany. I mention Helmholtz, duBois-Reymond, Ludwig, Fick. In the field of cellular physiology, however, physiological and physical chemistry have to assume the leadership—not, however, by analyzing the dead material in regard to its constituents, but by studying the chemical dynamics of the processes of life. Almost a hundred years ago, Pasteur struck out on this path. With extraordinary success, Jacques Loeb, whom many of our younger generation call their teacher, has continued along these lines," p. 23.

"Fermentation never starts immediately after the mixing of sugar and yeast juice, but rises gradually to the maximum. This rise occurs more quickly on the addition of hexose diphosphoric acid and in proportion to its concentration. Since during the fermentation itself hexose diphosphoric acid is formed, this increase of fermentation is caused partly by autocatalysis of the hexose phosphoric acid. According to Harden, the initial delay in fermentation is due to the slow formation of acetaldehyde, which acts as H_2 acceptor in the sense of Neuberg's theory. Therefore, by adding acetaldehyde, the fermentation sets in with full strength without the "fermentation rise." It is not quite clear what rôle is played in this process by the hexose phosphate. In any case, it acts through itself and not through the hexose formed at its decomposition," p. 48.

"While the unfatigued muscle with a definite amount of lactic acid always develops a proportional amount of tension, the efficiency of lactic acid is lowered with fatigue and also with incomplete narcosis. This seems important for the elucidation of the more delicate events in the contractile mechanism. A still larger problem is connected with the disappearance of lactic acid in the oxidative recovery. Hill recognized the principle very accurately indeed when he compared the activity of muscle with the function of an accumulator. The electric energy which a charged accumulator delivers on closing the circuit originates in the end in the supply of energy in being charged. According to Hill, this charging is done in muscle during the recovery period, when by the expenditure of oxidations potential energy is accumulated. A certain amount of this is liberated on stimulation during contraction, just as in an accumulator on closing the circuit. Taking another simile, we may compare the working of muscle with a clockwork. In the recovery period the clock is wound up. Each stimulus liberates one stroke, and the single strokes are not distinguished from each other until the clockwork has run down. The cause for its having run down is clear to us already; it is the accumulation of lactic acid. But in what does the winding up consist? To be sure, in the removal of lactic acid. But as to how this is going on, opinions have differed for some time," p. 65.

Parnas thought to have proven that consumption of oxygen and disappearance of lactic acid in the recovery period corresponded with each other, p. 66. "In reality, the relation is a different one. It is true that after the anaerobic stimulation the oxygen intake is strongly increased for a definite period. This increase is closely connected with the disappearance of lactic acid, and the intake of oxygen above the resting value, which we may call "excess oxygen," only keeps on as long as lactic acid can be proven in muscle. But the total amount of this excess oxygen is only sufficient to oxidize about one-fourth of the disappeared lactic acid. As a matter of fact, the rest, i. e., three-quarters, are reconverted quantitatively into glycogen. Therefore in this recovery period a process is going on which we know already as partial process of muscle respiration. The other part, however, the reconversion of glycogen into lactic acid, belongs to the working phase."

"In order to increase the generally slight nitrate reduction in the alga, Warburg used a trick. The velocity of reduction depends on the concentration of undissociated HNO_3 molecules because they alone can penetrate into the cell. Since the algae cannot bear any high acid concentration, Warburg put them into a nitrate mixture of N/10 of sodium nitrate and nitric acid, by which the dissociation of nitric acid is strongly depressed. If you now watch the nitrate reduction in the dark, the respiratory quotient, being exactly unity in the solution free from nitrate, rises considerably. Simultaneously with the formed ammonia a certain amount of carbon dioxide is evolved, not derived from the respired oxygen. First there is no quantitative relation between this carbon dioxide and ammonia, because, as is very probable, part of the ammonia is used immediately for the formation of amino-acids. But when the N-requirement of the cells is covered, a constant relation is obtained of 2 mols. CO_2 excreted and 1 mol NH_3. Here the reaction takes place,

$$HNO_3 + H_2O + 2C = NH_3 + 2\,CO_2$$

C meaning carbon compound from the reduction stage of free carbon. We may assume this to be sugar," p. 93.

"The nitrate reduction, taking place in the light, has led us to the assimilation of carbon dioxide, and draws our attention to one of Warburg's most recent works, (performed in co-operation with Negelein) in which the exchange of energy is determined on the assimilation of carbon dioxide itself. We notice there that under suitable experimental conditions we can obtain a yield of work surpassing everything we have learned so far of chemical metabolism. Measuring, as Warburg did, with utmost precision the total radiation absorbed by the suspension of the algae, and at the same time the amount of assimilated carbon dioxide, we find that the utilization of radiation, thus calculated, is by no means constant. In the first place the photochemical efficiency depends on the intensity of illumination. It is the greater, the less the light. The maximum efficiency can therefore only be determined as the limit under the very lowest intensity of light. Second, the algae among themselves show a different capacity of utilization. If they have been kept in weak light for a long time, dark colored cells are obtained, containing abundant chlorophyll, which possesses an especially high power of assimilation. In this case the photochemical yield has been 60 percent in yellow light on the average in a long series of experiments. It is higher than any known photochemical yield of energy measured so far," p. 96.

Wilder D. Bancroft

Principles and Applications of Electrochemistry. Vol. I. *By H. Jermain Creighton. 23×16 cm; pp. ix + 446. New York: John Wiley and Sons, 1924. Price: $4.00.* In the preface the author says: "That division of theoretical or physical chemistry which deals with the relations between chemical and electrical energy and their applications has developed to such an extent during recent years, that it is convenient to treat it by itself. During the past decade a large amount of investigation has been carried out in this field, and a great deal of new knowledge has been accumulated; yet during this period no book on Electrochemistry has been published in English. The need of a new presentation of the principles involved in this field of chemistry and their applications has been largely responsible for the writing of this book."

The chapters are entitled: introduction; Faraday's laws of electrolysis; the theory of electrolytic dissociation; the process of electrolytic dissociation and conductance; electrolytic conductance of solutions; the migration of ions; electrokinetic phenomena; electromotive force; electromotive force of concentration cells; electromotive force of oxidation-reduction cells; polarization and electrolysis; depolarization and electrolysis; the application of the law of mass-action to electrolytic dissociation; relations between chemical structure and the dissociation constant; homogeneous equilibria; the dissociation of water; hydrolysis; the avidity of acids and bases; the theory of neutralization indicators and its application to volumetric analysis; ampholytes; heterogeneous equilibria; the electrochemistry of gases.

There are a great many nice things in the book. The reviewer did not know that Grubb has recently shown that, when solutions of sulphuric acid and potassium hydroxide are electrolyzed with a very high current density, the hydrogen formed at the cathode contains an active component which combines with pure nitrogen to form ammonia, p. 24. "The influence of the nature of the diaphragm on endosmosis is illustrated by the following data obtained by Remy. Using conductance water, he found that the endosmotic flow amounted to 373000, 23000, 2350, 886, and 372 cubic centimeters per faraday with Zsigmondy's membrane, clay, gelatine, parchment, and animal charcoal diaphragms respectively. Parchment is, therefore, an ideal diaphragm material to use for differentiating between electro-endosmotic and ionic transfer of water, especially as above a certain concentration the former decreases as the concentration of the electrolyte increases," p. 148. The author sides with the physicists and the world at large in considering the zinc electrode as negative, p. 174.

"The free electron theory of metallic conduction has apparently encountered insuperable difficulties in the "superconductance" of metals discovered by Onnes at about 4°K., at which temperature the conductance becomes about 10^{11} times that at 0°C.; for as Thomson has pointed out, no permissible increase in the number of free electrons or in their mean free path would explain this enormous increase in the conductance. Accordingly, the free electron theory has been abandoned by Thomson, who has put forward a modification of a theory suggested by him in 1881. This new hypothesis which has recently been shown to meet the difficulties imposed by "super-conductance," may be outlined briefly as follows:

"The atoms of a metallic conductor are supposed to be electrical doublets which are arranged in a haphazard fashion. When an electromotive force is applied to the end of the conductor, a certain fraction of the doublets, which is greater the lower the temperature, arrange themselves in a chain under the influence of the electric field, the others pointing in all directions. The doublets in the atoms produce intense electric forces in their neighborhoods, which tend to drag electrons out of one atom into another. In this manner, the electrons pass along the line of doublets," p. 64.

The author believes that absolute ionic velocities have been measured by Whetham and by Steele, p. 132. If so, this should be extended to concentrated solutions. With an absolute value and the transference number at that concentration, one could calculate the real value for the electrolytic dissociation.

"In recent years attempts have been made to apply Stokes' well-known equation to the motion of ions in an electric field. According to this equation, the velocity of an ion should vary inversely as its radius. Although this has been found to be more or less true for a considerable number of large and heavy ions, the relation does not hold in the case of many simple ions, especially those of the alkali metals. Whilst it is to be expected that of the ions of the alkali metals the lithium ion should migrate the most rapidly and the caesium ion the least rapidly, since the atomic volumes of these elements increase from lithium to caesium, this, however, is the reverse of what is found. This behavior has been ascribed to solvation of the simple ions; the smaller the actual size of the ion, the more intense the electric field at its surface and, consequently, the greater its tendency to combine with solvent molecules. It has been shown by von Hevesy that nearly all univalent organic ions are so large, and the strength of the electric field with which the ions act on the solvent molecules so correspondingly small, that hydration does not occur. This is in agreement with the results obtained by Lorenz," p. 138.

"A recent successful technical application of cataphoresis is found in an electrolytic process for waterproofing textile fabrics. In this process finely divided alumina or aluminum hydroxide is carried into the interstices of the fabric by cataphoresis," p. 158.

"When a drop of mercury is placed in a tube containing a solution of an electrolyte, in which there is a fall of potential, the drop moves towards the positive or negative electrode, depending on the concentration of the mercurous ions contained in the solution. This behavior has been used recently by Bodforss to determine the absolute null-point of electric potential. The drop of mercury was placed in a tube containing a solution of potassium and sodium nitrates, to which had been added a small quantity of mercurous ions. The tube was directly connected to a normal calomel electrode. Varying amounts of potassium cyanide were then added to the solution, and the direction of the movement of the drop of mercury observed. The results of Bodforss' experiments showed that the charge on the drop of mercury changed from positive to negative when the potential between the drop and the calomel electrode was equal to -0.40 ± 0.02 volt. Hence if the drop of mercury was actually without charge, the absolute potential of the normal calomel electrode is $+0.40$ volt, a value very much lower than those previously obtained," p. 187.

The author recognizes that the activity is simply the value necessary to make the formula hold, though he does call the activity coefficient the thermodynamic degree of dissociation, p. 218. "From the results given in Table LIV, it is apparent that the activity coefficient and the degree of dissociation of potassium chloride are not identical at the concentrations employed. This may arise from the fact that the degree of dissociation is equal to the conductance ratio, only when it can be assumed that the velocities of the ions at a concentration, *c*, are equal to their velocities at zero concentration. While this assumption has been amply justified with weak electrolytes, it is not even approximately true with strong electrolytes. Therefore, with electrolytes of the latter class, the thermodynamic degree of dissociation, or the activity coefficient, is preferable to the degree of dissociation."

The reviewer was interested in Newbery's conclusion that the magnitude of the hydrogen overvoltage of a metal is determined by its position in the periodic table, the overvoltage increasing to Group II and thereafter decreasing gradually to Group VIII, p. 239.

"It has been shown that the law of mass-action, in the form of Ostwald's dilution law, expresses correctly the dissociation equilibrium in aqueous solutions of weak binary electrolytes. With aqueous solutions of strong electrolytes of this type, as well as with many non-aqueous solutions, the law appears to fail entirely, except at very low concentrations. Various formulae, many of which approach the dilution law as a limiting form, have been proposed to represent the variation of the conductance of solutions of strong electrolytes with concentration. Most of these expressions have no theoretical significance, and all are limited in their application.

"During the past two decades, various explanations have been put forward to account for the anomaly of strong electrolytes; and the effects of various factors have been studied without throwing much light on the causes of the deviations from the simple law of mass-action. The failure to account satisfactorily for the behavior of strong electrolytes has led a number of investigators to reject the fundamental assumptions of Arrhenius, and to substitute an hypothesis of complete dissociation, variations in conductance with concentration being attributed to the action of the electric field on the mobilities of the ions and not to changes in their number. Two new theories of electrolytic solutions, based on this concept, have been put forward, but it has been shown that they cannot be accepted in their present form," p. 295.

Somebody should repeat Thomsen's work on the relative avidities of the acids. It is not right that the dissociation of trichloracetic acid should be 36% by this method and 73% by the cane sugar method or that the corresponding values for orthophosphoric acid should be 25% and 6% unless some reason is given for these discrepancies.

On p. 376 the author points out correctly that one cannot use a weak acid indicator for titrating a weak base or a weak basic indicator for titrating a weak acid; but how is one to know in any given case whether an indicator is a base or an acid? Ostwald was wrong with methyl orange and others have followed in his footsteps.

The paragraphs on the solubility product, p. 395, are well worth quoting, lest we forget. "According to theory, the value of the solubility-product of an electrolyte should be independent of the concentration of the added electrolyte. That this is not strictly true is shown by the results of the investigations of Hill and Simmons, Hill, Bray and Winninghof, Kendall, and others. It has been found that the solubility-product law becomes more and more nearly true, the less soluble the electrolyte and the more dilute the solution. For the most purposes, however, the solubility-product may be regarded as constant, when the solubility of the salt and the concentrations of the ions in the solution are small. Although the values of the concentration of the undissociated electrolyte and the solubility-product should remain constant in any saturated solution with respect to a given electrolyte, Bray has found that the former decreases markedly, and that the latter increases slightly, as the total concentration of the salts and ions in the saturated solution increases. This behavior indicates that the deviation from the dilution law is mainly due to abnormal behavior of the undissociated electrolyte, and only secondarily to abnormal behavior of the ions.

"With the object of testing the constancy of the solubility-product law, Kendall measured the solubility of a number of slightly soluble acids in aqueous solutions of a second acid. The results of his investigation show that the solubility of an acid in an aqueous solution of another may be regarded as consisting of two parts: one of which (a) increases or decreases regularly according as the acid is more or less soluble in the second acid than in water, whilst the other (b) decreases more or less rapidly according to the ionic strength of the second acid. The divergencies between the experimental solubility values and those required by the theory of the constant solubility-product can be accounted for in all cases by the solvent effect (a). According as to whether the acids are chemically similar (e. g., salicylic and ortho-nitrobenzoic acid) or dissimilar (e. g., hydrochloric and salicylic acid), the divergencies are positive or negative.

"It should be remembered, as Arrhenius has pointed out, that the inconstancy of the solubility-product under certain conditions may be due to the fact that the solvent medium is somewhat changed by the presence of the other electrolyte."

This is a good book, though more electrochemistry and less physical chemistry would have been better. One wishes that the author had not given cupric chloride, p. 13, as an electrolyte from which one gets copper and chlorine on electrolysis. It would have been perfectly simple to have taken zinc chloride, thus sidestepping the intermediate stage of cuprous chloride. While it may be perfectly true that in the Cottrell process the dust particles go to the positive electrode, it is unwise to say so, p. 143, because they go always from the point to the plate electrode. That the plate electrode should be the positive electrode is not essential, though it may be helpful.

Wilder D. Bancroft

Metallographie. *By W. Guertler. Vol. II: Die Eigenschaften der Metalle und ihrer Legierungen. Part II: Physikalische Metallkunde. No. 6: Die elektrische und Wärme-Leitfahigkeit. By A. Schulze. Berlin: Gebrüder Borntraeger, 1924. Price: 48 gold marks.* These two sections of Dr. Guertler's monumental handbook on "Metallography" deal with Electrical Conductivity, the first part being concerned with pure metals, the second with alloys. The author, Dr. Schulze, states that it has been his endeavour to bring into review all the literature bearing on the subject although it has not been easy for German writers to obtain access to foreign publications. The work is principally intended for practising electricians and engineers and therefore the theoretical aspects of the subject are only briefly treated. Considerable stress is rightly laid on the influence of purity on Electrical Conductivity.'

Fully two-thirds of the first volume are concerned with the electrical conductivity of pure metals and its dependence upon temperature. The remainder of the volume deals with such aspects of the subject as the supraconducting state, changes of conductivity on melting and on deformation, the influence of pressure, of magnetic fields, and of direct and alternating currents. The volume closes with a brief reference to the influence of crystal structure and theories of electrical conductivity.

The second section—a volume of 560 pages—is based upon a knowledge of the constitutional diagrams of binary metallic systems and the experimental work on conductivity carried out by Matthiessen, H. LeChatelier, Guertler and Kurnakow and their co-workers. The general classification adopted is one which groups the alloys under three heads:—(1) The components are completely insoluble in one another and the alloy consists of a conglomerate of crystals of the two components. (2) The components are either completely or partially soluble in one another. In the former case the alloy consists of a one-phase system the composition of whose crystals varies continuously from one pure metal to another. In the latter case we have to deal with a solid solution on each side of the diagram whose range depends on the solubility. The intermediate area consists of a mixture of the two saturated solid solutions whose proportions depend upon the composition. (3) The components are able to combine forming one or more compounds with one another. These compounds may possess varying degrees of solubility. Such cases may give rise to very complicated diagrams. Corresponding to this the electrical conductivity may show considerable variations in any given alloy series. The investigation of systems containing inter-metallic compounds presents problems owing to the extraordinary hardness and brittleness of the alloys which renders the preparation of suitable rods or wires very difficult. Emphasis is rightly laid upon the necessity of ensuring that any given alloy is in thermal equilibrium before the electrical conductivity can be correctly determined.

This volume also deals with the electrical conductivity of fluid alloys—principally the work of Bornemann and his pupils. The two volumes are excellently printed and illustrated and will undoubtedly be found of great service by those who are interested in the properties of metals and alloys with which they deal.

H. C. H. Carpenter

The Kinetic Theory of Gases. *By Eugène Bloch. Translated by Philip A. Smith. 20×13 cm; pp. xiv + 178. London and New York: Methuen and Co.; E. P. Dutton Company. Price: 7 shillings; $3.00.* The complete and rigorous development of the kinetic theory involves a mathematical equipment which many physical chemists do not possess. Such will welcome Professor Bloch's modified exposition, now accessible in English, more especially as the volume is largely devoted to the bearing of the theory on a number of interesting questions not commonly raised in this connexion.

Thus, for example, the properties of highly rarefied gases are discussed in some detail in relation to the mean free path. The mean free path, which is about 0.0001 mm. at ordinary pressures, assumes at very low pressures values of the same order as the dimensions of the containing vessel. The governing factor is accordingly no longer the mutual collisions of the molecules, but the collisions of the molecules with the walls of the container. The bearing of this on molecular flow and effusion at low pressures (Knudsen), and on the principles underlying the molecular, diffusion and condensation pumps (Gaede, Langmuir) is clearly set out.

Among other collateral topics which come under review are the equations of state, the specific heat of solids and the theory of quanta, the width of spectrum lines, Perrin's work on Brownian movement and his determination of the Avogadro constant. In a useful chapter summarising the recorded figures for the various molecular magnitudes the most probable value of that constant is correctly given as 60.64×10^{22}; on p. 15, on the other hand, it is stated that the numerical value of the constant is in the neighbourhood of 65×10^{22}. This presumably is a misprint.

One misses an index, and throughout the book there are no references to original papers. The latter defect has been remedied to some extent by the translator, who has added a short bibliography embodying references to important books and memoirs on the subjects discussed.

The exposition itself is lucid and concise, as one might expect from a French writer, and the translator has done his work well.

J. C. Philip

The Elements of Colloidal Chemistry. *By Herbert Freundlich. Translated by George Barger. 19×14 cm; pp. vii+210. New York: E. P. Dutton and Company. Price: $3·00.*

In the preface the author says: "Suggestions have reached me from various quarters, that by abbreviation and excision of mathematical deductions and numerical data, my *Kapillarchemie* might become an introduction to the chemistry of colloids for a larger number of students of medicine and technology. Since several books of the kind already exist, I at first viewed this plan with misgivings, but ultimately overcame them, when I realized that the facts and ideas, which to my mind are of special importance to colloidal chemistry, had not yet been presented in simple language. I hope that I have succeeded in doing this in the present book."

The book is divided into two parts: the physico-chemical foundations of colloidal chemistry, with capillary chemistry, the rate of formation of a new phase, and the Brownian molecular movement as the three sub-heads; and colloidal-disperse systems, with colloidal solutions, sols and gels, and with colloidal-disperse structures of a different kind as the two sub-heads.

Freundlich believes in the contact angle, p. 27. He considers the Hofmeister or lyotropic series as depending on the affinity of the ions towards water, p. 27, "for it may be taken as certain, that every ion binds a considerable number of water molecules, and is to a certain extent therefore surrounded by an aqueous envelope. Unfortunately we have as yet no reliable means of measuring this power of binding water, the degree of hydration of the ions. If we had such means, we should at once be able to elucidate quantitatively a large number of phenomena which at present remain more or less obscure. Such scanty and rather uncertain measurements of the hydration of ions, as have been made, point however to the conclusion, that the Li$^{\cdot}$-ion is more strongly hydrated than the Na$^{\cdot}$-ion, and this more strongly than the K$^{\cdot}$-ion. Among anions the sulphate ion is more strongly hydrated than the Cl$'$-ion, and this more than the Br$'$-ion. The lyotropic series therefore also applies to the hydration of the ions."

Speaking of the adsorption of argon by charcoal, p. 46, Freundlich says that "this loose union of argon with charcoal can hardly be regarded as a chemical combination in the ordinary sense, since no chemical compounds of argon are known. This does not imply that adsorption must be regarded as a "physical combination," sharply differentiated from a chemical union. Adsorption does, however, belong to some such class of loose combinations, as are attributed in chemistry to the action of subsidiary valencies."

"Until recently the strong condensation, to which gases in the adsorption layer are subject, was considered a sufficient explanation of the extraordinary acceleration of gas reactions. A numerical estimate shows, however, that this condensation can hardly account for the phenomenon. We shall rather have to assume with Polanyi that hydrogen, oxygen, nitrogen, etc., dissociate much more strongly in the adsorption layer than in the gas space at the same temperature; it is therefore the larger content of atoms of these gases in the adsorption layer, which may explain the increased reaction velocity at a surface," p. 52.

"Now the adsorption of methylene blue by kaolin differs in various ways from the adsorption of non-ionized or slightly ionized substances by charcoal and analogous adsorbents. One difference is that in the former case only one ion is adsorbed, the dye-stuff cation, whilst the anion (generally a Cl$'$-ion, since we are mostly concerned with methylene blue chloride) remains behind in the solution in approximately unchanged concentration. Now in solution a definite number of anions must of course correspond to an equivalent number of cations. In place of the adsorbed dye-stuff ion other cations are found in the solution, and these are derived from the adsorbent; in the case of kaolin Ca$^{\cdot\cdot}$-ions are chiefly involved. This kind of adsorption is therefore termed an exchange adsorption and is polar in character. In contradistinction to it, the adsorption of non-electrolytes described above, will be termed an apolar adsorption. The designation "polar" is chosen on account of the electrical antithesis between anion and cation, both of the adsorbent and of the adsorptive. We may imagine the exchange adsorption to take place as follows: the silicate ions of the kaolin constitute a solid framework, because they are, so to speak, difficulty soluble. The cations of the kaolin, especially the Ca$^{\cdot\cdot}$-ions, are mobile, i.e. they can wander out of the surface molecules into the solution, provided that other cations, such as the dye-stuff ions in the above example, can replace them in the silicate frame-work," p. 63.

There is a discussion, p. 73, of the poisoning of catalytic agents. "A still deeper insight into the mechanism of such a reaction is afforded by the investigation of the oxidation in aqueous solution of amino-acids, such as cystine, on the surface of charcoal. While neither the original substance nor the reaction products strongly retards the reaction, a number of foreign substances do so powerfully. Among these substances two groups may be distinguished. There are in the first place capillary-active organic substances, which act quite like the urethanes in the previous example. Their retarding action is therefore found to increase like their adsorbability, in accordance with Traube's rule. The action is probably due to these substances displacing the less adsorbable amino-acid from the surface and thus lessening its surface concentration and thereby also the velocity of its oxidation.

"There is, however, a second group of substances which retard the reaction about 1,000 times as strongly as the organic substances and yet are not appreciably capillary-active, nor are they strongly adsorbed; hydrocyanic acid is a striking example of this second group. Otto Warburg explains its peculiar action as follows: By no means the whole surface of the charcoal takes part in the reaction, but only certain portions are active, where iron compounds (or compounds of other heavy metals) occur. The importance of iron results from the fact, that all charcoals containing iron accelerate the oxidation of the amino-acids, whilst varieties completely free from iron are not active at all, but become so when a minute quantity of iron has been incorporated in them in a suitable form. The hydrocyanic acid is considered to be loosely bound, especially by the iron compounds, which thus lose their catalytic activity. The interpretation of the behaviour of capillary-active substances, given above, remains unaffected, for when the latter are adsorbed by the charcoal, they cover the whole of the charcoal surface, including the ferrous portions, and displace the amino-acid from them. Charcoal and iron are therefore in the same relation as are glass wool and copper in the previously discussed example of the decomposition of hydrogen peroxide."

Freundlich defends the view, pp. 78-86, that the electro-kinetic potential difference is not identical with Nernst's potential difference at a single electrode. He deduces that the electrokinetic potential difference, unlike the Nernst potential difference, is influenced greatly by the adsorbability of the ions.

When discussing orientation in interfacial layers, Freundlich points out, p. 93, the bearing of this on contact catalysis. "Considerations of this kind are also important in connexion with catalysis in an adsorption layer. A reaction between two molecules with polar ends will be accelerated, if the ends, which are required to react, come into contact in the surface. But if this is not the case, if a hydrophobic end is required to react with a hydrophilic one, and the hydrophobic ends of the molecules are directed towards the absorbent, while the hydrophilic ones point to the water, the reaction is not accelerated by the adsorbent, and may even be retarded by it."

Under amorphous solids Freundlich states, p. 104, that "a remarkable difference between the crystalline and the amorphous-solid state is presented by their thermal conductivity, which in crystals rapidly increases at very low temperatures near the absolute zero, but in glasses diminishes in this region and becomes apparently constant near -273°.

Under amorphous solids Freundlich states, p. 104, that "a remarkable difference between the crystalline and the amorphous-solid state is presented by their thermal conductivity, which in crystals rapidly increases at very low temperatures near the absolute zero, but in glasses diminishes in this region and becomes apparently constant near -273°. The utilization of this property is, however, not so simple experimentally, and is particularly difficult in the case of powders."

"The Tyndall effect is simply the so-called primordial phenomenon of Goethe, on which the latter based his theory of colour. He expressed it somewhat as follows: A turbidity seen against a dark background appears blue, against a light background it appears yellowish red. The physicists of Goethe's time were unable to explain the phenomenon, which was first done by Lord Rayleigh in 1870, in the manner outlined above. No wonder that Goethe placed little confidence in the science of physics, because of its inability to explain so familiar a phenomenon, shown by any milk-glass or smoke," p. 126.

Freundlich apparently wishes to postulate something more than an agglomeration to account for the change in the properties of leather with time, p. 185. "A similar succession of processes is found in tanning. The hide is an amorphous adsorbent, the solution of tannic acid (and of many other vegetable tanning agents) is semi-colloidal. The tannin is in the first instance taken up by hide powder according to an ordinary adsorption isothermal, but the adsorption compound so formed from hide and tannin, has not yet the properties of leather. It only acquires these gradually, becomes brown, no longer gives off tannin on washing, and becomes more resistant to dilute alkali. The adsorption is followed by another process, a chemical action or a coagulation, by means of which the adsorption compound acquires the properties of leather."

Wilder D. Bancroft

Chemistry and Atomic Structure. *By J. D. Main Smith. Introduction by G. T. Morgan. 21-1/2×15 cm; pp. 221. London and New York: Ernest Benn: D. Van Nostrand Company. 1924. Price: 12 shillings, 6 pence, $3.70.* In these days a chemist finds himself in a very difficult position. That portion of the science—and it is the major portion—which may take as its basis the atom of Dalton is growing at an ever increasing rate so that it is an almost impossible task to keep pace with it, especially when such ramifications as physical chemistry, biochemistry, etc., are taken into account. The burden of the task is increased by the fact that during the last decade or so, and especially in the last few years, physicists have made very great advances towards unravelling the mystery of the atom and the chemist can no longer afford to neglect the results obtained and must bring them within the ambit of his knowledge. In attempting to do this, however, he had hitherto been confronted with the difficulty that, as is natural in the early stages of investigation, the views of the physicist have been in a state of flux; also, the bias of the chemist is towards stereochemical ideas whereas the physicist is inclined more towards kinetic theories. The result of this is that many chemists are content to assume the attitude of "wait and see"; they do not wish to take up a definite position until matters have become more stabilised. Such being the case, the chemist would naturally look forward to the appearance of a book, written by a chemist, dealing with results so far obtained in the attempts to probe atomic structure and their application to chemical phenomena. It must be stated frankly, however, that the book is disappointing. It is written too much from the specialist's point of view, that is to say, the reader, unless he is already well acquainted with the subject, will not get his ideas clarified but will only become more confused. For example, when dealing with Werner's Co-ordination Theory nineteen generalisations are given which can only be appreciated by one who is already *au fait* with the subject. Again, one is suddenly introduced to Sommerfeld's theory of elliptic orbits, to radial and azimuthal quanta, notation of orbits, etc., without any explanation, and the chemist who is not already a specialist will become hopelessly lost. At the same time the author occasionally introduces physical theories of his own, which appear not to have been subjected to mathematical analysis, and the reader will feel somewhat dubious about them when, in another connexion, he finds it suggested, for example, that the variation in mass with velocity may really be due to a variation in the factor depending on the electric charge; it is difficult to imagine that this possibility has not already been considered and rejected by physicists. Again, the author's suggestion that the formation of hydrogen on the bombardment of certain elements by α-particles may be due to the breakdown of the α-particles themselves has been considered and rejected by Rutherford.

The first chapters in the book, where the author deals with the fundamental topics of atoms, molecules, valency, electrochemistry and the classification of the elements are well done, and the reader will be interested in the new points of view obtained, and by the way in which well-known facts are marshalled and critically examined.

In an appendix on "The relativity effect on mass" it is stated that ideas based on the conception of shared-electron orbits pursuing paths represented by the "ovals of Cassini" have acted as guiding principles in the Birmingham research school under Professor Morgan. One's curiosity is whetted considerably by this statement, since the application to the very complex compounds studied at Birmingham has not yet been published.

Finally, it may be stated, with regret, that the book is not suitable for the student or for the non-specialist chemist. The specialist will find much to interest him, much to criticise, and much with which he will not agree.

T. Slater Price

Technical Methods of Chemical Analysis. *By Chas. A. Keane and P. C. L. Thorne. Vol. I, second edition. 24×16 cm; pp. xx+702. New York: D. Van Nostrand Company, 1924. Price: $18.00.* "The English translation was edited in conjunction with Professor Lunge, and was adapted to English conditions of manufacture by collaboration with specialists fully familiar with the methods of work in use in this country. Although this adaptation was made as complete as possible, it was necessarily somewhat hampered by the character and subject-matter of the German text, and it has accordingly been considered preferable to make this new edition more independent, and each of the contributors entirely responsible for his section.

From this consideration many of the sections have been largely rewritten, several new sections have been added, and the whole of the subject-matter has been thoroughly revised and brought up to date. The arrangement of the contents of each volume has also been modified so as to group the sections dealing with correlated industries more advantageously than in the previous edition."

"The new sections included in the present volume are—"Electrolytic Methods of Chemical Analysis" and "Physical Methods employed in Chemical Analysis." "

"The work will be published in six separate volumes, and in addition to the index with each volume, a complete index for the whole will be provided. The tables of general applicability are printed for reference at the end of each volume, and an index of tables has been added."

The new edition of the first volume of this well-known set of books is well written throughout and contains very valuable information with regard to all the technical analyses discussed. At least one method is given in detail for each determination and besides this most of the other methods available are mentioned, with complete references to the original work. The book also contains many illustrations and useful tables.

The work applies mainly, however, to English industrial practice and in certain cases, especially with regard to nitrometers, gas and fuel calorimeters and automatic gas analysis apparatus the discussions do not include those forms in general use in the United States.

In the opinion of the reviewer some of the methods given are not the most satisfactory available as, for example, the authors state that the titration of sodium oxalate with a solution of potassium permanganate is made at 40°-50°, while it has been shown that this titration should be made at 80°-90°, not allowing the temperature to fall below 60° by the time of the completion of the titration. Also the method given in detail for the standardization of a solution of sodium thiosulphate is by titration against pure iodine, while some of the other methods mentioned are less troublesome and of sufficient accuracy.

Also in the case of gas analysis the book could have been made more complete by mentioning at least another reagent for the absorption of oxygen, the rapid volumetric methods for the determination of hydrogen sulphide and the volumetric and turbidimetric methods for the determination of total sulphur in connection with the "Referees" method.

This new edition, however, is an improvement upon the first and should continue to enjoy the popularity of the first edition for use in connection with technical analytical work.

M. L. Nichols.

Colloid Chemistry. *By Jerome Alexander. Second edition, revised and enlarged. 22×14 cm; pp. viii+216. New York: D. Van Nostrand Company, 1924. Price: $2.00.* The first edition was reviewed nearly six years ago (23, 442). This edition is more than double the size of the old one. Among the new things are the colloid mill, p. 25; Vegard's work on frozen nitrogen as the source of the aurora, p. 58; the behavior of a charged cloud, p. 62; the dispersal of fog, p. 67; the use of bentonite as a beauty clay; Hildebrand's experiments on emulsions, p. 96; Thiessen's work on coal, p. 105; Sheppard's work on colloidal fuel, p. 106; the principle of plural protection, p. 114; Loeb's views on sodium gelatinate, p. 135; the work of Jeffreys and Archer on duralumin, p. 144; antiseptics, p. 168; cytology, p. 171; just to mention a few points.

It was new to the reviewer that "Sodom and Gomorrah were probably destroyed by a colloidal cloud of petroleum ignited by local fires or lightning. Analogous phenomena are known in the Caucasus Mountains today," p. 66.

There are several points on which the reviewer does not agree with the author. The color of the ruby is due to chromium and not to iron p. 72; it was Emil Fischer and not van't Hoff, p. 169, who said that enzyme and substrate fit like lock and key. If one is going to call solid solutions a case of a solid dispersed in a solid, p. 26, why not call a mixture of gases a colloidal system? The author is consistent in his evil ways and calls alpha brass an adsorption compound between copper and zinc, p. 156; but, if everything is to be colloidal, the term becomes valueless. Fuchsine, p. 51, is a basic dye and not an acid one. The observation probably refers to a sulphonated magenta.

The real quarrel between the reviewer and the author is over the question whether one can pass continuously by subdivision from a solid or a liquid to a gas, or from a sparingly soluble solid and a liquid to a solution, as is assumed in the "zone of maximum colloidality", p. 17. The reviewer is not yet prepared to accept, as a satisfactory working hypothesis, either the actual statement, p. 14, that "the practical distinction between homogeneity and heterogeneity depends entirely upon the refinement of our means of observation" or the implied statement, p. 17, that one can follow "the gradual dispersion of a substance from gross visible particles all the way down to true molecular subdivision."

If we take a definite amount of solid and assume that we can grind this as fine as we please, we shall find that, at a certain degree of fineness, the vapor pressure becomes so high that the whole of the solid will vaporize, presumably precipitating promptly as coarser crystals. In other words there will come a point below which it is impossible to grind a finite amount of solid and one cannot grind an infinite amount of solid. It seems therefore theoretically impossible to pass continuously, by subdivision, from gross visible particles to true molecular subdivision. People, like the author, who argue to the contrary, are only considering one set of factors and are overlooking or ignoring what will really happen.

The author's praiseworthy desire to use, as far as possible, "non-technical language and homely illustrations, so as to enable the reader's interest to aid memory" leads him occasionally into rather startling metaphors, p. 36. "Without an understanding of the underlying principles of colloidal protection, isolated facts have long lain like individual gems, scattered or even lost in the wide fields of human experience. A theory is necessary to string them together, each in its proper place, to form a beautiful necklace; or rather, a theory to serve as a matrix that forms of them a cutting drill, with which we may bore into the hard rocks of the still unknown."

On p. 14 the reviewer was delighted to read that Bridgman has found that "a fresh iron surface absorbs atmospheric constituents so quickly that, although a piece of cast iron broken under mercury is amalgamated at its new surfaces, the same iron is not amalgamated at all if broken above the mercury and instantly dropped in."

Wilder D. Bancroft

Physical Basis of Heredity. *By T. H. Morgan. Third impression. 20×14 cm; pp. 305. Philadelphia and London: J. B. Lippincott Co., 1919. Price: $3.00.* The subject is presented under the general headings: Mendel's first law; the mechanism of segregation; Mendel's second law; the mechanism of assortment; linkage; crossing over; crossing over and chromosomes; the order of the genes; interference; limitation of the linkage groups; variation in linkage; variation in the number of the chromosomes and its relation to the totality of the genes; sex-chromosomes and sex-linked inheritance; parthenogenesis and pure lines; the embryological and cytological evidence that the chromosomes are the bearers of the hereditary units; cytoplasmic inheritance; maternal inheritance; the particulate theory of heredity and the nature of the gene; mutation.

"That the fundamental aspects of heredity should have turned out to be so extraordinarily simple supports us in the hope that nature may, after all, be entirely approachable. Her much-advertised inscrutability has once more been found to be an illusion due to our ignorance. This is encouraging, for, if the world in which we live were as complicated as some of our friends would have us believe we might well despair that biology could ever become an exact science," p. 151.

"Segregation and independent assortment were the two fundamental principles of heredity discovered by Mendel. Since 1900 four other principles have been added. These are known as linkage, the linear order of the genes, interference, and the limitation of the linkage groups. In the same sense in which in the physical sciences it is customary to call the fundamental generalizations of the science the 'laws' of that science, so we may call the foregoing generalizations, the six laws of heredity known to us at present. Despite the fact that the use of this word 'law' has been much abused in popular biological writing we need not apologize for using it here, because the postulates in question have been established by the same scientific procedure that chemists and physicists make use of, viz., by deductions from quantitative data. Excepting for the sixth law they can be stated independently of the chromosomal mechanism, but on the other hand they are also the necessary outcome of that mechanism," p. 16.

"Mendel succeeded in discovering the principle of segregation because he simplified the conditions of his experiments so that he had to deal with one process at a time. Others before him had failed because they worked with too complex a situation. In each case Mendel picked out for study a pair of contrasted characters of a kind that were sharply distinguishable from each other whenever they appeared. He chose plants that normally self-fertilize and are little liable to accidental cross-fertilization, which made it possible easily to obtain in the second generation numbers large enough to give significant results. To Mendel's foresight in arranging the conditions of his work, as much as to his astuteness in interpreting the data, is due his remarkable success," p. 19.

"That Mendel's principles apply to animals was first made out by Bateson and by Cuénot in 1902. Since then many characters both in domesticated and in wild animals and plants have been studied, and there can be no question of the wide application of Mendel's discovery," p. 25.

"Mendelism rests on the theory of a clean separation of the members of each pair of factors (genes). In every heterozygote the factor for the dominant and that for the recessive are supposed to come into relation to each other and then to separate at the ripening of the germ-cells. If we think of the two genes coming together and afterwards separating, it would seem that a favorable situation might exist for the two to become mixed, and one 'contaminate' the other. If any extensive process of this kind occurred, the Mendelian phenomena would be so irregular and erratic that they would have little interest. But even those who are inclined to appeal to contamination as an exceptional phenomenon, grant that clean separation of the genes is the rule. The best critical evidence against contamination is in cases in which for many successive generations breeding has taken place from heterozygous forms only (which creates a favorable situation for contamination to take place were it possible). No influence of contamination has been found in such cases," p. 34.

"As has been stated, Mendel did not make it clear that there exists in the normal animal or plant the same duality that comes to light when a hybrid is produced; nevertheless this condition is implied, at least, in his paper, and has been taken for granted in practically all of the modern work on heredity. The demonstration that such is the case is, however, not a simple matter. It could not have been made by Mendel or in the earlier days after the rediscovery of Mendelism (1900). An attempt to furnish this demonstration is given in Chapter XX. Assuming the demonstration to be satisfactory, we reach the highly important conclusion that segregation is not something peculiar to hybrids, but something most readily demonstrated by means of hybrids, and that in all probability the germ-plasm is at first made up of pairs of elements, but at the ripening of the germ-cells these elements(genes) separate, one member of each pair going to one daughter cell, the other member to the other cell. The mechanism by means of which such a process might take place had been known for several years before its relation to Mendel's principles of segregation was realized. This mechanism is to be found in the conjugation and reduction processes that take place in the maturation of egg and sperm-cell. An account of this process is given in the next chapter," p. 37.

"One of the most secure generalizations of modern work on the cell is that every cell of the individual contains a *constant number* of self-perpetuating bodies (called chromosomes), half of which are traceable to the father and half to the mother of the individual. No matter how specialized cells may be, they contain the same number of chromosomes. Equally important is the fact that after the eggs of the female and the sperm-cells of the male have passed through the ripening of maturation divisions the number of chromosomes is reduced to half. Lastly, there is convincing evidence that the reduced number of chromosomes is brought about as the result of a separation of such a kind that each mature germ-cell gets only a paternal or a maternal member of each chromosome pair," p. 39.

"The evidence from studies of the maturation of eggs and spern shows that the paternal and maternal chromosomes come together at this time in pairs, and subsequently separate, so that each egg comes to contain one or the other member of a pair. The same process takes place in the formation of the sperm-cells. It is obvious that if one member of any pair contains material that produces an effect on some character as one of the end results of its activity, and the other member of the pair contains a different material, the behavior of the chromosomes at the time of maturation supplies exactly the mechanism that Mendel's law of segregation calls for," p. 57.

"Crossing over is not absolutely fixed in amount, but is variable. This statement does not refer to variability in the number of crossovers due to random sampling, but to variability due to fluctuation in environmental conditions, or due to internal changes in the mechanism of crossing over itself. For example, it has been shown that the amount of crossing over in *Drosophila* is different at different temperatures, and it has also been shown that there are factors (genes) carried by the chromosomes themselves that affect the amount of crossing over. These questions, that have already been touched upon in other connections, may be taken up here in more detail," p. 139.

"The theory that the chromosomes are made up of independent self-perpetuating elements or genes that compose the entire hereditary complex of the race, and the implication contained in the theory that similar species have an immense number of genes in common, makes the numerical relation of the chromosomes in such species of unusual interest. This subject is one that could best be studied by intercrossing similar species with different numbers of chromosomes, but since this would yield significant result only in groups where the contents of the chromosomes involved were sufficiently known to follow their histories, and since as yet no such hybridizations have been made, we can only fall back on the cytological possibilities involved, and on the suggestive results that cytologists have already obtained along these lines," p. 147.

"Color blindness in man appears to follow exactly the same procedure as sex-linked inheritance in the vinegar fly—at least certain kinds of color blindness have been shown to do so. Haemophilia also is sex-linked, and there are four or five other defects in man that appear to come under this head. According to several accounts there is an unpaired sex-chromosome (or two of them) in man, which is also called for by the genetic evidence relating to sex-linkage in man, but since the female number of chromosomes in man is stated by Guyer to be 24, and by von Winiwarter to be 48, it is unsafe as yet to appeal to this evidence as showing the identity of the sex-determining mechanism of man and the vinegar fly," p. 170.

"Variations in the ordinary sex-determining mechanism account in some cases for the normal output of males and females produced by parthenogenesis, and determine the exceptional sex-ratios of such species. The honey bee furnishes the best known example. The queen comes from a fertilized egg, and has therefore the double (2N) number of chromosomes. Her eggs give off two polar bodies, hence have the reduced, or single number of chromosomes. Any egg that is not fertilized develops parthenogenetically into a male. If there are two X-chromosomes in the bee, as in some of the other insects, the egg is expected to contain only one of them after the extrusion of the polar bodies. Hence, if it develops with out doubling its chromosomes, it should give rise to a male," p. 180.

"In so far as parthenogenetic reproduction takes place without reduction in number of the chromosomes, the expectation for any character is that it will have the same frequency distribution in successive generations, because the chromosome group is identical in each generation. There are a few cases where parthenogenetic inheritance has been studied. The results conform to expectation.

"The only difference between a species reproducing by diploid parthenogenesis and one propagating vegetatively is that in the latter group of cells starts the new generation and in the former only one cell, viz., an egg, that no longer undergoes reduction, or needs to be fertilized. In both, the chromosome complex remains the same as in the parent. Strictly analogous to the two foregoing methods of propagation are the cases of sexual reproduction in a homozygous group of individuals, composed of males and females or in a group of hermaphroditic forms that are homozygous. Successive generations are here also expected to have the same frequency distribution, whether selected or not, because they have the same germ-plasm. Johannsen's pure lines furnish an example of the last case, for, in principle, pure lines, parthogenetic reproduction, and vegetative propagation, are concerned with nearly the same situation," p. 204.

"Young aphids reared on the salts of the heavy metals as well as on magnesium salts and the sugar became winged, while those reared on the other substances in the list became apterous," p. 210. With nickel sulphate there were 955 winged individuals to 5 wingless ones. With magnesium salts the corresponding figures were 840 to 9, while there were 2 winged individuals to 1029 wingless ones when sodium salts were the food.

"In the preceding pages so much emphasis has been laid on the chromosomes as bearers of the hereditary material that it may appear that no very important rôle is left to the rest of the cell. Such an impression would be quite misleading, for the evidence from the embryology appears to show that the reactions by means of which the embryo develops, and many physiological processes themselves, reside at the time in the cytoplasm. Furthermore, there is also genetic evidence to show that certain forms of inheritance are the outcome of self-perpetuating bodies in the cytoplasm, most of which go under the name of plastids. Recognition of plastid inheritance carries with it the idea that if there are such materials in the cytoplasm that are self-perpetutating they will have to be taken into account in any complete theory of heredity," p. 219.

"The attempt to explain biological phenomena by means of representative particles has often been made in the past. The superficial resemblance of the theory of the gene to some of the older theories, long since abandoned, has furnished the opponents of the Mendelian theory of heredity an opportunity to injure the latter by pretending that the modern idea of the gene is the same as the older ideas of Herbert Spencer concerning physiological units, of Darwin relating to pangenes, and especially of Weismann about biophors. There is no need for such confusion, for even a little knowledge of the evidence on which the old and the new views rest ought to have sufficed to make evident some important and essential differences. It need not be denied, however, that there is an historical connection between the mediaeval theory of preformation and the particulate theory of heredity. Bonnet, one of the best known adherents of preformation, believed at first in 'whole' germs, but later admitted that pieces of germs might be stowed away in regions likely to be injured. Weismann, also, the most prominent modern adherent of preformation, held that whole germs, ids, are present in the germ-plasm, each standing for a whole organism—each (or most or one?) becoming unravelled as the embryonic development proceeded. In fact, Weismann's entire theory was invented primarily to explain embryonic development rather than genetics. Its connection with the modern idea of the germ-plasm is little more than an analogy—for reduction in Weismann's original sense meant the sorting out of the wholes of ancestral germ-plasms with which he peopled the chromosomes," p. 234.

"Our present conception of the relation of the germ-plasm to developmental phenomena has then only a most superficial resemblance to the older theories. The newer point of view may be summed up in a few words, and has in fact been stated already. First, that each gene may have manifold effects on the organism, and second, that every part of the body, and even each particular character, is the product of many genes. The evidence for these two conclusions has been so repeatedly referred to in the preceding pages that it is not necessary to go over it again, but it may be worth while to emphasize that these two conclusions are not pure speculations, but derived from the evidence itself. It may also be well to point out that even if the whole germ-plasm—the sum of all the genes—acts in the formation of every detail of the body, still the evidence from heredity shows that this same material becomes segregated into two parts during the maturation of the egg and sperm, and that at this time individual elements separate from each other largely independently of the separation of other pairs of elements. It is in this sense, and in this sense only, that we are justified in speaking of the particulate composition of the germ-plasm and of particulate inheritance," p. 243.

"Concerning the origin of the germinal differences that give rise to mutant characters very little is known at present except, (1) that they appear infrequently, (2) that the change is definite from the beginning, (3) that some of the changes at least are recurrent, and (4) that the difference between the old character and the new one is small in some cases and greater in others. I do not think that any of the work purporting to produce specific mutational changes has succeeded in establishing its claims, at least in the sense that we can pretend at present to control the appearance of specific mutant changes, and until this is done we can not hope to find out very much as to the nature of these changes. Our study of the germ-plasm is largely confined, therefore, for the present, to a study of transmission of the genes, to the kinds of effects they produce on the organism, and to the special relations of the genes in the chromosomes where they are located," p. 247.

"The question of lethal genes has attracted in recent years increasing attention, both on account of their frequency and because of a curious complication they may produce in hiding the effects of other genes also present. In *Drosophila* we have records of more than 20 sex-linked lethals, and about 15 not sex-linked, and scattering records of many others. Gametic lethal genes are those that destroy eggs or pollen cells that contain such genes. Zygotic lethal genes affect the embryo, the larva, or the adult, so that it dies. In the case of the garden plant known as double 'stocks', the genetic evidence obtained by Miss Saunders indicates that certain kinds of pollen are not produced, and presumably die because of a contained factor. The same factor does not kill the ovules, which may therefore transmit the recessive lethal gene to half the progeny. How far the frequent occurrence of imperfect pollen grains in many species of plants is due to such factors is still uncertain," p. 254.

"The 'yellow mouse case' is an example of a *zygotic lethal* effect. The gene that produces the dominant yellow color is lethal in double dose, so that all homozygous yellow mice die, as Cuénot first discovered, and as has been more positively demonstrated by the work of Castle and Little. There is some evidence indicating that these homozygotes die as young embryos. Little has also shown that black-eyed white mice carry a lethal, that acts in the same way. In *Drosophila* there is a sex-linked recessive lethal factor that causes the development of tumors in the larvae, destroying every male larva that contains the sex-chromosome carrying this gene, p. 256.

The author falls in line with the fanciers in using blue as interchangeable with gray, p. 26. "Another example of failure of complete dominance is shown in the race of Andalusian fowls. In this race there are blue, splashed-white, and black birds, the blue birds going under the name of Andalusians.....Evidently the blue birds are the heterozygous type. Their feathers show under the microscope less black pigment, somewhat differently distributed from that in the black birds. The intermediate blue color is due in this case to the less dense distribution of the pigment in the heterozygote. Lippincott, who has recently examined this cross in greater detail than heretofore, states that the colored areas or splashes in the white males are either blue or blackish according to the part of the body on which they occur, and that this corresponds with the distribution of the color on the Andalusian, for while the latter is said to be blue, this applies strictly only to the hen and to the lower parts of the body in the cock whose upper surface is very dark blue or even black."

Wilder D. Bancroft

PHYSICO-CHEMICAL STUDIES ON PROTEINS. II. ALKALI BINDING. A COMPARISON OF THE ELECTROMETRIC TITRATION OF PROTEINS AND OF PHOSPHORIC ACID WITH SODIUM AND CALCIUM HYDROXIDES*

BY WALTER F. HOFFMAN AND ROSS AIKEN GORTNER

When a protein, such as casein, is titrated electrometrically with sodium hydroxide, we have shown[1] that a curve similar to the titration of mono-sodium phosphate is obtained. In the range between the isoelectric point of the casein-water suspension and about pH 7, there is approximately one equivalent of alkali bound, if the combining weight of casein is assumed to be about 1100[2]. The curve rises sharply, resembling the titration curve for the second hydrogen of phosphoric acid. Between pH 7 and pH 10 there is a second equivalent of sodium hydroxide bound. If a protein like durumin is titrated in a similar manner, very little if any alkali is bound before a hydroxyl ion concentration greater than pH 10.5 is reached.

From the data obtained for a large number of titration curves with different proteins, using both acid and alkali[3], the postulation was made that two factors are involved when a protein combines with an acid or an alkali, i.e. stoichiometrical combination and combination due to adsorption. The former holds for the hydrogen ion concentrations represented between about pH 2.5 and 10.5 while the latter apparently holds for hydrogen ion concentrations greater than pH 2.5 and hydroxyl ion concentrations greater than pH 10.5.

The combination of alkali with proteins below a hydroxyl ion concentration of pH 10.5 resembles that of alkali and weak acids. Proteins, of which casein is a type, resemble weak acids such as monosodium phosphate while proteins, of which gliadin is a type, resemble much weaker acids. To ascertain, if possible, to what extent the behavior of proteins and acids are similar when titrated with alkali, a weak acid (phosphoric acid) was titrated in the same manner as the proteins, with both sodium and calcium hydroxide.

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[1] Colloid Symposium Monograph. Papers presented at the Second National Symposium on Colloid Chemistry. Chapter 20 (1925).

[2] This is within the experimental error of the average equivalent weight of casein, (about 1120) as given by different workers. Cf. Van Slyke and Bosworth: J. Biol. Chem. 14, 227-230 (1913) give 1111; Laquerer and Sackur: Beitr. Chem. Physiol. Path. 3, 193-224 (1903) give 1135; Long: J. Am. Chem. Soc. 28, 372-384 (1906) give 1124; Bleyer and Seidel: Biochem. Z. 128, 48-75 (1922) give 1145; and Mattaiopoulos: Z. anal. Chem. 47, 492-501 (1908) gives 1131.5. This gives casein a valency of eight, as the smallest possible molecular weight as calculated from the sulfur and phosphorus content is 8708 and 8744 respectively.

[3] Colloid Symposium Monograph. Chapter 20 (1925).

Experimental

These experiments were carried out as follows: 2 grams of casein[1] were suspended in 200 cc. of water and this suspension titrated electrometrically with sodium hydroxide. A titrating vessel as described by Bovie[2] was employed. The potential of the hydrogen ion electrode was measured in the usual manner by using a normal calomel electrode, a Leeds and Northrup, Type K potentiometer with a high sensitivity galvanometer and a saturated potassium chloride salt bridge. The hydrogen ion concentration and pH values were obtained from the tables given by Schmidt and Hoagland[3].

Small increments of exactly normal sodium hydroxide were added and the equilibrium hydrogen ion concentration determined after each addition until a total of 6.0 cc. of normal sodium hydroxide had been added to the casein suspension and a hydroxyl ion concentration greater than pH 11.0 had been produced. We have shown that this hydroxyl ion concentration is outside of range of chemical combination between a protein and sodium hydroxide. At this stage, the addition of small increments of exactly normal hydrochloric acid began and the equilibrium hydrogen ion concentration was followed until exactly enough acid had been added to neutralize all of the initially added alkali. In this way we secured two titration curves, one beginning at pH 4.7 and ending at pH 11.0, and the other beginning at 11.0, and ending at pH 4.7. No correction was made for the small dilution error. Similar experiments were carried out with casein using normal calcium hydroxide[4].

Figures 1 and 2 show the results which were obtained. These curves are the average of two or more separate titrations. Durumin was also titrated with both sodium and calcium hydroxide and "back titrated" with hydrochloric acid. The results obtained are shown in Figures 3 and 4. The proteins, teozein and fibrin, were also titrated with alkali and "back titrated" with hydrochloric acid. Results similar to those for durumin and casein were obtained.

The curve for casein and sodium hydroxide, Figure 1, resembles a typical titration curve for an acid. However, when this casein-sodium hydroxide solution is "back titrated" with hydrochloric acid, the curve does not fall exactly on the casein-sodium hydroxide curve. The points are identical until the hydrogen ion concentration has been increased to about pH 10.5, the point at which it has been suggested that the type of alkali binding by protein changes. When more hydrochloric acid is added, the solution has at equilibrium a greater hydrogen ion concentration than is indicated by the protein-sodium hydroxide titration curve. In other words, the "back titration" curve is not identical with the original titration curve.

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[1] The method of preparation and the analyses of the proteins used in this paper have been reported in an earlier paper.

[2] J. Am. Chem. Soc. 44, 2892-2893 (1922).

[3] Univ. of California Publications in Physiology, 5, 23-69 (1919).

[4] A normal solution of calcium hydroxide was obtained by using calcium sucrate. To prepare this, a 33% sucrose solution was saturated with calcium hydroxide, the excess calcium hydroxide was filtered off and the filtrate standardized.

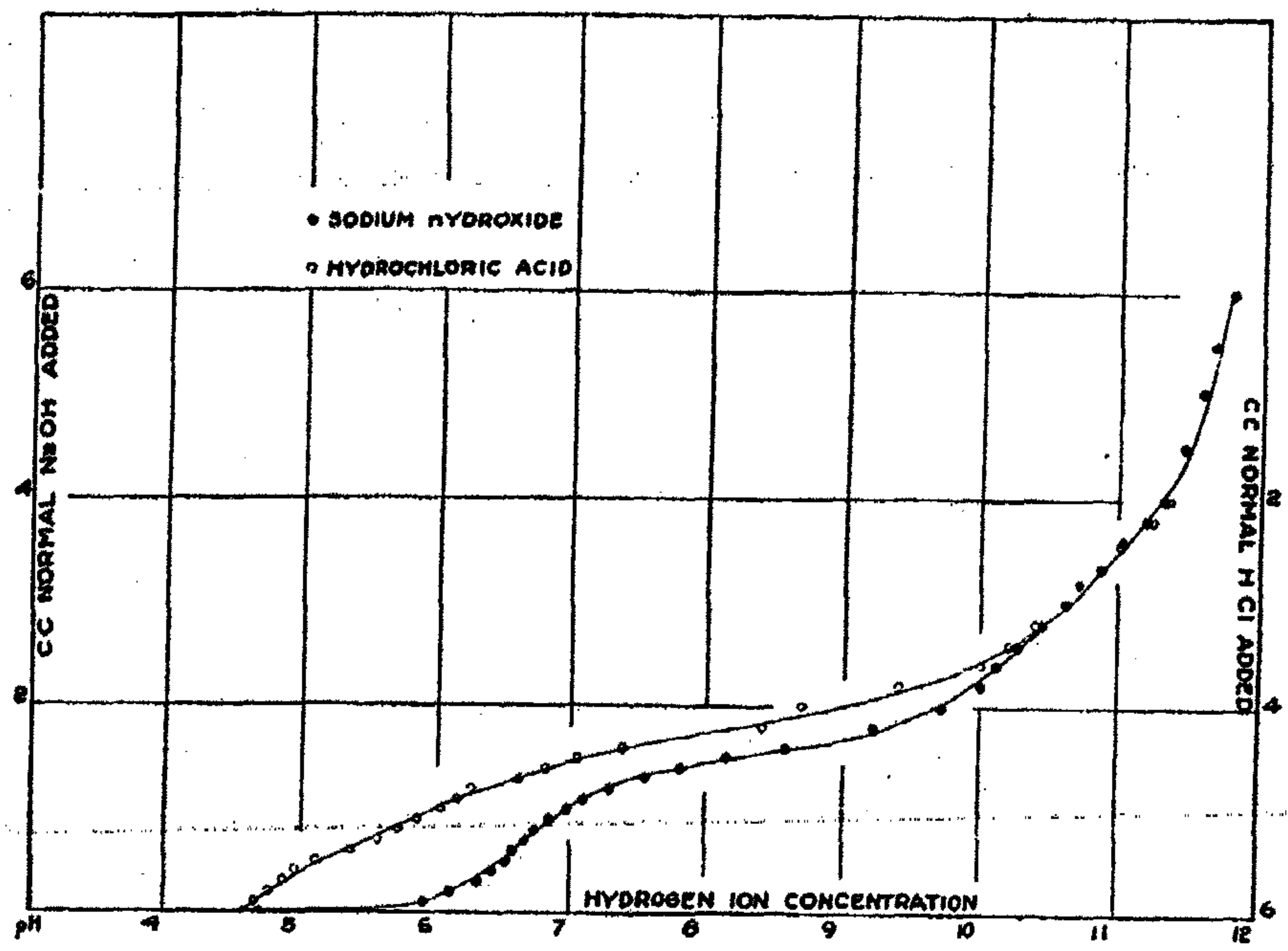

FIG. 1
Titration curve of casein with sodium hydroxide and the back titration curve of the casein-sodium hydroxide mixture with hydrochloric acid.

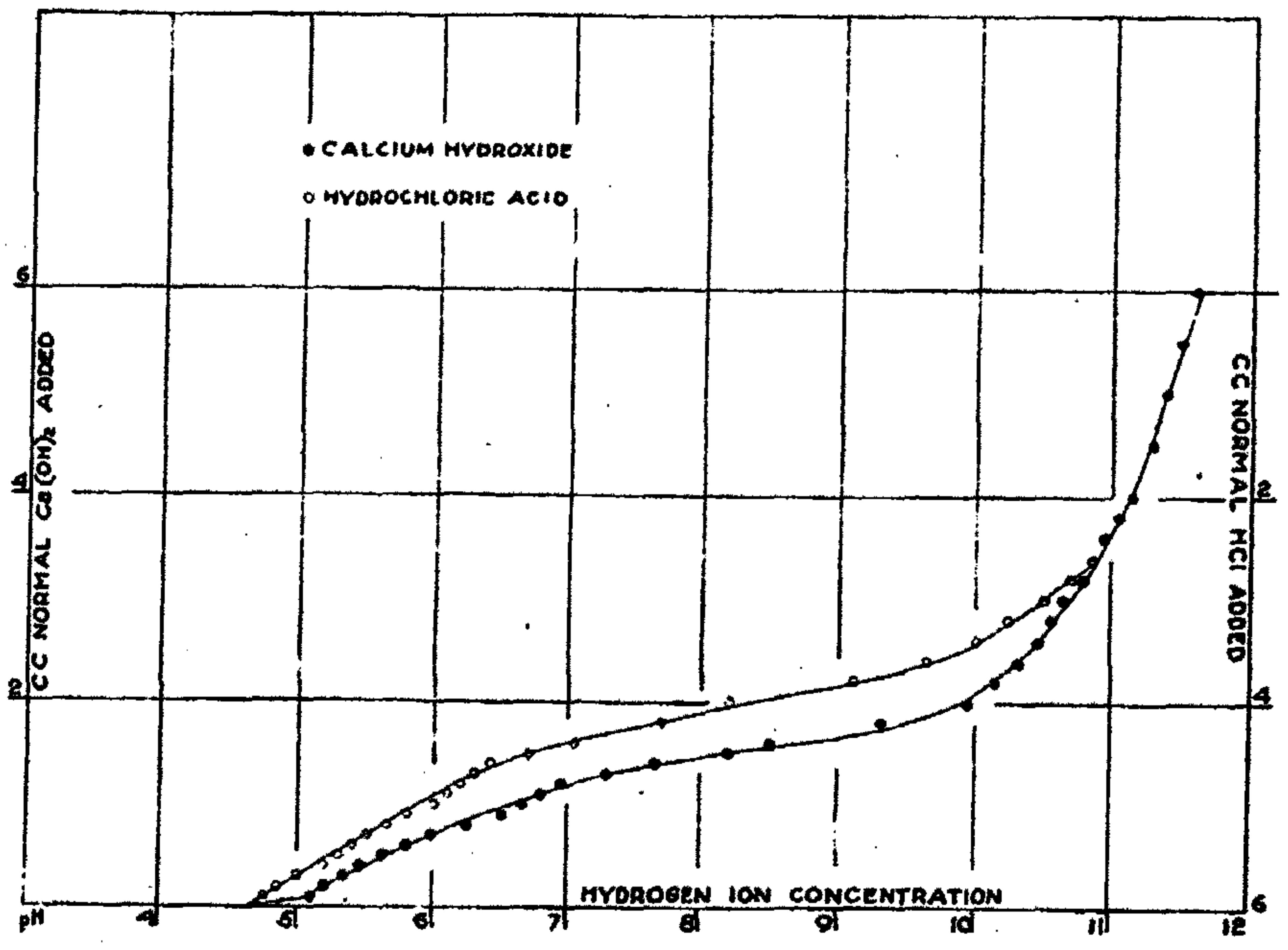

FIG. 2
Titration curve of casein with calcium hydroxide and the back titration curve of the casein-calcium hydroxide mixture with hydrochloric acid.

Casein was also titrated with calcium hydroxide, Figure 2, and a curve very similar to that of casein and sodium hydroxide was obtained. The only difference between the two curves being that casein appears to begin to bind calcium hydroxide at a slightly greater hydrogen ion concentration. At about pH 7.0 the same amount of calcium hydroxide as sodium hydroxide is bound and the remainder of the curve is practically the same as the sodium hydroxide curve.

These experiments show that proteins of which casein and fibrin are examples, contain groups which titrate as acids which have more or less definite end points. This type of proteins binds appreciable amounts of alkali even below pH 7.0. Another type of proteins of which durumin and teozein are examples shows very little if any acidic properties as they bind no alkali below pH 7.0 and very little below pH 10.5.

In order to compare these alkaline titration curves of proteins with those of acids, phosphoric acid was titrated in an identical manner. Two hundred cc. of M/100 phosphoric acid was titrated electrometrically with normal sodium hydroxide, Figure 5, and with normal calcium hydroxide, Figure 6. After 7.2 cc. of the alkali had been added, this being 1.2 cc. in excess of that theoretically required to completely neutralize the phosphoric acid, the solution, in the case of sodium phosphate, and suspension, in the case of calcium phosphate, was "back titrated" with an equivalent amount of hydrochloric acid.

The titration curve of phosphoric acid with sodium hydroxide, Figure 5, is very similar to the curve obtained by Bovie[1]. The first hydrogen is neutralized at about pH 3.5, the second is neutralized at about pH 7.5 and the third which corresponds to the tertiary sodium phosphate does not exist as such in this solution, and hence does not appear in the curve. Abbott and Bray[2] give the following ionization constants at 18° C. for phosphoric acid:

$$H_2PO_4' + H^+ = 1.1 \times 10^{-2}$$
$$HPO_4'' + H^+ = 1.95 \times 10^{-7}$$
$$PO_4''' + H^+ = 3.6 \times 10^{-13}$$

The curve obtained when back titrating the phosphoric acid-sodium hydroxide solution with hydrochloric acid differs very little from the phosphoric acid-sodium hydroxide titration curve. The differences are not much more than can be attributed to experimental errors.

The titration curve of phosphoric acid with calcium hydroxide, Figure 6, is distinctly different from that for phosphoric acid and sodium hydroxide. The first or primary hydrogen is titrated at about the same pH in both cases, i.e., one equivalent of calcium hydroxide completely neutralized the primary hydrogen at about pH 3.5. When the second equivalent of calcium hydroxide had been added there was no definite break in the curve as in the case of the sodium hydroxide curve. It was not until the third equivalent of calcium hydroxide had been added that the curve broke sharply toward the alkaline region. This break in the curve occurs at about pH 7.5. *When ortho-phosphoric acid is titrated with calcium hydroxide the secondary and tertiary hydrogens titrate as a single hydrogen, i.e. both appear to be equally active. Under these*

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[1] J. Am. Med. Assoc. 33, 295-322 (1915-1916).

[2] J. Am. Chem. Soc. 31, 729-763 (1909).

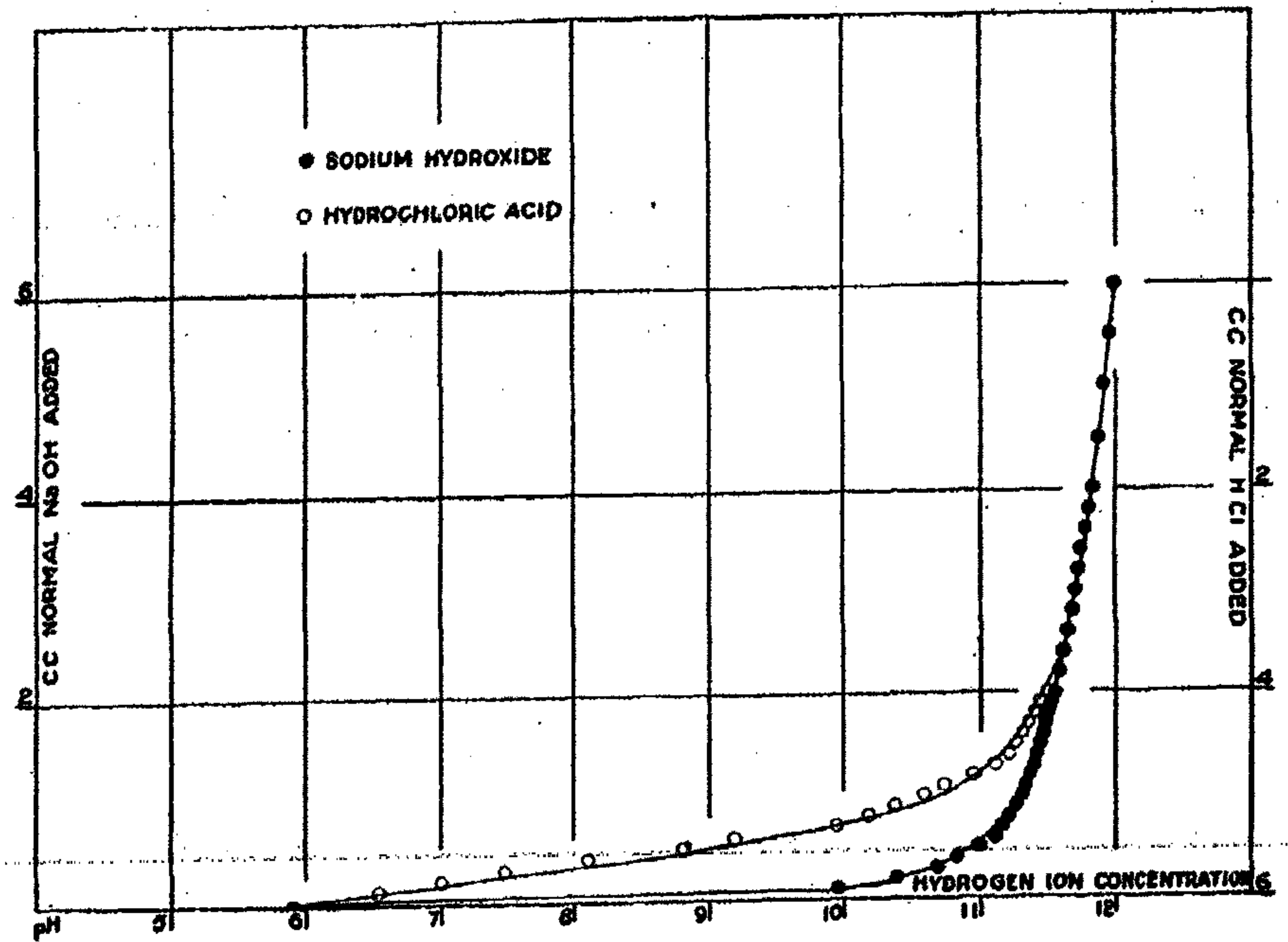

Fig. 3

Titration curve of durumin and sodium hydroxide and the back titration curve of the durumin-sodium hydroxide mixture with hydrochloric acid.

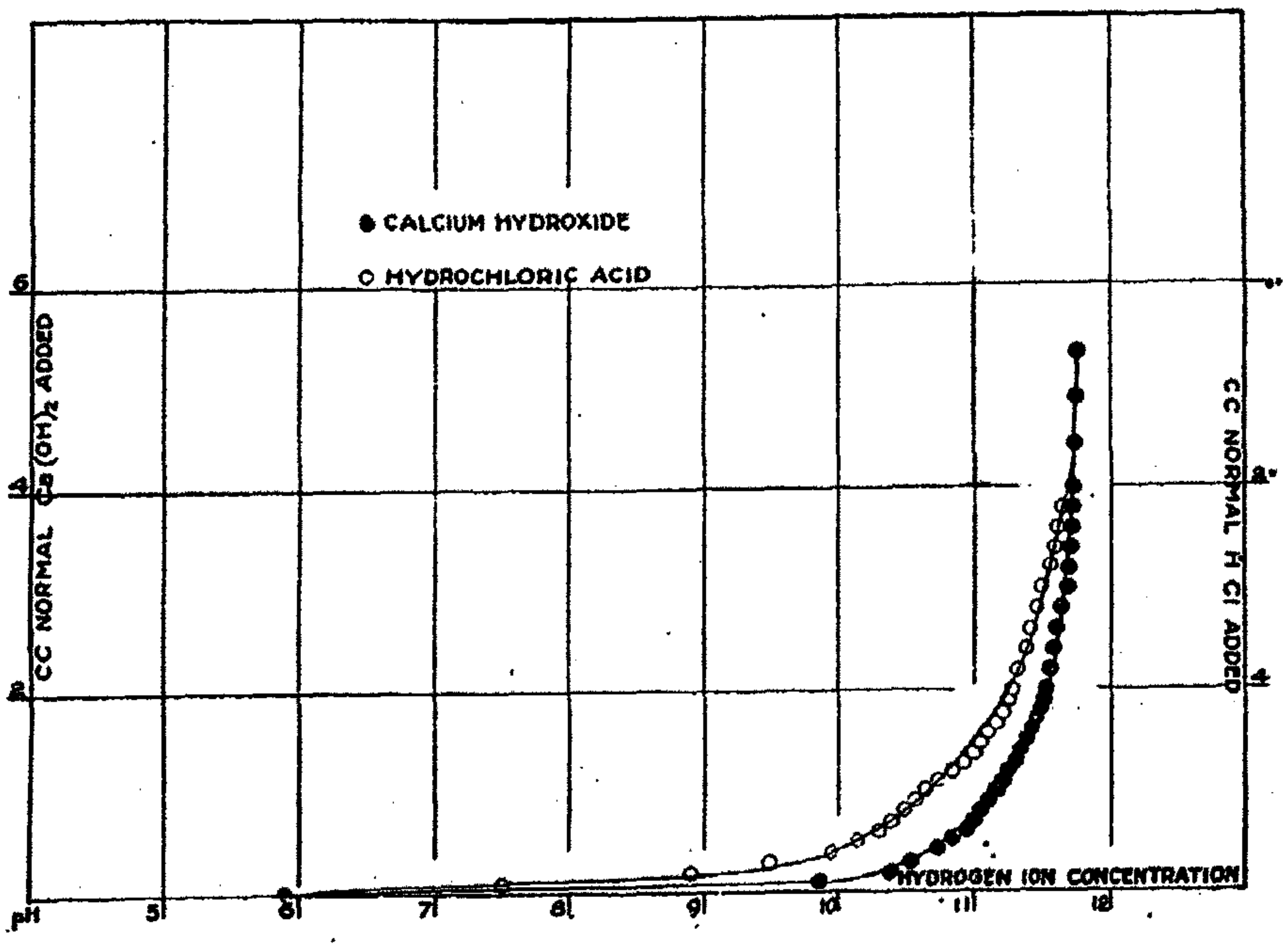

Fig. 4

Titration curve of durumin with calcium hydroxide and the back titration curve of the durumin-calcium hydroxide mixture with hydrochloric acid.

conditions, the tertiary hydrogen of phosphoric acid is neutralized at pH 6.8-7.5, although its ionization constant is given as 3.6×10^{-13}.

The curve obtained when the phosphoric acid-calcium hydroxide solution was back titrated with hydrochloric acid is distinctly different from the initial phosphoric acid-calcium hydroxide curve. When 1.2 cc. of hydrochloric acid had been added, the hydrogen ion concentration did not differ greatly from that obtained when 6.0 cc. of calcium hydroxide had been added to the phosphoric acid. However, after 3.2 cc. of hydrochloric acid had been added, the hydrogen ion concentration was appreciably greater (approximately 0.8 pH) than when 4 cc. of calcium hydroxide had been added to the phosphoric acid. The two curves are identical after 5.2 cc. of hydrochloric acid had been added. This "lag" in the hydrochloric acid back titration curve is very similar to that described above in the case of proteins (cf. casein curves).

Barium hydroxide was also used in titrating phosphoric acid. The titration curves thus obtained were so similar to those of calcium hydroxide and phosphoric acid, that their reproduction here is superfluous.

Several other acids, (uric, citric, tartaric and boric) were titrated with both sodium hydroxide and calcium hydroxide and the solutions were back titrated with hydrochloric acid. In all cases the hydrochloric acid back titration curve showed a "lag" over the initial acid and alkali curve, similar to the curves which are reproduced in the figures.

In another experiment, phosphoric acid was titrated with calcium hydroxide and this solution then back titrated with oxalic acid. Both of these curves were identical. *There was no "lag" in the oxalic acid curve.*

Two possible explanations suggest themselves to account for this difference or "lag" in the curves. These are; (1) that the solution did not come to equilibrium immediately after the hydrochloric acid had been added and sufficient time had not elapsed before the hydrogen ion concentration was measured; and (2) that the reaction,

$$Ca_2H_2(PO_4)_2 + 4HCl \rightleftharpoons 2CaCl_2 + 2H_3PO_4$$

did not go to completion but that some free hydrochloric acid remained in solution. As hydrochloric acid is much more active than phosphoric acid, the solution would then have a greater hydrogen ion concentration.

The first possibility was tested experimentally as follows: 7.2 cc. of normal calcium hydroxide was added to 200 cc. of M/100 phosphoric acid and then 3.2 cc. of normal hydrochloric acid was added to this suspension. The hydrogen ion concentration of this mixture was then measured at different intervals of time by use of the Bailey electrode[1]. Immediately after the addition of the hydrochloric acid, the solution had a hydrogen ion concentration equivalent to pH 5.342. Several measurements were made during the first hour after the addition of the hydrochloric acid but no appreciable change was observed. After 6 hours, during which time the flask had been shaken several times, the solution had a hydrogen ion concentration equivalent to pH 5.384. Another solution was tested, using the bubbling electrode. Immediately after the addition of the hydrochloric acid the solution had a hydrogen ion concentration

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[1] J. Am. Chem. Soc. 42, 45-48 (1920).

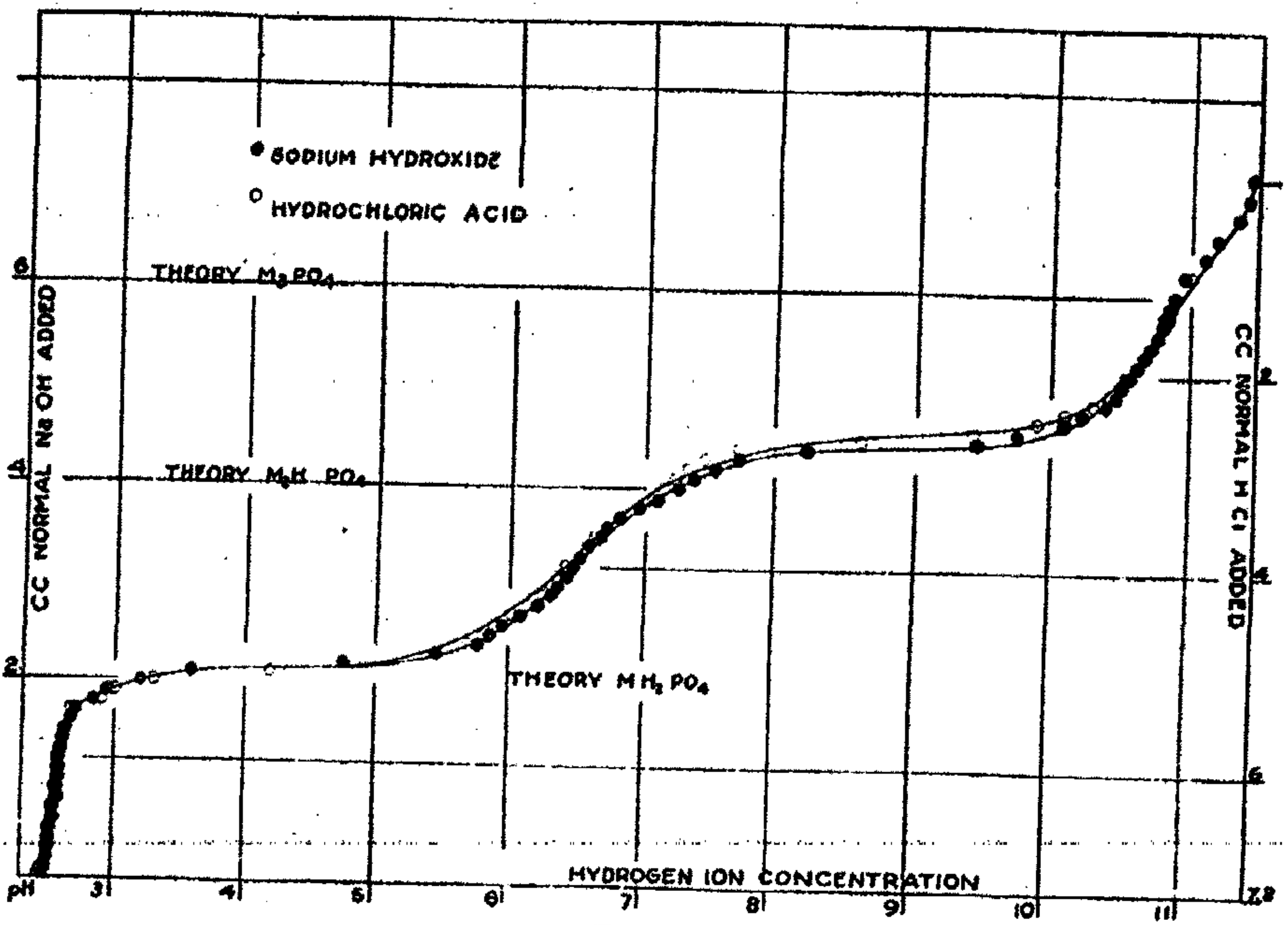


FIG. 5

Titration curve of phosphoric acid with sodium hydroxide and the back titration curve of the phosphoric acid-sodium hydroxide mixture with hydrochloric acid.

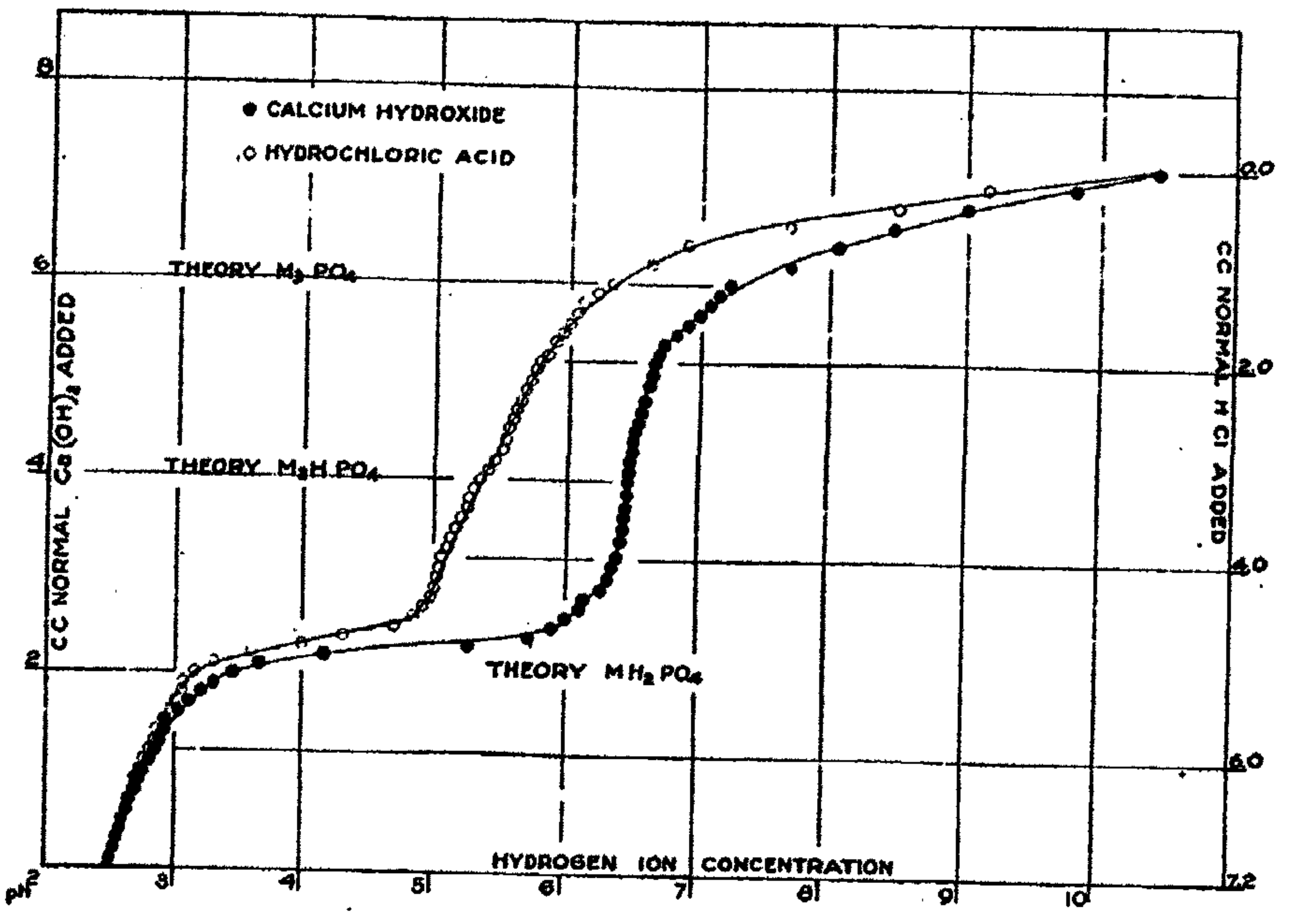


FIG. 6

Titration curve of phosphoric acid with calcium hydroxide and the back titration curve of the phosphoric acid-calcium hydroxide mixture with hydrochloric acid.

of pH 5.342. After 30 minutes, with a continual flow of hydrogen, no change was observed in the hydrogen ion concentration. These data indicate that the difference between the curves is not due to a time factor, and that equilibrium is established very soon after the addition of the hydrochloric acid.

The second possibility was tested by preparing solutions of phosphoric acid (200 cc. of M/100) and calcium hydroxide and then adding some calcium chloride, (approximately 0.20 gm. of *anhydrous* $CaCl_2$ reacting faintly alkaline to phenolphthalein[1].) The hydrogen ion concentration was measured both before and after the addition of calcium chloride. The results obtained were

pH before adding $CaCl_2$	pH after adding $CaCl_2$
5.334	5.094
6.120	5.495

Similar results were obtained with casein. A solution containing 100 cc. of 1 per cent casein suspension and approximately 0.7 cc. of normal sodium hydroxide had a hydrogen ion concentration equivalent to pH 7.455. After the addition of 0.20 gram of the calcium chloride, the solution had a hydrogen ion concentration equivalent to pH 6.424. These data show that when calcium chloride is added to calcium phosphate or calcium caseinate, the hydrogen ion concentration is increased, probably by the formation of some free hydrochloric acid. This accounts for the difference or "lag" between the two titration curves as shown in Figures 1 to 6.

The sodium salts of phosphoric acid as described in the literature are

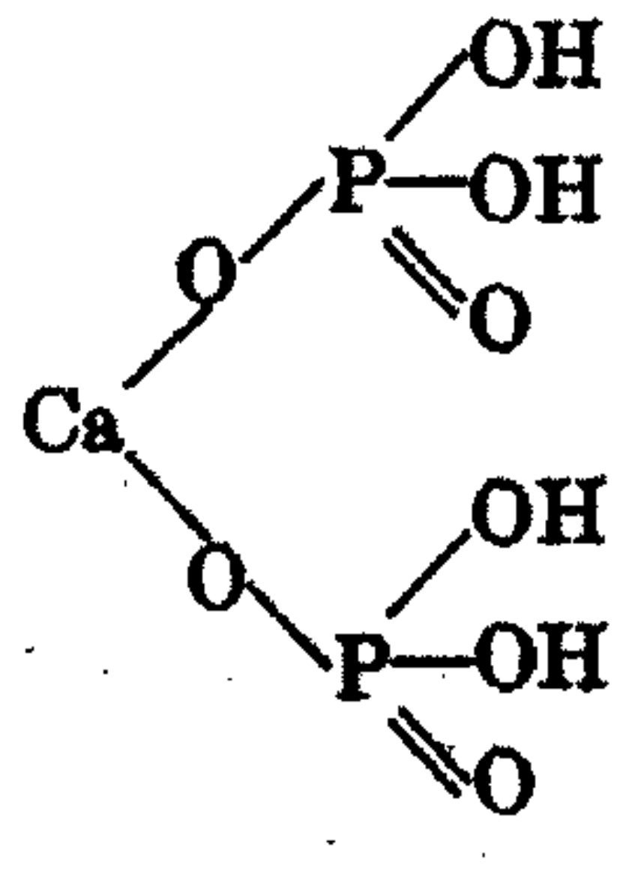
NaH_2PO_4	Monosodium phosphate (formed $<$ pH 3.5)
Na_2HPO_4	Disodium phosphate (formed between pH 6.0 – 7.5)
Na_3PO_4	Trisodium phosphate (formed $>$ pH 12.0)

The calcium salts as usually described in the literature are

$CaH_4(PO_4)_2$	Mono-calcium phosphate
$CaH\ PO_4$	Di-calcium phosphate
$Ca_3\ (PO_4)_2$	Tri-calcium phosphate

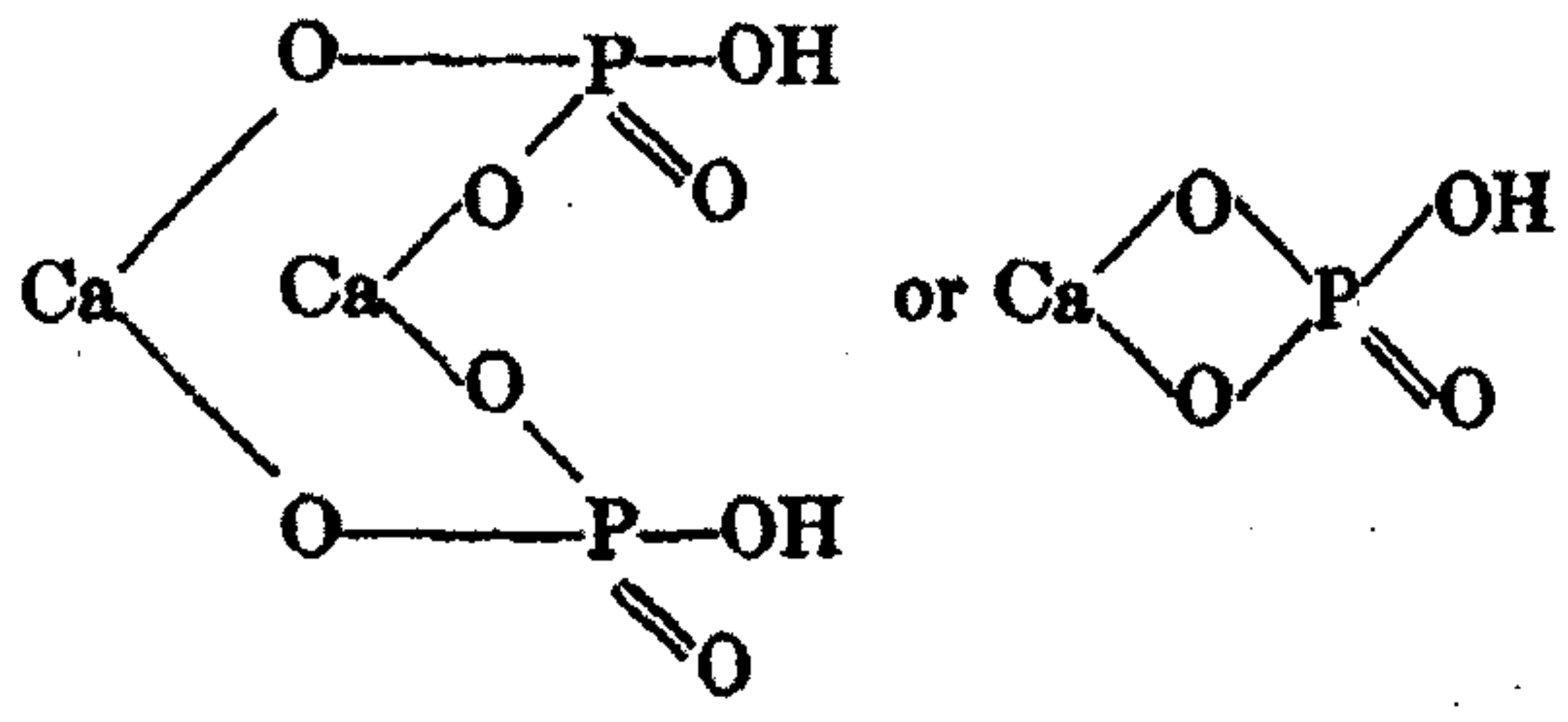
These are supposed to be formed at the same or approximately the same hydrogen ion concentrations as are the sodium salts.

The calcium salts of phosphoric acid expressed graphically as compared to the salts of sodium phosphate would be



I

Mono-calcium phosphate



II

Di-calcium phosphate

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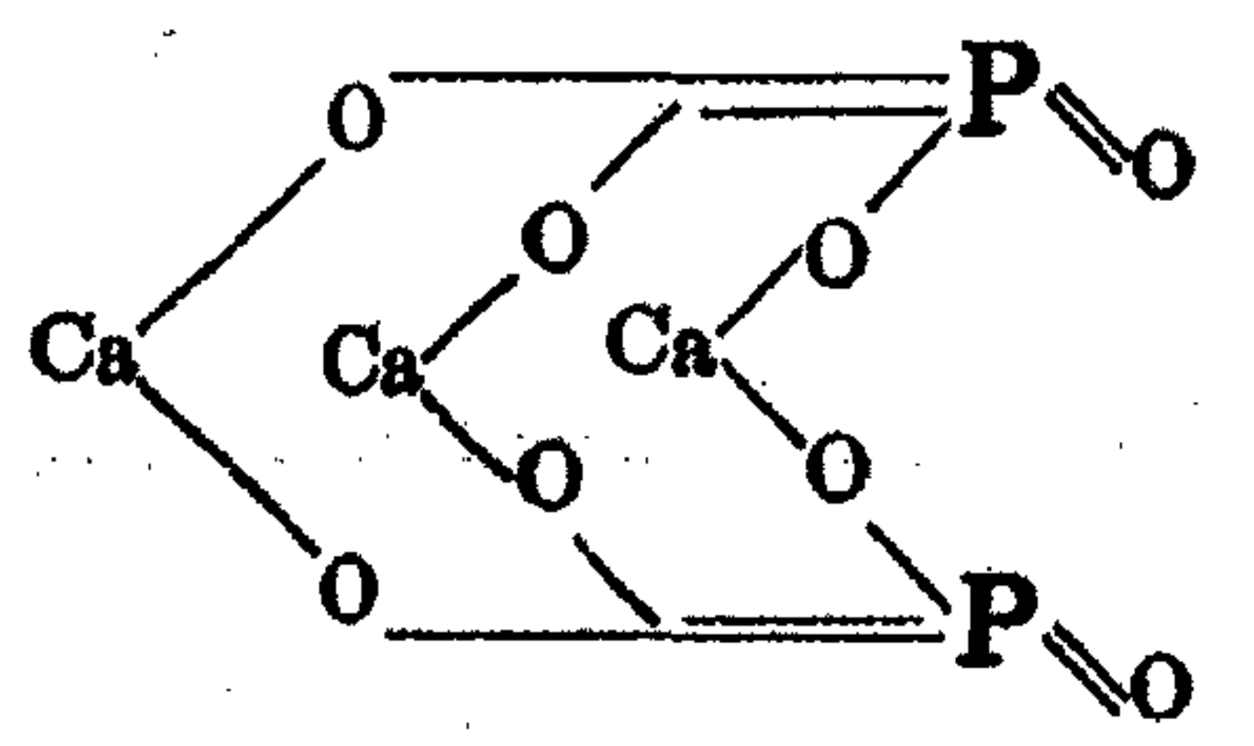
[1] An alkaline $CaCl_2$ was chosen so that any shift of the pH toward the acid side could no be attributed to the salt added.

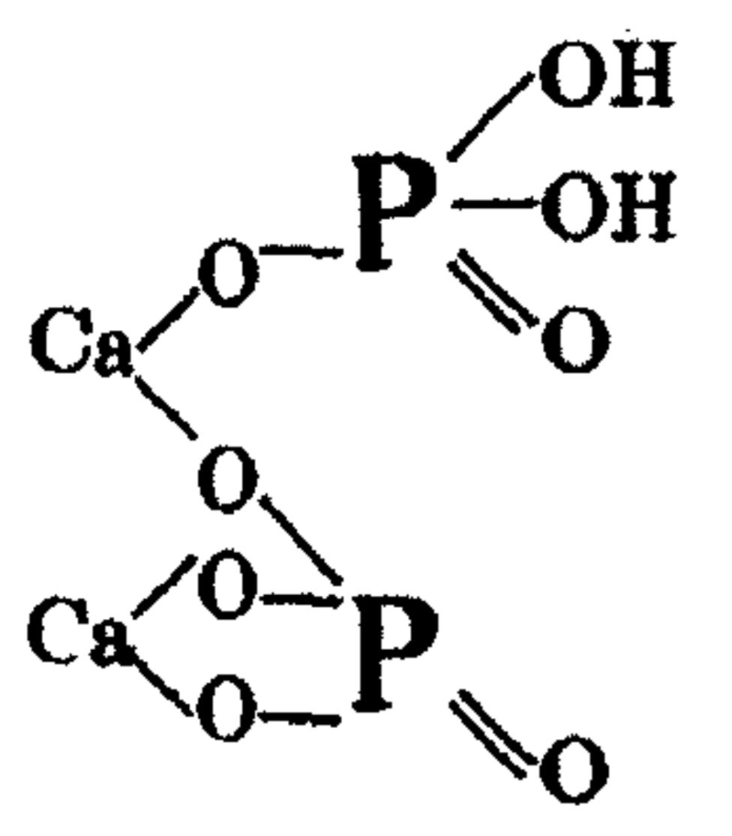


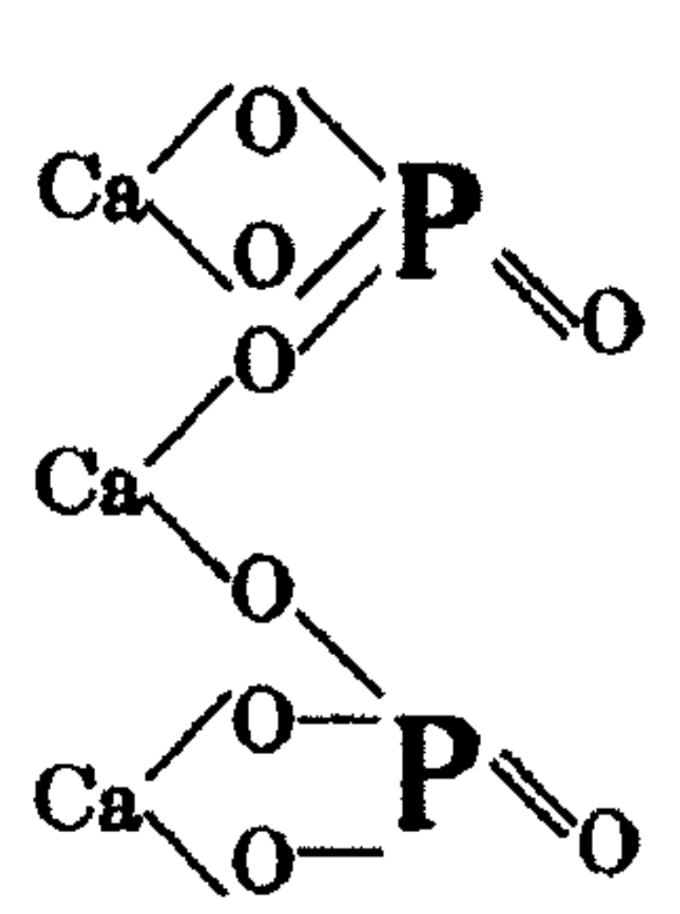
III

Tri-calcium phosphate

Our experimental data do not support the above structural formulae inasmuch as *dicalcium phosphate, tri-calcium phosphate and disodium phosphate are formed at the same hydrogen ion concentration.* This indicates that both the secondary and tertiary hydrogens of the phosphoric acid are neutralized by calcium hydroxide at the same time, regardless of the ionization constant of the tertiary hydrogen.

The following graphic formulae for the so-called di-calcium phosphate and the tri-calcium phosphate meet the requirements of our experimental data:





IV
Di-calcium Phosphate

V
Tri-calcium Phosphate

According to these formulae, the calcium salt of phosphoric acid which analyses for $Ca_2H_2(PO_4)_2$ or di-calcium phosphate, is actually a compound consisting of two molecules of phosphoric acid, one molecule of which has all of its hydrogens replaced by calcium and the other having only the primary hydrogen replaced by calcium. Evidence that this is the case is furnished by the following experiment. Two hundred cc. of molar phosphoric acid was titrated electrometrically with normal calcium hydroxide, until exactly enough calcium hydroxide had been added to form "di-calcium phosphate." At this point, the calcium hydroxide burette was replaced by one containing normal sodium hydroxide and the electrometric titration was continued with the sodium hydroxide. If at this point the salt in the titration vessel corresponds to formula II, only tertiary hydrogens of phosphoric acid are present and no sodium should be "bound" below pH 12.0. On the other hand, if formula IV is correct both a secondary hydrogen and a tertiary hydrogen are present and half an equivalent of sodium should be bound at about pH = 7.5 and an equal amount of pH greater than 12.0. Figure 7 shows that the titration corresponds to formula IV for sodium hydroxide was bound at pH 7.5 in approximately the required amount. After half of an equivalent of sodium hydroxide is added further additions of sodium hydroxide caused the hydroxyl ion concentration to progressively increase until it finally approaches that obtained when sodium hydroxide alone is employed in titrating phosphoric acid

Additional proof that this peculiar behavior of phosphoric acid and calcium hydroxide as compared to that of sodium hydroxide is correct is furnished by the work of Robb, Medes, McClendon, Graham and Murphy[1], who found that apatite when suspended in solutions of varying hydrogen ion concentrations did not dissolve when the hydrogen ion concentration was equivalent to pH 5.5, but did lose weight in solutions of pH 5.0. Briefly their results are

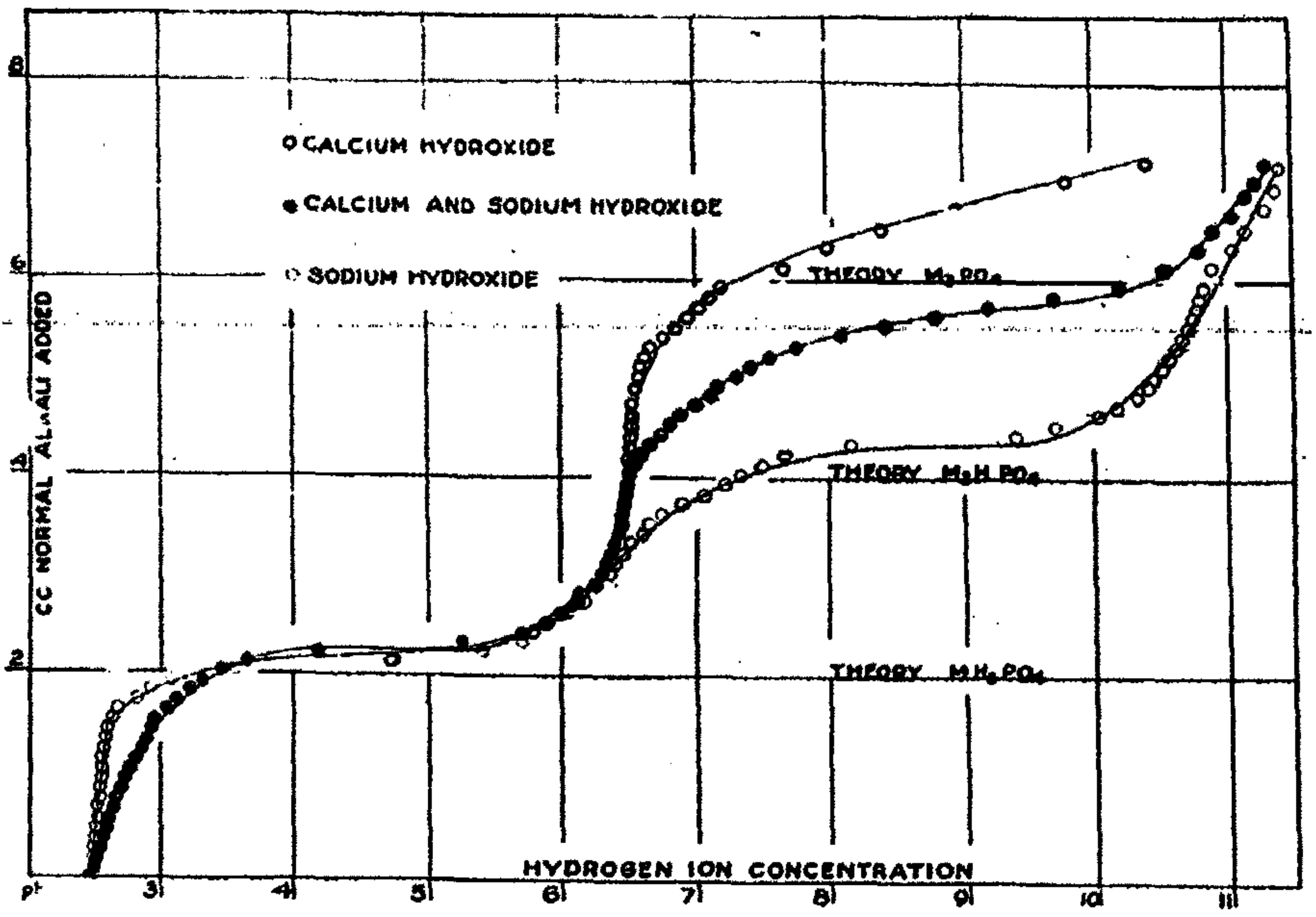


FIG. 7

Titration curves of phosphoric acid with sodium hydroxide, with calcium hydroxide and with sodium and calcium hydroxides.

Apatite Original Weight gms.	pH of solution	Loss of Weight after 2 months and 3 days mg.
2.7272	6.0	1.0
2.7024	5.5	0.3
2.5942	5.0	67.2

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[1] J. Dent. Res. 3, 39-61 (1921).

Atkins[1] has also shown that tri-calcium phosphate is much less soluble at pH 7.0 than at pH 5.1, changing from 114 to 786 parts per million. Both of these investigations show that tri-calcium phosphate is stable at pH 7 and is not decomposed until an acidity of about pH 5.0 is reached. The tri-calcium phosphate formed in nature further substantiates these data. If tri-calcium phosphate is not stable when the hydroxyl ion concentration is less than about pH 12.0, the teeth, bones, shells of aquatic animals, etc., could not exist at the acidity of the body fluids.

It has been suggested that the calcium salt of milk is di-calcium phosphate principally because of the assumption that it is impossible for tri-calcium phosphate to exist as such at the hydrogen ion concentration (pH 6.5) of milk. Our experimental data show that tri-calcium phosphate can exist and is stable when in solutions having a hydrogen ion concentration equivalent to that found in milk.

The results shown by the calcium hydroxide-casein curve and the calcium hydroxide-casein-hydrochloric "back titration" curve, are directly related to much of the work that has been done on the calcium salts of casein. Most of the calcium salts of casein have been prepared[2] by making "alkaline calcium caseinates" and then adding acid until the desired acidity is reached. From Figure 2 it is readily seen that at any particular hydrogen ion concentration between the isoelectric point of casein (pH 4.7) and pH 10.5 a calcium-casein salt of the same composition is not formed by the two methods of preparation, (1) direct addition of alkali to an isoelectric casein suspension, and (2) adding acid to an alkaline calcium caseinate. Our data indicate that this is a general rule and that it holds likewise for the sodium salts of casein and for the calcium or sodium salts of other proteins.

Addendum. Since writing the above our attention has been called to the work of Wendt and Clarke[3] who carried out a study of the electrometric titration of phosphoric acid with a solution of calcium hydroxide (saturated lime water). The curves which they present show striking differences from those which we obtained. We do not believe that these differences can be due to the fact that we used "calcium sucrate" as the alkali, for calcium sucrate readily hydrolyzes in dilute solution to calcium hydroxide and sucrose. The small amount of sucrose (2.376 gr. in 200 cc.) in our final mixture is too little to have a marked effect on the form of the curves. In certain of our experiments we have observed similar irregularities, i.e. an apparent *increase* in hydrogen ion concentration when an increment of the calcium hydroxide was added. We attributed such an abnormal behavior to a "poisoning" of the hydrogen electrode and in each instance where such an effect was observed we have found that replacing the electrodes with a new one previously checked against a buffer solution caused the abnormal dip in the curve to disappear. The fact that Wendt and Clarke were able to titrate calcium hydroxide with phosphoric

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[1] Nature, 114, 275 (1924).

[2] Bosworth and Van Slyke: J. Biol. Chem. 14, 207-209 (1913); Van Slyke and Hart: Am. Chem. J. 33, 461 (1905); Long: J. Am. Chem. Soc. 27, 372-384 (1906); Van Slyke and Bosworth: J. Biol. Chem. 14, 211-225 (1913).

[3] J. Am. Chem. Soc. 45, 881-887 (1923).

acid and not get the pronounced irregularities (Curve b, Fig. 1 W. and C.) but instead to get a curve very similar to our own is noteworthy. They state that this curve shows that "the two vertical drops correspond to the tri- and the mono-calcium salts, respectively. . . . . The volumes of acid solution added to produce them are 10 and 30 cc." Thus Wendt and Clarke have already presented data showing that the secondary and tertiary hydrogen of phosphoric acid titrate together when calcium hydroxide is used as an alkali and that there is no inflection of the curve for the secondary hydrogen as is the case when sodium hydroxide is used.

Wendt and Clarke believe that rearrangement takes place, that di-calcium phosphate is unstable and rearranges to form tri-calcium phosphate and mono-calcium phosphate. They believe that the irregular titration curve which they obtained in the titration of phosphoric acid with lime water indicates an unstable equilibrium. We have found no evidence for a shift in hydrogen ion concentration toward the acid side in our solutions on standing and prefer to accept our Formula IV for di-calcium phosphate until further evidence is available. Such a formula as already noted will adequately explain our findings as well as Curve b, Figure 1 of Wendt and Clarke.

Probably a phase rule study of the calcium-phosphoric acid equilibrium would decide these questions and it is to be hoped that some one will undertake such a study. If Formula IV is correct it should be possible to isolate a new series of salts of the general formula, $Ca_2MH(PO_4)_2$, where M is a monovalent metal.

Summary

1. Phosphoric acid and the proteins, casein and durumin, have been titrated electrometrically with both sodium and calcium hydroxide, and "back titrated" with hydrochloric acid.

2. The alkali titration curves of casein and fibrin show binding of alkali at about pH = 5.5 and resemble the curve for a weak acid such as mono-sodium phosphate. Other proteins, of which durumin is a type, behave as much weaker acids, beginning to bind alkali only at about pH = 10.0.

3. The same type of curves are obtained when a protein is titrated with either sodium hydroxide or calcium hydroxide.

4. When phosphoric acid is titrated with sodium hydroxide and calcium hydroxide, the two curves are not similar. In the latter case, both the secondary and tertiary hydrogens are replaced by calcium at the same pH at which di-sodium phosphate is formed.

5. The titration curves of protein + alkali and of phosphoric acid + alkali are not identical at similar hydrogen ion concentrations with the curves formed by a subsequent "back titration" with hydrochloric acid. There is a "lag" in the back titration curves.

6. This "lag" is shown to be due to the reaction

$$Ca_2H_2(PO_4)_2 + 4HCl = 2CaCl_2 + 2H_3PO_4$$

not going to completion resulting in an equilibrium and the presence of free hydrochloric acid which increases the hydrogen ion concentration.

7. All three hydrogens of phosphoric acid may be titrated by calcium hydroxide below a pH of 8.0. The bearing of this observation on the graphic structure of di-calcium phosphate and tri-calcium phosphate is discussed.

8. Tri-calcium phosphate is apparently stable in solutions as acid as pH 6.5. This has important bearings on physiological and biochemical problems.

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IONISATION OF TWO ELECTROLYTES IN ALCOHOL-WATER MIXTURES; INFLUENCE OF ENVIRONMENT ON IONISATION

BY F. BRADLEY AND W. C. M. LEWIS

Part I

While it is now fairly certain that strong electrolytes are almost completely ionised, the classical concept of degree of ionisation of an electrolyte can still be applied with advantage to weak or moderately strong electrolytes and the further classical assumption—that the degree of ionisation of an electrolyte at a given dilution is given by the ratio of the equivalent conductivity at that dilution to the equivalent conductivity at infinite dilution—may also be employed. These concepts are more particularly applicable to the interpretation of certain experimental data referring to the influence of environment upon the ionisation of weak and moderately strong electrolytes.

The ionisation of salicylic acid, cyanacetic acid and bromacetic acid has been investigated by Godlewski[1], and although this author's results are not too accurate they do show roughly the enormous influence that the solvent has upon the ionisation of these acids. According to Godlewski the ionisation constant of salicylic acid at 18° in alcohol is only one ten-thousandth of that in water. Neale[2] found much the same state of affairs for picric acid in acetone-water mixtures—the addition of acetone to an aqueous solution of picric acid diminishes the ionisation constant many times. Recently Pring[3] has shown the same to be true for weak bases in acetone-water mixtures.

Up to the present, however, the only relation which attempts to express, in a semi-quantitative manner, the influence of the solvent upon the ionisation of an electrolyte is the following:

$$\frac{K_1}{K_2} = \frac{D_1^3}{D_2^3}$$

where K_1 and K_2 are the ionisation constants of an electrolyte in two media of dielectric constants D_1 and D_2 respectively. In various forms this relation has been deduced by Baur[4], by Krüger[5] and by Walden[6], and it is really only a simple quantitative expression of the Nernst-Thomson rule. For electrolytes obeying the law of mass action, however, this relation is quite incapable of expressing the great changes in the ionisation constant K which occur while the dielectric constant D undergoes only relatively small change, and it was therefore obvious that a really satisfactory explanation of the behaviour of such

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[1] J. Chim. phys. 3, 393 (1905).

[2] Trans. Faraday Soc., 17, 505 (1921).

[3] Trans. Faraday Soc., 19 705 (1924).

[4] Z. Elektrochemie, 11, 936 (1905).

[5] Z. Elektrochemie, 17, 453 (1911).

[6] Z. phys. Chem. 94, 263 (1920).

electrolytes in different solvents would have to be based on different physical concepts.

The first step was the obtaining of reliable experimental data, and to this end the conductances of solutions of salicylic acid and of cyanacetic acid were measured over a complete range of alcohol-water mixtures at both 25° and 35°. In the course of this investigation it was found that a considerable number of the existing data on the subject were based upon erroneous values of the equivalent conductivity at infinite dilution, a fact which of course vitiates to a large extent their utility[1].

The usual method was used for determining the conductances of the solutions, employing a metre wire bridge which was carefully calibrated. The cells used were of the Arrhenius closed type, made of borosilicate glass, with rigidly supported vertical electrodes. The electrodes were either lightly platinised or simply of smooth platinum, since only with such electrodes was it found possible to obtain accurate values. The experimental error in measuring the resistance of a solution did not exceed 0.1 per cent. Conductivity water having a specific conductance of 0.7×10^{-6} to 1.0×10^{-6} mhos at 25° was employed throughout; the specific conductivity of the alcohol varied between 6.0×10^{-8} and 1.0×1.0^{-7} mhos at 25°. The alcohol used was the product of thorough drying with highly active quicklime (prepared by roasting marble at 800° to 1000° for some hours[2]) followed by several distillations in a special apparatus. The thermostats were maintained at 25° and 35° to within 0.02°. All the conductivities were corrected for the conductivity of the solvent by subtracting this quantity from the observed conductivity. Special attention was paid to the obtaining of accurate values of the equivalent conductivity at infinite dilution. It was concluded that the most reliable method of estimating these values was to determine the mobilities of the separate ions and to apply Kohlrausch's law of the independent mobility of ions. Consequently the conductances of dilute solutions of hydrochloric acid, of sodium chloride and of the sodium salts of the acids concerned were examined over the whole range

TABLE I

Equivalent Conductivity at Infinite Dilution

Per cent alcohol	Salicylic acid		Cyanacetic acid	
	25°	30°	25°	35°
0.0	382.5	439.0	392.0	449.0
16.2	248.6	299.0	255.7	307.5
33.2	160.0	202.0	165.3	209.0
52.0	105.8	135.8	110.6	141.7
73.5	66.0	84.4	68.5	87.4
85.7	52.0	66.1	54.0	68.0
95.0	46.0	57.0	48.0	59.5
100.0	86.0	107.0	87.0	108.0

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[1] Cf. Godlewski's results: loc. cit.

[2] J. Am. Chem. Soc., 30, 353 (1908).

of alcohol-water mixtures. The numerical values of the equivalent conductivity at infinite dilution for salicylic acid and cyanacetic acid are recorded in Table I. Throughout this paper the term "per cent alcohol" means per cent by weight, i.e., grams alcohol per 100 grams of alcohol-water mixture.

In all the alcohol-water mixtures the ionisation constants of salicylic acid were found to be nearly independent of the dilution. The same slight trend with dilution of the ionisation constant was observed in all cases, in the sense that the ionisation constant decreases as the dilution increases, but over the range of dilution studied, usually 8 to 1024[1] litres, the variations never exceeded 5% of a mean value and were often considerably less. Cyanacetic acid showed the same behaviour, although the variation with dilution of the ionisation constant was slightly greater. Table II gives the experimental values of the ionisation constants for salicylic acid and cyanacetic acid in alcohol-water mixtures.

TABLE II

Per cent alcohol	$K \times 10^5$ [2] Salicylic acid		$K \times 10^5$ Cyanacetic acid	
	25°	35°	25°	35°
0.0	100.0	103.0	320.0	304.0
16.2	66.0	65.3	190.0	180.0
33.2	26.0	25.0	94.0	88.0
52.0	9.0	8.8	36.0	33.9
73.5	1.8	1.7	8.4	7.4
85.7	0.45	0.40	1.7	1.4
89.0	0.25	0.23	1.0	0.9
93.3	0.08	0.07	0.37	0.33
97.8	0.01	0.01	0.05	0.045
100.0	0.00024	0.00026	0.0032	0.0030

Theoretical

Let AB be an unionised melecule about to undergo ionisation into ions A^+ and B^- in a solvent of dielectric capacity D. Assuming that the molecule AB requires on the average a critical amount of energy E, which it must absorb before it can ionise, the rate of ionisation will be

$$k_1 . e^{-E/RT} \times C_{AB}$$

where k_1 is a reaction velocity constant independent of temperature, and C_{AB} is the concentration of the unionised molecules. If we now identify the critical increment E with the electrostatic work expended in separating the charged ions A^+ and B^- (constituting the unionised molecule) to a distance beyond their sphere of mutual attraction we can write

$$E = E_0/D$$

where E_0 is the critical increment in a medium of dielectric capacity unity, i.e., in vacuo, or in the gaseous state.

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[1] Measurements were taken at dilutions of 8, 16, 32, 64, 128, 256, and 1024 litres.

[2] Rounded values, measured at a dilution of 1024 litres.

Applying similar ideas to the recombination of the ions to form the unionized molecule we obtain the rate of union

$$k_2 . e^{-E_o'/DRT} \times C_A \times C_B$$

where the sum of the critical increments of the ions E′, is identified with the work necessary to remove the solvent molecules with which the ions are hydrated.

Equating the expressions for the rate of ionisation and for the rate of recombination of ions we have at equilibrium

$$\frac{C_A \times C_B}{C_{AB}} = \frac{k_1}{k_2} e^{(E_o'-E_o)/DRT} \qquad (1)$$

and the left hand side of this equation is obviously the ordinary ionisation constant.

This relation embodies in simple form the purely physical influences operative in the ionisation of an electrolyte, and as will be seen from the comparison of calculated with observed ionisation constants which is contained in the following table, it represents the observed results much better than does the relation $K \propto D^3$. It is, however, by no means satisfactory. Nevertheless the physical picture which the above formula conveys is much more illuminating than that afforded by the old relation.

Table III

Salicylic acid, 25°

Percent alcohol	Dielectric constant	K obs. $\times 10^6$	K calc $\times 10^6$ (Equation 1)	K calc. $\times 10^6$ ($K \propto D^3$)
0.0	78.5	100.0	(100.0)	(100.0)
16.2	66.5	66.0	55.2	60.8
33.2	55.9	26.0	26.4	36.1
52.0	45.5	9.0	9.2	19.5
73.5	35.0	1.8	1.7	8.9
85.7	29.7	0.45	(0.45)	5.4
89.0	28.3	0.25	0.29	4.7
93.3	27.0	0.08	0.19	4.1
97.8	25.3	0.01	0.09	3.3
100.0	24.9	0.0002	0.08	3.2

Although not reproduced here the data for cyanacetic acid show precisely the same behaviour as those for salicylic acid in the above table.

To obtain the values of the constants k_1/k_2 and $(E_o' - E_o)$ in the expression (equation 1) for the ionisation constant two of the observed ionisation constants are substituted in the formula and the required terms are evaluated from the two simultaneous equations so obtained. In the case exemplified in the preceding table the data for 0.0 and 85.7 per cent alcohol have been used for this purpose, and the value of the composite critical increment term $(E_o' - E_o)$ is calculated to be − 153,700 calories. It will be seen that the agreement between the calculated and the observed ionisation constants is quite good up to about 90 per cent alcohol, and this is a considerable range of solvent. The discrepancies in solvents of higher alcohol content are sufficiently serious to indicate the necessity of further investigation of the particular mechanism concerned, and as will be shown later they lead to considerations of a *chemical* kind as distinct from the purely physical concepts employed in the present instance. These chemical considerations prove to be only of first importance, so far as numerical values are concerned, over the range of alcohol-water mixtures containing very little water, the values already calculated over the remaining range being comparatively little affected.

Part II

We now proceed to the "chemical" considerations, the object of which is an extension of the theory already developed so as to include, in what is believed to be a more satisfactory manner, the behaviour of these same electrolytes in alcohol-water mixtures containing very little water.

The principal feature to be noticed in these solvents is that the influence of slight variations in the water content of the solution is inordinately great, and indeed in the solvent region extending from 90 to 100 per cent alcohol the decrease in the strengths of the acids studied (salicylic acid and cyanacetic acid) as the amount of water grows less and less is much too rapid to be accounted for by the exponential formula already deduced (equation 1).

In the absence of any purely physical influence likely to be capable of explaining the exaggerated effect of small amounts of water recourse was had to the chemical concept of hydration. For the sake of brevity the full evidence for and the plausibility of the hypothesis will not be entered into since they have been treated at length by J. Kendall,[1] whose ionisation hypothesis is employed here. The basic idea is that "ionisation is a consequence of compound formation." In the present case it is assumed that the ionisation of weak acids in alcohol-water mixtures is preceded by *hydrate formation* according to the following scheme:—

$$H\,A + n\,H_2O = HA.\,n\,H_2O \qquad (2)$$

$$HA.\,n\,H_2O = H^+ + (A^-.\,n\,H_2O) \qquad (3)$$

$$H_4\,O_2 = 2\,H_2O \qquad (4)$$

Assuming that the concentration of the complex $HA.nH_2O$ is very small compared with that of the ions and of the unhydrated undissociated molecules,[2] it follows that K, the *observed* ionisation constant is given by:—.

$$K = \frac{[H^+]\,[A^-.n\,H_2O]}{[H\,A]} = K_1\,K_2\,[H_2O]^n$$

where K_1 is the equilibrium constant of reaction (2), i.e.

$$K_1 = \frac{[HA.nH_2O]}{[HA]\,[H_2O]^n}$$

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[1] J. Am. Chem. Soc., 39, 2303 2323 (1917).

[2] According to Faurholt (Soc. Chim. phys. June 1924) in the case of dissolved carbonic acid approximately 99.6% exists in the unhydrated form.

and K_2 the equilibrium constant of reaction (3). K_2 is the equilibrium constant of the true ionisation process, and may be replaced by the theoretical expression previously found for the ionisation constant of an electrolyte, (equation 1), thereby yielding the expression:—

$$K = K_1\left(\frac{k_1}{k_2}\right)[H_2O]^n\, e^{(E_o' - E_o)/DRT} \qquad (5)^1$$

The result of applying this expression to the experimental data for the acids is shown in tables IV and V.

In equation (5) *n* represents the number of molecules of monohydrol with which one molecule of the acid becomes hydrated, and must clearly be some small integer. The value found by trial was 2[2]. The values of the constants $K_1\left(\frac{k_1}{k_2}\right)$ and $(E_o' - E_o)$ were found by using the experimentally determined ionisation constants for two solvent mixtures in two simultaneous equations which were solved for the desired quantities.

The values of the term $(E_o' - E_o)$, which are independent of the units employed in the equation (5), are as follows

Salicylic acid.................... −113,900 calories per mole.
Cyanacetic acid.................. −112,600 " " "

these values being found from the ionisation constants enclosed in brackets in Tables IV-V.

TABLE IV

Salicylic acid, 25°

Per cent alcohol	Dielectric constant	Activity of water	K obs. $\times 10^5$	K calc. $\times 10^5$
0.0	78.5	23.7	100.0	(100.0)
16.2	66.5	21.4	66.0	56.0
33.2	55.9	19.5	26.0	27.0
52.0	45.5	18.1	9.0	10.7
73.5	35.0	15.5	1.8	2.2
85.7	29.7	12.0	0.45	(0.50)
89.0	28.3	10.1	0.25*	0.26
93.3	27.0	7.0	0.08*	0.09
95.0	26.0	5.3	0.04	0.04
97.8	25.3	2.5	0.01*	0.007

* These ionisation constants are due to Goldschmidt: Z. phys. Chem., 91, 46 (1916).

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[1] $[H_2O]$ denotes the activity of water and is measured by the partial vapour pressure of water over the solution.

[2] It may be seen from equation (5) that over a *small* range of alcohol-water mixtures $K \propto (H_2O)^n$. Now when the concentration of the water in the mixture is small it nearly all exists as monohydrol, and therefore $K \propto$ (total water concentration)^n. For salicylic acid in 90 to 98 per cent alcohol inspection shows that $K \propto$ (total water concentration)^2 roughly.

TABLE V

Cyanacetic acid, 25°

Per cent alcohol	Dielectric constant	Activity of water	K obs. $\times 10^6$	K calc. $\times 10^6$
0.0	78.5	23.7	391 to 318	(362)
16.2	66.5	21.4	231 to 188	191
33.2	55.9	19.5	116 to 94	92.5
52.0	45.5	18.1	46 to 36	36.8
73.5	35.0	15.5	9.5 to 8.4	7.8
85.7	29.7	12.0	1.8 to 1.7	1.8
91.0	27.3	8.8	0.73	0.55
92.7	26.8	7.7	0.45	0.36
94.4	26.3	6.5	0.26	0.22
95.0	26.0	5.3	0.14	(0.14)
96.2	25.8	4.8	0.12	0.11
98.1	25.4	3.0	0.05	0.04

As may be seen from Table II, the observed ionisation constants for these acids at 35° differ relatively little from those at 25°, and in fact these differences are somewhat less than those exhibited in Tables IV and V between the calculated and the observed values at 25°. In these circumstances, and in the absence of reliable direct data for the activities of water in alcohol-water mixtures at 35° it was considered unnecessary to attempt a test of equation (5) by reference to the experimental data obtained at 35°. It should be noticed that the observed ionisation constants, particularly for cyanacetic acid, are not wholly independent of dilution.

The agreement shown between the calculated values of the ionisation constants is satisfactory, especially in the region 90 to 98 per cent alcohol, where physical influences alone fail to account for the behaviour. The ionisation due to the alcohol has been neglected in the above theory and to be able to account for the ionisation in a solvent which contains 98 per cent alcohol is rather remarkable. The ionisation of both salicylic acid and cyanacetic acid in 100 per cent alcohol is very small; the ionisation constants at 25° are 2.2×10^{-9} and 3.2×10^{-8} respectively.

The term $(E_0' - E_0)$ in equation (5) deserves some consideration. Both E_0' and E_0 represent work terms, but it seems probable that they are of quite different magnitude. E_0 is the energy expended in separating two *oppositely* charged ions while E_0' is supposed to be the sum of the energies required to remove from the hydrated ions the water molecules that have been attracted to the ions or to overcome electrostriction. The attractive forces in hydration must be considerably less than those involved in the structure of a stable compound, and therefore it is conjectured that $-E_0$ itself (the critical increment of the undissociated molecule with sign reversed) is of sensibly the same magnitude as the whole term $(E_0' - E_0)$. If this is so, E_0 for the cases studied here has a value of about 100,000 calories. It is to be remembered that E_0

does not indicate the actual critical increment of ionisation of the molecule in a solution, but in a medium of unit dielectric constant, i.e., in the gaseous state. Considering the case of water it would follow that the critical increment of ionisation of salicylic acid in this solvent is of the order 1000 to 2000 calories. As regards E_0 it may be pointed out that quantities of the same order have already been found for the critical increments of substances in the gaseous state. The ionisation potentials met with in gases correspond to this order of magnitude, and the calculated heat of ionisation of one-gram molecule of crystal lattice is much the same.

Attention may be directed to the fact that the assumption that the critical increment of ionisation may be identified with a work term involving dielectric constant necessitates the drawing of a distinction between the influence of environment upon the breaking of a co-valent bond and its effect upon that of an electro-valent bond. The critical increment of an electro-valent bond would be expected to vary with the nature of the solvent, (in terms of the dielectric constant), while the critical increment of a co-valent bond might well be independent of the dielectric properties of the solvent. We have an illustration of this in the well known case of triethylsulphonium bromide, which can decompose in two distinct ways according to the nature of the solvent. In a large number of organic solvents it decomposes into ethyl bromide and diethylsulphide, evidently through the breaking of a co-valent bond. It is observed that the critical increment is sensibly the same in all these solvents, although the dielectric capacities of the solvents are different[1]. In water on the other hand the triethylsulphonium bromide splits up into bromine ion and the triethylsulphonium ion, an electrovalence being involved.

Finally it is of interest to see what is the order of magnitude of the heat of ionisation to be anticipated on the basis of equation (5). On taking logarithms of both sides and differentiating with respect to temperature we obtain

$$\frac{d \log K}{dT} = \frac{d \log K_1}{dT} + \frac{d \log \frac{k_1}{k_2}}{dT} + \frac{2\, d \log [H_2O]}{dT} + \frac{d}{dT}\left(\frac{E_0' - E_0}{D R T}\right) \qquad (6)$$

Since k_1 and k_2 are independent of temperature, and the activity of water does not vary with T, equation (6) becomes

$$\frac{d \log K}{d T} = \frac{d \log K_1}{d T} + \frac{d}{dT}\left(\frac{E_0' - E_0}{D R T}\right) \qquad (7)$$

On comparing with the van't Hoff isochore it follows that the heat of ionisation, Q, is given by

$$Q = \frac{R T^2 . d \log K_1}{dT} - \frac{E^{\circ\prime} - E^{\circ}}{D} - \frac{T . d \log D}{d T} \times \left(\frac{E_0' - E_0}{D}\right) \qquad (8)$$

In equation (8) the term $\frac{R T^2 . d \log K_1}{d T}$ is equivalent to the net heat effect, Q_1, of the hydration of the undissociated molecule HA. Hence

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[1] Cf. Taylor and Lewis: J. Chem. Soc., **121**, 665 (1921).

$$Q = Q_1 - \frac{E_0' - E_0}{D} - \frac{T.d \log D}{dT} \times \left(\frac{E_0' - E_0}{D}\right) \qquad (9)$$

Q_1 is the only unknown term on the right side of equation (9), but assuming that it remains constant in all alcohol-water mixtures it may be evaluated by using the experimental Q for one case, when it becomes possible to calculate Q for the other solvent mixtures and to compare these calculated values with the experimentally observed ones. For the case of salicylic acid in water at 30° the observed Q is + 500 calories, and on inserting the appropriate numerical values for the other terms in equation (9) we find that $Q_1 = + 1300$ calories[1].

Using the equation

$$Q = 1300 - \frac{E_0' - E_0}{D} - \frac{T.d \log D}{dT}\left(\frac{E_0' - E_0}{D}\right) \qquad (10)$$

the values of Q for the other alcohol-water mixtures may be obtained. They are compared with the observed values in table VI.

TABLE VI

Heat of ionisation of salicylic acid at 30°

Per cent alcohol	Observed heat	Calculated heat
0.0	+ 500 cals.	(+ 500) cals.
16.2	− 200	+ 200
33.2	− 300	− 200
52.0	− 400	− 900
73.5	− 1200	− 2100
85.7	− 2200	− 3100
95.0	− 1700	− 4000
100.0	+ 800	− 4300

The agreement between calculated and observed values in Table VI is evidently not satisfactory. The electrolytes studied in the present work, however, are not suitable for a rigorous examination of the heat effect of ionisation, owing to the fact that this quantity happens to be very small in these cases and consequently liable to error. The trend of the calculated heats of ionisation agrees with that observed up to about 80 to 90 per cent alcohol, but the minimum in heat effect is not reproduced. It may be pointed out that the term $T \frac{d \log D}{dT}\left(\frac{E_0' - E_0}{D}\right)$ has quite a large value compared with the other terms in equation (10), and especially in the alcohol-water mixtures of higher alcohol content has a preponderating influence its effect being to make the net heat of ionisation heat evolved.

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[1] It will be observed that this quantity is positive, i.e. heat absorbed. At first sight it might have been thought that the effect should be heat evolved. It is to be remembered, however, that Q_1 is actually the sum of the true heat of the reaction $HA + 2\,H_2O \longrightarrow HA\,2\,H_2O$, and also of the heat of depolymerisation of a molecule of dihydrol, which depolymerisation is a consequence of the removal of two molecules of monohydrol by the reaction (water being assumed to be practically all dihydrol). Hence + 1300 cals is quite a possible value for the term Q_1.

Summary

(1) The ionisation of salicylic acid and of cyanacetic acid has been investigated in alcohol-water mixtures ranging from pure water to pure alcohol, at 25° and 35°.

(2) A quantitative relation between the ionisation constant and the dielectric capacity of the medium has been developed, and the concept of the existence of critical increments of ionisation of an undissociated molecule and of recombination of ions has been given concrete expression. In addition to purely physical considerations a chemical hypothesis as to the mechanism of the ionisation process has been used. The ionisation of salicylic and cyanacetic acids has been satisfactorily accounted for in all solvents up to 98 per cent alcohol.

(3) It is pointed out that the order of the critical increment of ionisation deduced in the present work for a medium of unit dielectric constant is in agreement with that of the ionisation of other compounds in the gaseous state.

(4) The preceding treatment demands a distinction between electro- and co-valency, according to which the critical increment of a co-valent bond should be independent of the dielectric capacity of the solvent while that of an electro-valent bond will vary inversely as the dielectric capacity of the solvent.

(5) It has not been found possible satisfactorily to account for the variation of the heat effect of ionisation with changes of solvent, but the electrolytes studied do not afford very favourable instances for this purpose.

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THE INFLUENCE OF HYDROGEN-ION CONCENTRATION ON THE PROTECTIVE ACTION OF GELATIN ON ZSIGMONDY'S STANDARD GOLD SOL

BY HERMAN V. TARTAR AND JAMES R. LORAH

Introduction

In 1901, Zsigmondy[1] proposed the determination of the "gold number" as a measure of the protective action of colloids. He defined the gold number as the number of milligrams of the protective colloid necessary just insufficient to prevent the change in color to violet of 10 cc. of a bright-red, standard gold sol by the addition of 1 cc. of a 10% solution of sodium chloride. A number of investigations[2] have since been made of the gold numbers of different protective colloids and this method for the determination of protective action is now included in practically all text books and laboratory manuals on colloid chemistry.

During recent years a considerable amount of work has been done on the influence of hydrogen-ion concentration on the properties of proteins. Thus far, however, but little systematic work has been done on the effect of hydrogen-ion concentration on the protective action of colloids. Zsigmondy[3] states that in a few cases he determined the gold number by the use of hydrochloric acid (1 cc. of sp. gr. 1.14) instead of 1 cc. of sodium chloride and found the values became considerably larger (about 10 times) for gelatin, bone glue, casein, and albumen. Doerinckel[4] found that using a gold sol prepared by the reduction of gold chloride with hydrogen peroxide gave abnormally high gold numbers but when sufficient potassium carbonate was added the values were in good agreement with those of Zsigmondy. Reitstötter[5] determined the gold number of sera from a number of animals; he found that the relative protective action expressed as gold number is altered by the acidity of the medium. Since the completion of the experimental work reported in this paper, Thomas[6] has stated "that the pH of the solutions will certainly affect the values" (gold numbers).

The work presented herein is a study of the effect of hydrogen-ion concentration on the protective action of gelatin on Zsigmondy's standard gold sol.

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[1] Zsigmondy: Z. anal. Chem. 40, 687 (1901).

[2] Schulz and Zsigmondy: Beitr. chem. Physiol. Path 3, 137 (1902); Doerinckel: Z. anorg. Chem. 63, 344 (1909); Menz: Z. physik. Chem. 66, 129 (1909); Heubner and Jacobs: Biochem. Z. 58, 352 (1914); Gortner: J. Am. Chem. Soc. 42, 595 (1920); Elliott and Sheppard: J. Ind. and Eng. Chem. 13, 699 (1921); and others.

[3] Zsigmondy: Z. anal. Chem. 40, 697 (1901).

[4] Doerinckel: Z. anorg. Chem. 63, 344 (1909).

[5] Reitstötter: Oesterr. chem. Ztg. 25, 29 (1922); through Chem. Abstracts 17, 290 (1923)

[6] Bogue: "Theory and Application of Colloidal Behavior," 1, 351 (1924).

Experimental Part

(a) *Preparation of the Gold Sol.*

In the preparation of the gold sol, the directions of Zsigmondy[1] were followed with only slight changes in the quantities of the solutions. The writers have found that the procedure for reducing the gold must be carefully followed in detail in order to secure satisfactory and reproducible results. The gold chloride solution was made by dissolving 1 g. of $AuCl_3.HCl.3H_2O$ in 333.3 cc. of distilled water. For each 240 cc. of gold sol prepared, 0.087 g. of potassium carbonate was used. The formaldehyde solution was obtained by diluting 5 cc. of 40% "formalin" solution to 100 cc.

The potassium carbonate was placed in a well-cleaned, tared pyrex beaker and 10 cc. of the gold chloride solution added. Enough distilled water was added to make 240 g. of solution. The beaker was then placed on a tripod covered with a wire gauze and a thin sheet of asbestos, and two burners were turned on full blast under it. The solution was brought near boiling in approximately 5 minutes. A rotary motion was imparted to the solution and as soon as gentle ebullition began at the center of the vortex, 3 drops of formaldehyde (1 drop every 30 seconds) were added, the solution being stirred and kept boiling. The heating was continued until the deep red color appeared. Sufficient distilled water was then added to replace that lost by evaporation and the sol was transferred to a pyrex storage flask. This procedure gave a sol of uniform concentration and quite reproducible. It was deep red in color and did not appear turbid by transmitted or by reflected light. The color change during the reduction was always the same: First, a faint pink (1.5-2 minutes after the addition of the first drop of formaldehyde) which slowly darkened, then a more rapid change (lasting about 2 minutes) to cherry red, which gradually darkened.

The writers have confirmed the results of Faraday[2] and of Zsigmondy[3] that two primary precautions in the preparation of a finely dispersed gold sol, are the purity of the water and the cleanliness of the glassware. "Conductivity water" with a conductance of 2×10^{-6}, was used. A Barnstead still with block tin condenser was used in the distillation. Great care was taken to have the glass vessels chemically and physically clean.

The gold sols prepared by the above procedure did not show perceptible change on ageing in tightly stoppered flasks, with small air space. Four liters of the sol were kept in a sealed pyrex flask for six months without any visible change taking place. In the experimental work reported herein a large quantity of sol was made by preparing a series of small quantities of gold sol and mixing these in a large pyrex flask in which the colloid was stored.

(b) *Preparation of the Gelatin.*

A commercial gelatin ("Silver Label" brand) of good quality was purified and made isoelectric according to the procedure recommended by Loeb[4] then

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[1] Zsigmondy: Z. anal. Chem. **40**, 687 (1901)

[2] Faraday: Phil. Trans. **147**, 145 (1857).

[3] Zsigmondy: Z. anal. Chem. **40**, 697 (1901).

[4] Loeb: "Proteins and the Theory of Colloidal Behavior," 35 (1922).

dried in vacuo at 60°. A sufficient amount of the dry gelatin was prepared to afford a supply of uniform composition for all the experiments.

When a gelatin sol was needed, the requisite amount of gelatin was added to 50 cc. of water and the mixture then heated at 50° for 4 hours to permit the sol to come to "equilibrium." This temperature and duration of heating were found by Elliott and Sheppard[1] to be satisfactory for the production of a reproducible sol. Upon cooling, the sol was diluted to the required volume, usually to give a concentration of 0.0001 g. of gelatin per cc. Only a few tenths of a cubic centimeter of the diluted sol were required for a given experiment. The diluted sol was used within a few hours after its preparation so that no change took place due to ageing.

(c) *Preparation of the Precipitating Agents.*

The sodium chloride solutions used as precipitating agents were made up with sufficient acid to give the desired hydrogen-ion concentration. A series of solutions were prepared containing the same concentration of sodium chloride but increasing amounts (exact multiples of the lowest concentration) of acid. In one series, the concentration of sodium chloride was 10%, as recommended by Zsigmondy. Because of the possible danger that this high concentration might obscure some of the phenomena taking place, a second series of precipitating agents was prepared containing 4% sodium chloride. Different acids (hydrochloric, acetic, oxalic and phosphoric) were used to show that the effects secured were due largely to hydrogen-ion concentration and not to any specific property of the acid employed.

(d) *Method of Procedure.*

A 40 cc. portion of the gold sol was transferred to a large test tube. The gelatin sol was placed in another test tube of the same size. These sols were mixed by first pouring the gold sol into the gelatin sol then back and forth from one test tube to the other 8 times. The sodium chloride solution was then placed in a test tube and this was mixed with the gelatin gold sol in a manner similar to that just described. The time between the addition of the gelatin sol and of the sodium chloride solution was approximately 2 minutes. The test tube containing the mixture was then tightly stoppered to prevent evaporation and allowed to stand 12 hours. By using a series of test tubes the minimal amount of gelatin required to prevent complete precipitation in 12 hours was determined. In some cases all of the flocculated gold did not settle rapidly and the last portion of the precipitate was removed by centrifuging 15 minutes at 2500 revolutions per minute. In most instances, supernatant liquid could be decanted from the precipitate without the necessity of centrifuging.

The hydrogen-ion concentration of the supernatant liquid was determined electrometrically. The writers have confirmed the finding of Adolf and Pauli[2] that in the presence of traces of gold, either dissolved or suspended, the hydrogen electrode gives erratic results. No difficulty was experienced in the measurement of the hydrogen electrode potentials in the clear, colorless, supernatant liquid from the completely precipitated gold. A Leeds and Northrup

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[1] Elliott and Sheppard: J. Ind. and Eng. Chem. 13, 699 (1921).

[2] Adolf and Pauli: Kolloid-Z. 34, 29 (1924).

potentiometer was used with a galvanometer sufficiently sensitive, to make determinations of potential to 0.2 millivolt. The hydrogen-electrode vessel was connected by a saturated potassium chloride solution as a bridge to the normal calomel electrode to reduce the liquid-liquid potentials to a minimum. The hydrogen-electrodes used were checked with standard buffer solutions. The determinations were corrected for temperature. Trial runs were made to ascertain if gelatin alone had any influence on the potentials. These runs showed the variations to be small and to be within the error of the experiments.

Zsigmondy in the determination of the gold number used the change of color from red to blue to indicate the end-point of the protective action of the colloid used. In the work presented in this paper, the point of complete precipitation of the sol was used. The end-point is essentially the same as that used by Zsigmondy. The point of complete precipitation was ascertained in the following manner: A series of tests were made to ascertain the amount of gelatin just necessary to leave only a faint tinge of pink (purple) 5 minutes after the addition of the precipitating agent. The sol was completely precipitated in 12 hours.

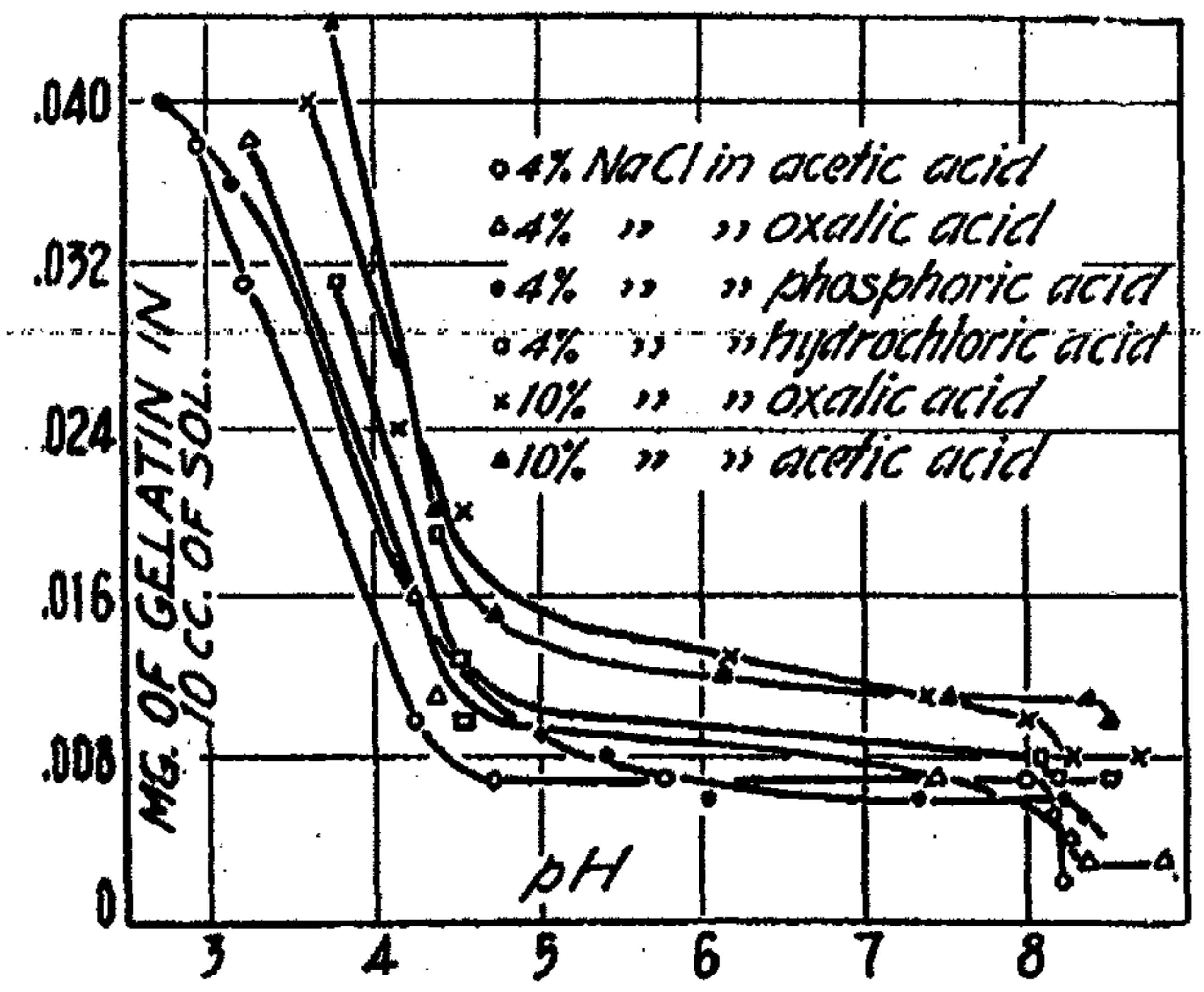

Fig. 1

In cases where large amounts of gelatin were required—acidic solutions—the time for the actual color change after adding the precipitating agent, required a longer time, perhaps 15 minutes, and often the precipitate does not settle completely in 12 hours. In these cases centrifuging for a brief time was necessary to secure a clear supernatant liquid.

In order to secure some information of the influence of the acids themselves on the stability of the gold sol, precipitations were made with the acids alone.

Results and Discussion

The data obtained are given in Tables I and II and presented graphically in Fig. 1. Because of the abrupt change in the pH values when the 10% solution of sodium chloride was used with hydrochloric acid, no attempt has been made to graph the data in Fig. 1. The curve for the data obtained using acetic acid with gold sol No. 70 has also been omitted; the results are essentially the same as those with sol No. 71 using 4% sodium chloride as the precipitating agent. The different amounts of gelatin are given for 10 cc. of sol in order to afford easy comparison with the gold numbers reported by previous workers.

TABLE I

Change of the Protective Action of Gelatin with Change of Hydrogen-Ion Concentration with Different Acids

Number of gold sol used	Concentration of the NaCl solution %	Milligrams of gelatin for 10 cc. of gold sol	Hydrogen-ion concentration pH
	Acetic acid (see curve Fig. 1)		
71	4	0.002	8.27
"	"	0.005	8.17
"	"	0.007	8.00
"	"	0.007	5.78
"	"	0.007	4.72
"	"	0.010	4.24
"	"	0.031	3.20
"	"	0.038	2.93
	Acetic acid (see curve Fig. 1)		
"	10	0.010	8.50
"	"	0.011	8.39
"	"	0.011	7.50
"	"	0.012	6.13
"	"	0.015	4.75
"	"	0.020	4.38
"	"	0.075	2.93
	Acetic acid (not included in Fig. 1)		
70	10	0.003	8.40
"	"	0.005	7.98
"	"	0.005	5.27
"	"	0.014	4.92
"	"	0.015	4.40
"	"	0.020	3.10
	Oxalic acid (see curve Fig. 1)		
72	4	0.003	8.85
"	"	0.003	8.37
"	"	0.004	8.26
"	"	0.007	7.43
"	"	0.011	4.38
"	"	0.016	4.25
"	"	0.038	3.26

TABLE I (Continued)

Number of gold sol used	Concentration of the NaCl solution %	Milligrams of gelatin for 10 cc. of gold sol	Hydrogen-ion concentration pH
	Oxalic acid (see curve Fig. 1)		
72	10	0.008	8.69
"	"	0.008	8.30
"	"	0.010	8.00
"	"	0.011	7.40
"	"	0.013	6.18
"	"	0.020	4.57
"	"	0.024	4.16
"	"	0.040	3.61
"	"	0.055	3.15.
	Hydrochloric acid (see curve Fig 1)		
"	4	0.007	8.53
"	"	0.007	8.18
"	"	0.008	8.08
"	"	0.010	4.55
"	"	0.013	4.50
"	"	0.019	4.40
"	"	0.031	3.78
	Hydrochloric acid (not included in Fig. 1)		
69	10	0.009	8.75
"	"	0.011	8.35
"	"	0.050	4.03
"	"	0.065	3.20
"	"	0.075	2.75
	Phosphoric acid (see curve Fig. 1)		
72	4	0.005	8.37
"	"	0.006	8.23
"	"	0.006	7.33
"	"	0.006	6.03
"	"	0.008	5.44
"	"	0.009	5.01
"	"	0.016	4.73
"	"	0.031	3.78
"	"	0.036	3.14
"	"	0.040	2.70

TABLE II

The Precipitation of Gold Sols with Acids Alone

Number of Gold Sol used	Acid	Hydrogen-ion concentration pH
70	Hydrochloric	2.10
73	Acetic	1.96
72	Phosphoric	1.88

The results show that the amount of gelatin required to protect the gold changes markedly when the pH of the medium falls below approximately 4.7, the isoelectric point of the gelatin[1]. For a change of pH from 8.0 to 5.0 very little effect is shown, particularly when 4% sodium chloride solution was used. The sudden increase in the amount of gelatin below pH 4.7 (approximately) is not due to reaching the isoelectric point of the gold sols through change of hydrogen-ion concentration: the data of Table II show that the isoelectric point (the point of complete precipitation) with acids is approximately pH 2.0. The gelatin exerts a large protective action when it is isoelectric or possesses a charge similar to that of the gold (negative). When the gelatin becomes positive (below pH 4.7) then its protective power for the gold is rapidly reduced by lowering of the pH of the medium. This finding affords corroboratory evidence in support of Thomas'[2] statement that "a hydrophile colloid will protect a less stable dispersion at all concentrations of the former provided its sign is like that of the latter."

The "gold number" determination proposed by Zsigmondy gives the protective action only for a certain condition. The pH of the medium may affect markedly the values.

Summary

1. A study has been made of the influence of hydrogen-ion concentration on the protective action of gelatin on Zsigmondy's standard gold sol.

2. Between pH values 8 to 5 the hydrogen-ion concentration has practically no influence on the protective action. Below a pH of approximately 4.7 the protective action decreases very rapidly with increase of hydrogen-ion concentration.

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Feb. 23, 1925

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[1] Loeb: "Proteins and Theory of Colloidal Behavior," 1922.

[2] Bogue: "Theory and Application of Colloidal Behavior," 1, 349 (1924).

INDUCED OXIDATION OF CARBOHYDRATES

BY C. C. PALIT AND N. R. DHAR

It is well known that carbohydrates are not ordinarily oxidised by air at the ordinary temperature, but in the animal body they are oxidised readily mainly into carbon dioxide and water, and this oxidation is the main source of animal heat. Generally speaking two thirds of the energy produced by the animal organism is derived from the oxidation of carbohydrates. Not without reason is bread considered the staff of life.

The gastro-intestinal tract converts starch into glucose, inverts sucrose into glucose and fructose and lactose into glucose and galactose, so that these soluble mono-saccharids become fuels transported by the blood for the nourishment of the body cells. The enzymes, maltase, invertin and lactase which respectively convert maltose, sucrose and lactose into mono-saccharids, are present in the intestinal mucosa of the new-born infant.

In previous papers we have proved qualitatively that substances like starch, sugar, etc., can be oxidised by air or oxygen at ordinary temperature by mixing the above substances with sodium sulphite, ferrous hydroxide, cerous hydroxide and other reducing agents. In other words the slow oxidation of these reducing agents induces or sets up the oxidation of starch, sugar and other substances which are not oxidised at the ordinary temperature. In the foregoing papers we have also insisted that these induced reactions are helpful in understanding bio-chemical oxidations and possibly are imitations of bio-chemical oxidation of starch, sugar, etc.

In this paper a systematic and quantitative study has been made on the oxidation of such carbo-hydrates as starch, cane sugar, maltose, galactose, laevulose, arabinose, lactase, and glucose. It will be shown in the subsequent pages that in presence of large excess of alkali, these substances can be readily oxidised into carbon dioxide and water in presence of cerous hydroxide and ferrous hydroxide.

Experiments

In these experiments a slow current of air was passed through a series of bottles containing solutions of carbohydrates and the reducing agent containing an excess of alkali. Each of these bottles contained 20 cc of cerium chloride solution ($\equiv$0.07838 grm of Ce or $\equiv$ 0.1069 grm of cerous hydroxide) or 20 cc of ferrous sulphate solution ($\equiv$ 0.04029 grm of Fe or $\equiv$ 0.06476 grm of ferrous hydroxide) and 10 cc of the solution of carbohydrate but contained alkali of different concentrations in increasing order, the first bottle containing just an equivalent amount of alkali. In each case the total volume of the solutions was 100 cc and the volume of air passed,—after being purified and bubbled through water,—was about 36.5 litres in 5.5 hours in each case. In the case of cerous hydroxide, the precipitate is at first white, then becomes slightly

TABLE I

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of $CeCl_3$ used was 20 cc [≡ 0.1069 grm. of $Ce(OH)_4$].

No. of Expt.	Carbohydrate used for the experiment	Actual weight of carbohydrate in 10 c.c. of the solution taken in grm.	Amount of carbohydrate oxidised in grm. in presence of caustic soda in grm. containing									
			(1) 0.10	(2) 0.15	(3) 0.20	(4) 0.25	(5) 0.30	(6) 0.35	(7) 0.40	(8) 0.50	(9) 0.60	(10) 0.70
1	Starch	0.1050	0.0690	0.0804	0.0850	0.0936	0.0954	0.0985	——	0.1010	0.1018	complete oxidation
2	Maltose	0.1097	0.0494	0.0797	0.0970	0.1000	0.1021	0.1028	——	Complete oxidation		
3	Arabinose	0.1000	0.0462	0.0687	0.0935	0.0978		Complete oxidation				
4	Laevulose	0.09185	0.0342	0.0582	0.0800	0.0868	0.0904	0.0908	0.0910	Complete oxidation		
5	Galactose	0.08613	0.0315	0.0464	0.0732	0.0754	0.0784	0.0797	——	Do	Do	
6	Glucose	0.0962	0.0224	0.0570	0.0774	0.0897	0.09055	0.09133	——	Do	Do	
7	Lactose	0.0997	0.0189	0.0314	0.0573	0.0753	0.0911	0.0927	——	0.0928	0.0929	0.0929
8	Cane Sugar	0.1080	0.0126	0.0160	0.0172	0.0174	0.0228	0.0235	——	0.0253	0.0265	0.0283

TABLE II

(Analysis of the precipitate of cerium hydroxide).

In each of these experiments the volume of air passed was 36.5 litres in 5.5 hours and the volume of $CeCl_3$ used was 20 cc [≡0.1069 grms. of $Ce(OH)_4$].

No. of Expt.	Carbohydrate in presence of which the experiment is performed	Percentage amount of cerium peroxide, CeO_3, in grm. present in the precipitate in presence of caustic soda in grm. containing									
		(1) 0.10	(2) 0.15	(3) 0.20	(4) 0.25	(5) 0.30	(6) 0.35	(7) 0.40	(8) 0.50	(9) 0.60	(10) 0.70
1	Maltose	77.2	80.4	85.3	85.3	85.3	85.3	85.3	85.3	85.3	85.3
2	Arabinose	91.7	88.5	53.1	38.6	32.2	32.2	——	——	——	——
3	Laevulose	42.5	37.0	20.9	45.7	56.3	54.6	——	——	——	——
4	Galactose	29.0	35.4	20.9	29.0	45.7	57.9	51.5	35.4	37.0	56.3
5	Glucose	19.3	20.9	20.9	16.1	16.1	18.5	——	——	——	——
6	Starch	——	——	——	22.5	23.3	24.9	——	——	——	——
7	Lactose	88.5	91.7	47.3	56.3	56.3	56.3	——	37.0	62.5	32.2
8	Cane Sugar	77.2	80.4	85.3	85.3	85.3	85.3	85.3	85.3	85.3	85.3

TABLE III

In each of these experiments, the volume of air passed was 36.5 litres in 5.5 hours and the volume of $CeCl_3$ used was 20 cc [≡ 0.1069 grm. of $Ce(OH)_3$].

No. of Expt.	Substance used for the experiments	Actual weight of the substance in 10 c.c. of the solution taken in grm.	Amount of the substance oxidised in grm. in presence of caustic soda in grm. containing									
			(1) 0.10	(2) 0.15	(3) 0.20	(4) 0.25	(5) 0.30	(6) 0.35	(7) 0.40	(8) 0.50	(9) 0.60	(10) 0.70
1	Chromium sulphate	0.0175 Cr. [≡0.06586 $Cr_2(SO_4)_3$]	0.0004 Cr. [≡0.00135 Na_2CrO_4]	0.0015 Cr. (≡0.0046 Na_2CrO_4)	0.0028 Cr. (≡0.0089 Na_2CrO_4)	0.0029 Cr. (≡0.0092 Na_2CrO_4)	0.0033 Cr. (≡0.0102 Na_2CrO_4)	0.0037 Cr. (≡0.0116 Na_2CrO_4)	——	0.0043 Cr. (≡0.0135 Na_2CrO_4)	0.0055 Cr. (≡0.0173 Na_2CrO_4)	0.0062 Cr. (≡0.0194 Na_2CrO_4)
2	Manganese sulphate	0.0364Mn (≡0.1000 $MnSO_4$)	Analysis done qualitatively			0.0007Mn (≡0.0021 Na_2MnO_4)	0.0010Mn (≡0.0029 Na_2MnO_4)	0.0012Mn (≡0.0037 Na_2MnO_4)	——	0.0019Mn (≡0.0066 Na_2MnO_4)	0.0033Mn (≡0.0099 Na_2MnO_4)	0.0036Mn (≡0.0107 Na_2MnO_4)
3	Potassium oxalate *	0.0998	Nil	Nil	Nil	Nil	Nil	Nil	——	Nil	Nil	Nil
4	Sodium nitrite	0.0100	Do	Do	Do	Do	Do	Do	——	Do	Do	Do

* In last two cases, namely, potassium oxalate and sodium nitrite, the amounts of potassium oxalate and sodium nitrite after the experiment were exactly the same as the amounts of each of these present before the experiment.

TABLE IV

(Analysis of the precipitate of cerium hydroxide).

In each of these experiments, the volume of air passed was 36.5 litres in 5.5 hours and the volume of $CeCl_3$ used was 20 cc [≡0.1069 grm. of $Ce(OH)_3$].

No. of Exp.	Substance in presence of which the experiment is performed	Percentage amount of cerium peroxide, CeO_2 in grm. in presence of caustic soda in grm. containing					
		(1) 0.25	(2) 0.30	(3) 0.35	(4) 0.50	(5) 0.60	(6) 0.70
1	Chromium sulphate	88.5	91.7	91.7	91.7	91.7	91.7
2	Manganese sulphate*	—	—	—	—	—	—
3	Potassium oxalate	88.5	91.7	91.7	—	—	—
4	Sodium nitrite	91.7	91.7	91.7	—	—	—

* In the second case, namely, manganese sulphate, the precipitate of cerium hydroxide—which also contained manganese dioxide formed by the oxidation of manganous hydroxide by air—was not analysed simply due to the presence of manganese dioxide which also liberates iodine on treatment with hydrochloric acid and potassium iodide.

TABLE V

In each of these experiments, the volume of air passed was 36.5 litres in 5.5 hours and the volume of ferrous sulphate used was 20 cc [≡ 0.06476 grm. of $Fe(OH)_2$].

No. of Expt.	Carbohydrate used for the experiment	Actual weight of carbohydrate in 10 c.c. after solution taken in grm.	Amount of carbohydrate oxidised in grm. in presence of caustic soda in grm. containing									
			(1) 0.10	(2) 0.15	(3) 0.20	(4) 0.25	(5) 0.30	(6) 0.35	(7) 0.40	(8) 0.50	(9) 0.60	(10) 0.70
1	Maltose	0.1097	0.0516	0.0779	0.0829	0.0849	0.0943	0.0999	——	Complete oxidation		
2	Lactose	0.0997	0.0258	0.0388	0.0797	0.0832	0.0926	0.0992	——	Do		Do

N. B. The experiments with other carbohydrates in presence of ferrous hydroxide are in progress and the results will be communicated in our next paper.

pinkish and finally as the oxidation proceeds the colour becomes reddish brown. In the case of the oxidation of potassium oxalate, the colour of the cerous hydroxide on passing of air becomes yellow. As the ceric hydroxide or ferric hydroxide was in the peptised condition due to the presence of sugar and alkali[1] it was coagulated by boiling with potassium sulphate and the solution was filtered and the carbohydrates were estimated after hydrolysis when necessary by reduction of Fehling's solution. The cuprous oxide obtained was collected, dried and ignited in a crucible and weighed as cupric oxide, CuO.

In all cases, the precipitate of ceric hydroxide after coagulation was washed free of alkali and carbohydrates and dissolved in potassium iodide and hydrochloric acid and the liberated iodine was estimated by standard thiosulphate and hence its constitution was examined.

From the foregoing results, it will be seen that with cerous hydroxide and ferrous hydroxide, the greater the alkali the greater is the amount of oxidation of the carbohydrates. More or less similar results were obtained by Mittra and Dhar[2] in the oxidation of nickelous hydroxide by air in presence of ferrous hydroxide.

It will be very interesting to observe that in presence of 0.7% solution of caustic soda and 0.1069 grm of cerous hydroxide, $Ce(OH)_3$, or 0.06476 grm of ferrous hydroxide, $Fe(OH)_2$, about 0.1 grm of each of the carbohydrates becomes practically completely oxidised in 5.5 hours.

It will also be seen that starch is more readily oxidised than the other carbohydrates investigated in this paper and the order in which they are oxidised is the following:—

starch > maltose > arabinose > laevulose > galactose > glucose > lactose > cane sugar. In other words, starch is most readily oxidised, whilst cane sugar is least readily oxidised among the carbohydrates investigated.

These results are very important from another point of view. The analysis of ceric hydroxide, $Ce(OH)_4$, shows that in several cases the substances obtained after the passage of air and oxidation of the carbohydrates, is practically pure ceric hydroxide, $Ce(OH)_4$. In other words, a molecule of cerous hydroxide, $Ce(OH)_3$, becomes oxidised to a molecule of ceric hydroxide, $Ce(OH)_4$, and this oxidation induces the oxidation of the carbohydrates to carbon dioxide and water. Consequently most of these cases are typical cases of induced oxidation and not cases of catalysis. Job[3], Baur, and others have assumed the formation of unstable peroxide of cerium of the following composition:— $Ce(OH)_3-O-O-Ce(OH)_3$. This peroxide is supposed to be decomposed by water into $Ce(OH)_4$ and $Ce(OH)_3-O-OH$, thus:—

$$Ce(OH)_3 + O_2 + Ce(OH)_3 = \underset{\text{Unstable Peroxide}}{Ce(OH)_3-O-O-Ce(OH)_3} \quad (1)$$

$$Ce(OH)_3-O-O-Ce(OH)_3 + H_2O = Ce(OH)_4 + Ce(OH)_3-O-OH \quad (2)$$

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[1] Compare Chatterji and Dhar: Trans. Faraday Soc. **16**, 122 (1921); Sen and Dhar: Kolloid-Z. **33**, 193 (1923).

[2] Z. anorg. Chem. **122**, 146 (1922).

[3] Job: Ann. Chim. Phys. (7) **20**, 207 (1900); Baur: Ber. **36**, 3038 (1903)

The ceric hydroxide then reacts on the carbohydrates and oxidises them and is itself converted into cerous hydroxide which in its turn is again oxidised when air is passed to ceric hydroxide and the cycle is repeated. In other words, the cerium salt is supposed to act as a catalyst in the oxidation of carbohydrates by air[1]. But from our investigations, it is clear that most of these reactions are not cases of catalysis as ordinarily understood. On the other hand, they are typical cases of induced reactions, because the composition of the ceric hydroxide which is finally obtained after the oxidation of the carbohydrates shows that it is practically $Ce(OH)_4$ and hardly contains any $Ce(OH)_3$. Moreover, we find that 0.1069 gram of cerous hydroxide or 0.06476 grm of ferrous hydroxide can oxidise by induction practically about 0.1 grm of carbohydrates. Hence practically no reduction of ceric hydroxide to cerous hydroxide in the process of oxidation takes place. Consequently we are strongly of opinion that majority of cases of oxidation are not cases of oxidation by catalysis as has been formerly assumed but are typical cases of induced reactions in which the oxidation of cerous hydroxide or ferrous hydroxide induces the oxidation of carbohydrates.

Alkalies are given with great advantage as medicine in the treatment of diabetes. They neutralise an excess of acid in the blood and tissues and are as essential in the treatment of severe cases of diabetes as are the dietic restrictions. The amount of sugar in the urine has been observed to diminish steadily under alkaline treatment. The bicarbonates of sodium and potassium have been used, and so also the citrates and tartrates. These facts are capable of interpretation in view of the results obtained by us. We have shown that in presence of alkalies, the induced oxidation of carbohydrates is greatly facilitated and we have shown that greater the amount of alkali, other things remaining constant, the greater is the oxidation of the carbohydrates. It seems probable therefore, that the addition of alkali, alkaline carbonates or bicarbonates is associated with greater oxidation of the carbohydrates in the animal body. It will be interesting to observe that Rona and Wilenko[2] have shown that an increase in hydrogen ion ($H^\cdot$) concentration greatly reduces the utilisation of glucose by an excised beating heart. Hence the alkali treatment is favourable. From our results it will be seen that glucose is more readily oxidised than cane sugar and it seems probable that in animal body it will be more readily oxidised than cane sugar. Consequently medical people are right in prescribing small quantities of glucose in preference to cane sugar. According to our investigations maltose seems to be the best among the sugars for sweetening purposes in diabetic food.

Moreover the addition of alkalies, sodium bicarbonate, etc., will decrease the concentration of hydrogen ion ($H^\cdot$) in the system and consequently the hydrolysis of starch, etc., into glucose will be decreased. Now we have proved that in all concentrations of alkalies, starch is more readily oxidised than glucose and it is quite possible that in the animal body also, starch as such before

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[1] Compare Sabatier: "La Catalyse en chimie organique," 54.

[2] Biochem. Z. 59, 173 (1913).

it is converted into glucose, is more readily oxidised than glucose itself. Now by the addition of alkalies, the conversion of starch into glucose is retarded and consequently in diabetic patients on the addition of alkalies the starch is oxidised in the body as such. As we have proved starch is more readily oxidised than glucose, consequently in diabetic patients, the addition of alkalies is favourable, because it helps the retention and oxidation of starch as such and which is found to be more readily oxidised than glucose.

At the suggestion of Voit who believed that certain withdrawal of carbohydrates from food would increase protein metabolism and would explain the high tissue waste in diabetes, Lusk[1] showed that that is actually so. Other workers also proved that the withdrawal of carbohydrate from food increases the protein metabolism. Thus Landergren proved the above fact by some beautiful experiments.

The above results can be explained from the following point of view. In foregoing papers it has been proved that substances which are readily oxidised act as marked negative catalysts in the oxidation of other substances. Thus the oxidation of sodium sulphite or benzaldehyde is markedly retarded by sodium arsenite, carbohydrates and other reducing agents, which themselves are also oxidised. Consequently it seems likely that the carbohydrates when present in the animal body act as a marked negative catalyst in the oxidation of proteins by air. Hence in the absence of carbohydrates as negative catalyst, the proteins are more readily oxidised in the body than in the absence of carbohydrates.

Lusk[2] has shown that laevulose exerted a more powerful influence on metabolism than glucose. He also showed that galactose is oxidised with much greater difficulty in dog than laevulose or glucose and that lactose was not oxidised at all and therefore caused no increase in the heat production. This latter fact must have been due to the absence of lactase from the intestines. Weinland[3] has shown that galactose does not form glycogen as readily as do glucose and laevulose. From these facts it is most probable that glactose does not as readily dissociate into easily oxidisable molecules as do glucose and laevulose. By similar reasoning one can explain the difference in behaviour between glucose and laevulose. Glucose molecules require simple dehydration for conversion into glycogen and may in that fashion be removed from the tissue fluids. Laevulose cannot be thus removed. It must first undergo chemical change before it can be synthesised into glycogen.

Ishimori[4] has reported that galactose is less readily oxidised at least in the adult organism than are glucose and laevulose, although it may be that the condition for its break-down are more favourable in the suckling.

In a recent paper, Spoehr[5] has made the following statements:—

"In strongly alkaline solution, glucose is oxidised by air, but these conditions have only remote physiological influence because it has not been pos-

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[1] Z. Biol. 27, 459 (1899).

[2] J. Biol. Chem. 20, 555 (1915).

[3] Z. Biol. 38, 16, 607 (1899).

[4] Biochem. Z. 48, 332 (1912).

[5] J. Am. Chem. Soc. 40, 1494 (1924).

sible to oxidise glucose with air in solutions of hydroxyl ion (OH′) concentrations approximating those found in the living organism even in presence of iron salts or phosphates."

In view of our experimental results, the above remarks need correction, because we have been able to oxidise eight carbohydrates in practically neutral solutions by passing air through the solutions of the carbohydrates in contact with cerous hydroxide or ferrous hydroxide.

We have also attempted to induce oxidation of sodium chromite, sodium manganite, sodium nitrite and potassium oxalate by passing air in contact with cerous hydroxide (vide Table Nos. III and IV). Only sodium chromite and sodium manganite were partly oxidised into sodium chromate and sodium manganate. Recently Wood and Miss Black[1] have obtained traces of oxidation of solutions of chromic hydroxide in presence of caustic soda into sodium chromate by air. It is very interesting to note that we could not oxidise sodium nitrate and potassium oxalate, which are so readily oxidised under other conditions by this method.

We are further investigating the problem and the experiments are in progress, the results of which will be communicated in our next paper.

Summary

(1) In this investigation a systematic study has been made on the oxidation of carbohydrates such as starch, cane sugar, maltose, lactose, glucose, arabinose, laevulose, etc. It has been found that when a stream of air is allowed to pass slowly through an alkaline solution of carbohydrates, namely starch, maltose, arabinose, laevulose, galactose, glucose, lactose and cane sugar in presence of freshly precipitated cerous hydroxide or ferrous hydroxide, the carbohydrates get oxidised into water and carbon dioxide in about 5.5 hours.

(2) It has also been observed that as the concentration of the alkali increases, the amount of oxidation of the carbohydrates also increases.

(3) There are some carbohydrates such as galactose, laevulose, arabinose, maltose, etc., which can be completely oxidised with ease into water and carbon dioxide, whereas there are others such as cane sugar, etc., which can be oxidised to a less extent under the same conditions. It has been conclusively proved by experiments that oxidation does take place in each case.

(4) This experiment has also been extended to certain other inorganic substances such as the oxidation of oxalates, nitrites, chromites, manganites, etc., and it has been found that oxalates, nitrites, etc., cannot be oxidised at all, whereas chromites and manganites can be oxidised by air in presence of ex-

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[1] J. Chem. Soc. 109, 104 (1916).

cess of alkali into chromates and manganates under the same conditions, though the latter to a less extent than the former one.

(5) An explanation of the internal use of alkali and alkaline carbonates in diabetes has been suggested based on increased oxidation of carbohydrates by air in presence of alkali.

(6) The experiments in this investigation are in reality imitations of Nature's process of oxidation (slow) of food materials in the animal body.

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ADSORPTION OF DYES BY SOILS

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The method of determining the amounts of colloidal matter in clays and soils by measuring the amount of some dye taken up has been developed by Rohland[1], Ashley[2], Lord[3] and others. The method is based on the assumption that the dye is taken up by adsorption which is a property of surfaces and hence is a measure of the colloidal matter. Therefore, the amount of dye taken up is considered a measure of the colloidal matter in the soil.

Bancroft[4] has shown that the dyeing of textiles is essentially an adsorption phenomenon and the dyeing of soils should be of a similar nature. The amount of dye taken up will depend on the following factors; (a) nature of the soil, (b) nature of the dye, (c) acidity or alkalinity of the soil solution, (d) acidity or alkalinity of the dye solution, (e) presence of other salts in solution, (f) a possibility of base exchange between the dye and the minerals in the soil.

(a) & (b) From Bancroft's theory that dyeing is an adsorption phenomenon, a soil containing a positive colloid such as ferric hydroxide will adsorb more of an acid dye such as diamine sky blue than it will if it contains a negative colloid such as silicic acid. This is what is found experimentally by Beaumont[5]. Similarly a basic dye such as methylene blue will be more adsorbed by a negative colloid like silicic acid. Rohland[6] has shown that the amount of dye adsorbed is in general greater the more complex its nature and the more colloidal it is. The dyes usually used for determining the amounts of colloids in clays and soils have been basic dyes such as malachite green chloride or oxalate, methyl violet, methylene blue, crystal violet and aniline blue. These will measure chiefly the negative colloids. It is obvious therefore that the nature of both the dye and the soil colloid will have a large effect on the amount of adsorption.

(c) As Bancroft has shown with textiles an acid dye will be more adsorbed from an acid solution because of the high adsorption of the H ion by the fiber and a basic dye will be less adsorbed from an acid solution than it will be from a neutral or alkaline solution due to the high adsorption of OH ions from the latter. Rohland[7] has shown that the amount of methyl orange (an acid dye) taken up by a given soil is greater from an acid solution than from one which is neutral or alkaline. He concludes that the acid forms more colloidal material in the soil but the more probable explanation is that the dye anion is more highly adsorbed due to the H ion of the acid being first adsorbed.

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[1] Rohland: Farben-Zeitung **18**, 522 (1913).

[2] Ashley: Trans. Am. Cer. Soc. **11**, 530 (1909).

[3] Lord: U. S. Bur. of Public Roads. Laboratory Tests for determining the Physical Properties of Subgrade Soils.

[4] Bancroft: J. Phys. Chem. **18**, 1, 118, 385 (1914).

[5] Beaumont: Cornell Ag. Exp. Sta. Mem. **21**, 494 (1919).

[6] Rohland: Kolloid-Z. **16**, 16 (1915).

[7] Rohland: Glasind. **26**, Nos. 19-22 (1915).

(d) The amount of dye taken up will depend not only on the acidity or alkalinity of the soil solution when it is treated with water but also on the acidity or alkalinity of the dye solution used. If one had a soil that gave a basic solution on treatment with water the amount of an acid dye taken up from this solution would probably be very small.

(e) Just as H ions cause a variation in the amount of dye adsorbed other ions, especially metals, will have a similar effect and a soil or clay that will give a water solution containing salts of Ca, Mg, Fe, and Al will adsorb more of an acid dye than will one that gives none of these. Similarly, the presence of anions as nitrate, sulphate or chloride in the soil solution will increase the amount of a basic dye that will be adsorbed[1]. In the case of malachite green which is sold either as the oxalate or the chloride the amount of dye adsorbed will be different depending upon which one is used. It should be less in the case of the chloride since the bivalent negative oxalate is more adsorbed than the univalent chloride and hence will cause more of the dye ion to be adsorbed.

(f) A basic dye such as malachite green has in addition to the adsorption of the positive dye ion a possibility of exchanging some of its positive ion for the metal ions of the soil particle and thus fix more dye by chemical action or base exchange. Ashley[2] says that this is the way malachite green is taken up rather than by adsorption.

With these points in view the experiments were planned to find the effect of the concentration of acid and base upon the amount of dye adsorbed by different soils and to look for evidence of any base exchange between the dye and the soil. It was thought that by adding varying amounts of acid to the soil one should be able to saturate the soil colloids with H ions and thus increase the amount of an acid dye held to a maximum and decrease the amount of a basic dye held and by using a base increase the amount of a basic dye held and decrease the amount of an acid dye. Six soils were used, (1) and (2) were Kansanian clays, (3) and (4) were Iowa drifts, (5) a black loam and (6) a dark red sandy clay very high in iron content.

An endeavor was made to find a dye that had the same color in acid and alkaline solution but none was found. Next search was made for dyes that had definite colors in both acid and alkaline solutions even though the colors were different. The two that were used were diamine blue 3 B and methylene blue. The former is blue in acid solution and purple in neutral and alkaline solution. The latter is blue in neutral and acid solution and pink in alkaline solution. Neutral violet, which is violet in neutral and acid solution but is insoluble in an alkaline solution, was used also for neutral and acid solution. Diamine blue 3 B is an acid dye while the other two are basic dyes.

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[1] Bancroft: loc. cit. p. 120

[2] Ashley: Bur. Standards Tech. Paper, **23**, 41 (1914).

Procedure

The amount of dye adsorbed was determined by placing one gram of the soil in a large test tube and adding sufficient dye solution to saturate it and still leave some excess which was determined colorimetrically using a Duboscq colorimeter. The test tubes were then stoppered with paraffined corks and placed in a shaking machine and shaken vigorously for a given time. The soil was then allowed to settle, the concentration of the dye solution determined and the loss taken as the dye adsorbed. To determine the time necessary to reach equilibrium a series was shaken for different lengths of time and the adsorption measured. This was done with several dyes and different soils. The following table is typical of the results.

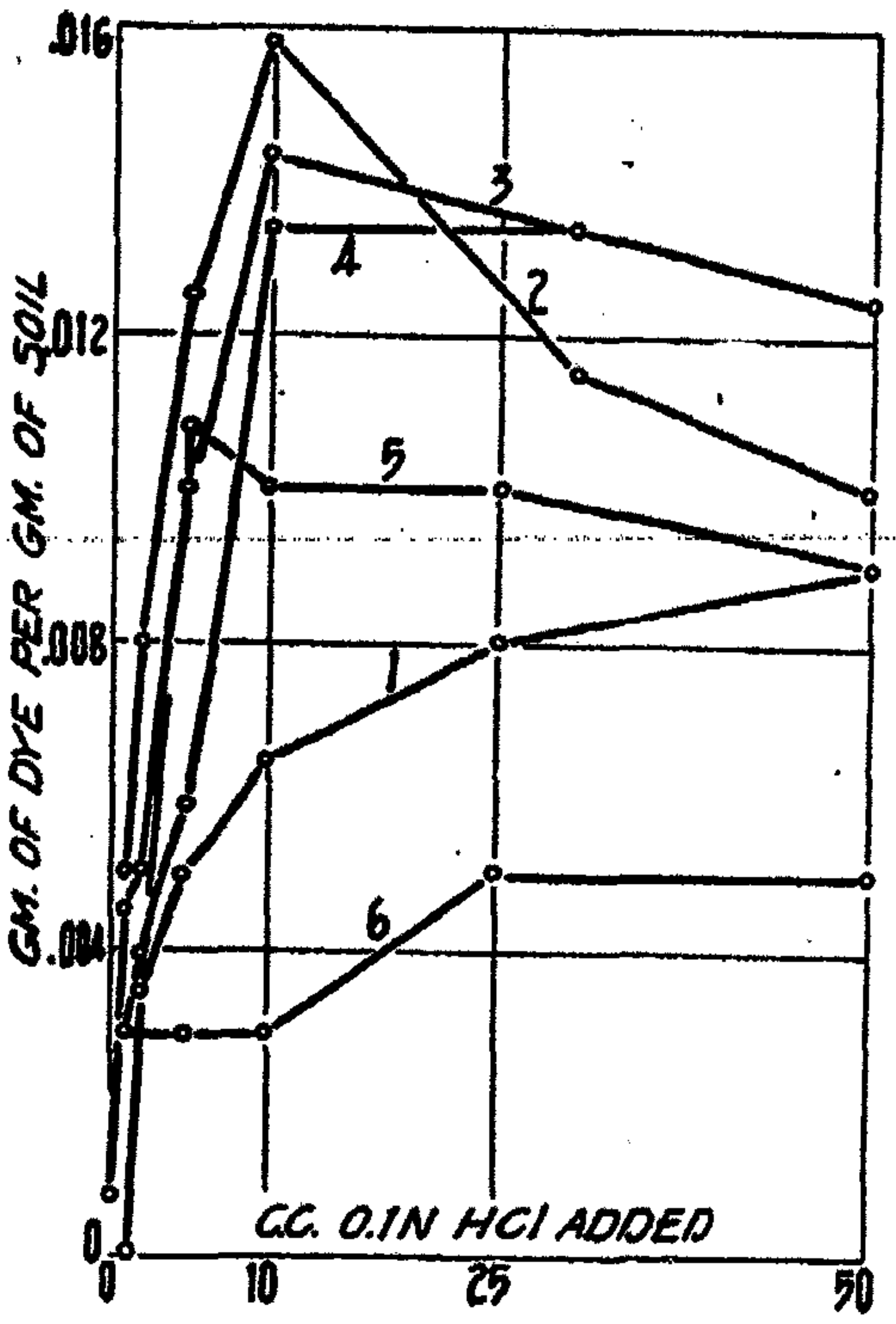

Fig. 1
Adsorption of Diamine Blue

Table I
Rate of Adsorption of Dye by Soil

Time (hours)	gm dye adsorbed	gm dye adsorbed
0.25	0.0453	0.0455
0.50	0.0457	0.0457
1	0.0475	0.0475
2	0.0482	0.0483
3	0.0483	0.0484
6	0.0487	0.0488
8	0.0489	0.0489

TABLE II

Adsorption of Diamine Blue 3 B from Acid Solution
gm of dye adsorbed per gram of soil

cc. 1N HCl	Soil (1)	Soil (2)	Soil (3)	Soil (4)	Soil (5)	Soil (6)
0	0.0015	0.0015	0.0008	None	None	None
1	0.0015	0.0050	0.0045	0.0029	None	0.0029
2	0.0034	0.0080	0.0050	0.0039	0.0029	0.0029
5	0.0050	0.0125	0.0100	0.0059	0.0108	0.0029
10	0.0065	0.0158	0.0143	0.0134	0.0100	0.0029
25	0.0080	0.0115	0.0134	0.0134	0.0100	0.0050
50	0.0090	0.0100	0.0125	0.0125	0.0091	0.0050

TABLE III

Adsorption of Diamine Blue 3 B from Alkaline Solution
Diamine Blue 3 B adsorbed per gm of soil

cco.IN KCH	Soil (1)	Soil (2)	Soil (3)	Soil (4)	Soil (5)	Soil (6)
0	0.0007	None	0.0015	None	None	None
1	0.0015	"	0.0015	"	"	"
2	None	"	0.0015	"	"	"
5	0.0007	"	0.0015	"	"	"
10	0.0015	"	0.0030	0.0029	"	"
25	0.0015	"	0.0040	0.0039	"	"
50	0.0025	0.0029	0.0040	0.0039	"	"

TABLE IV

Adsorption of Neutral Violet
gm of dye adsorbed per gram of soil

cco 1 N HCl	Soil (1)	Soil (2)	Soil (3)	Soil (4)	Soil (5)	Soil (6)
0	0.0791	0.0728	0.0806	0.0750	0.0605	0.0113
1	0.0758	0.0723	0.0781	0.0750	0.0531	0.0113
2	0.0692	0.0657	0.0727	0.0710	0.0527	0.0113
5	0.0653	0.0600	0.0713	0.0713	0.0485	0.0100
10	0.0630	0.0650	0.0758	0.0727	0.0490	0.0123
25	0.0603	0.0550	0.0758	0.0750	0.0510	0.0137
50	0.0603	0.0600	0.0806	0.0781	0.0531	0.0142

TABLE V

Adsorption of Methylene Blue
gm of dye per gram of soil

cco.1 N HCl	Soil (1)	Soil (2)	Soil (3)	Soil (4)	Soil (5)	Soil (6)
0	0.0425	0.0430	0.0575	0.0568	0.0360	0.0073
1	0.0479	0.0437	0.0586	0.0568	0.0384	0.0073
2	0.0479	0.0413	0.0600	0.0518	0.0366	0.0073
5	0.0477	0.0413	0.0575	0.0520	0.0294	0.0073
10	0.0476	0.0413	0.0584	0.0557	0.0313	0.0084
25	0.0467	0.0407	0.0600	0.0586	0.0313	0.0097
50	0.0462	0.0372	0.0600	0.0586	0.0360	0.0104

In all cases it was found that over 95% of the total dye adsorbed was taken up in an hour of shaking and in later experiments an arbitrary time of one hour was used in determining the amount of dye adsorbed. This agrees with the results of Morse and Curry[1] who found that while most of the dye was taken up in an hour or so it did not reach an equilibrium until after 72 hours.

The Effect of Acidity and Alkalinity

The effect of acidity and alkalinity was determined by mixing varying quantities of 0.1 N HCl or NaOH with water and dye solution so that the total volume in each case was 50 cc and adding to this one gram of soil. The amount of dye that will be taken up is of course dependent upon the excess of dye present and so a preliminary run was made with each soil to find the approximate amount of dye that would be taken up and slightly more than this amount was introduced for the final run so that the adsorption was always determined in the presence of a very small excess of the dye. After shaking vigorously for an hour in a mechanical shaker the samples were allowed to settle and the concentration of the dye remaining in the liquid determined. The results obtained are shown in Tables II, III, IV and V, and in Figs. 1, 2, 3 and 4.

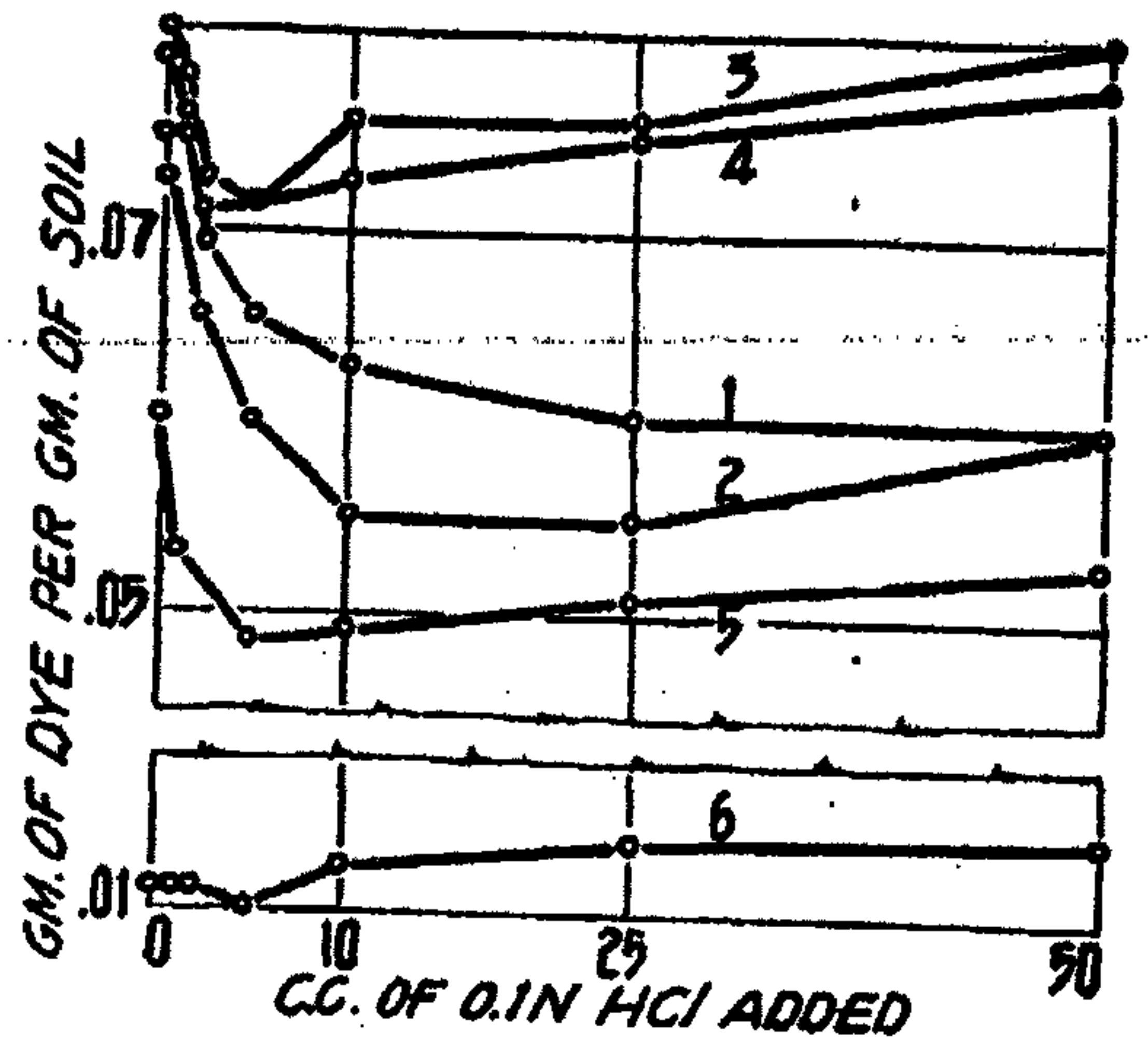

FIG. 2
Adsorption of Neutral Violet

Discussion of Results

Diamine Blue 3B is an acid dye, being the sodium salt $Na_4C_{34}H_{24}N_6O_{14}S_4$, and should therefore be more adsorbed from an acid solution and it is found to be so with every soil that was examined as is shown in Table II and Fig. 1. The form of the curves agrees with what one should get since an increase in the H concentration will increase the amount of dye adsorbed up to a certain point

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[1] New Hampshire Agr. Expt. Sta. Reports 19 and 20, p. 275 (1908).

and beyond that the adsorption of the negative Cl will tend to replace the negative dye ion and the amount of dye held will be less.

It will be observed that the soils arrange themselves in the same order for all the dyes, the only exception being Soil No. 1 with diamine blue in acid solutions. The red sandy clay shows the least adsorption in every case and the Iowa drift soils the most.

Table III shows that the addition of base decreases the amount of diamine blue taken up compared to that from the acid solution. With two of the soils no dye was adsorbed at all and with one it is only when the solution is 0.1N with respect to the base that adsorption took place. With the other three soils the amount is only about one third as much as from acid solutions. This adsorption may be due to the presence of a positive colloid in the soil or to the sodium ion of the base being adsorbed enough to partly overcome the effect of the OH ion.

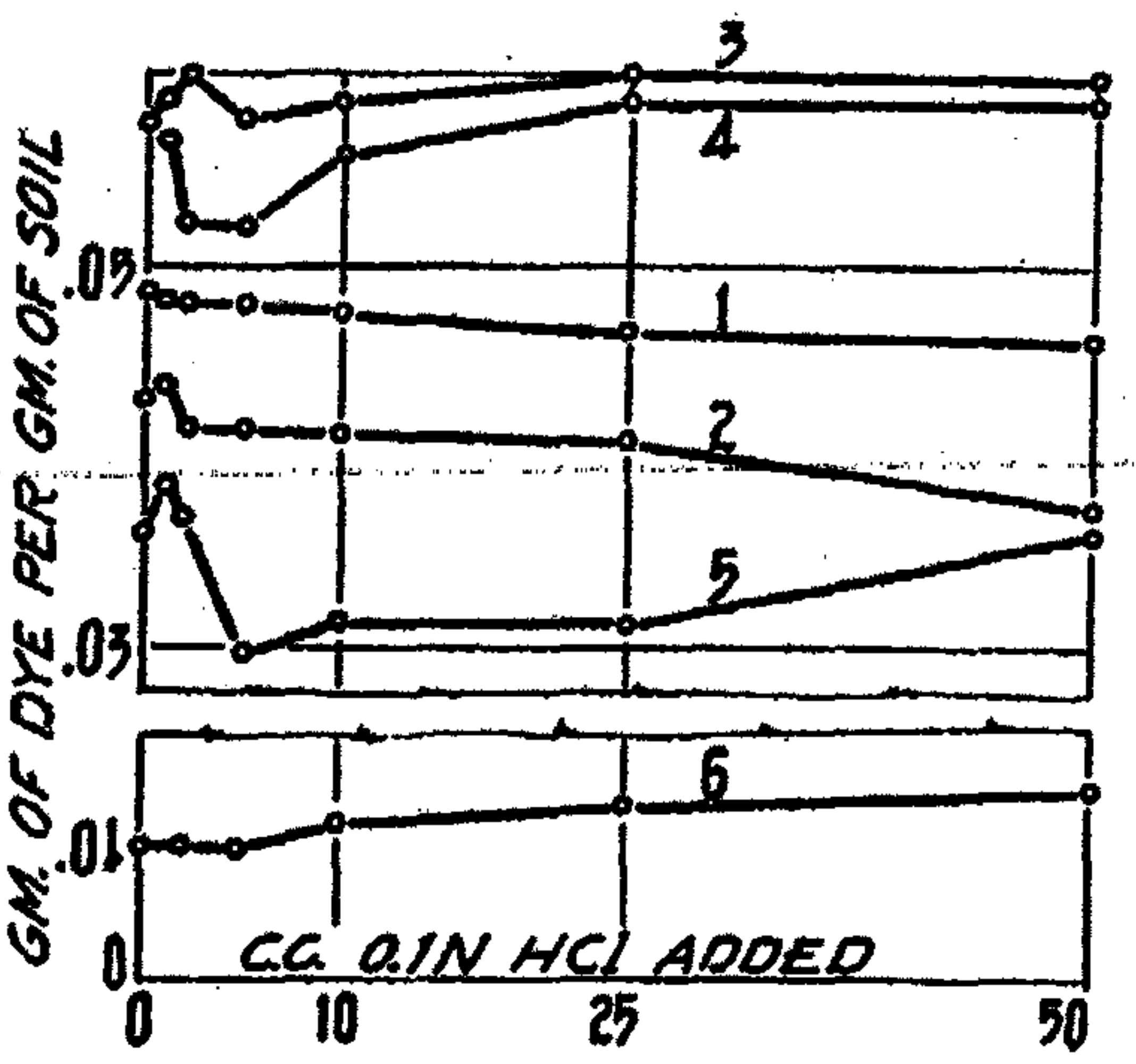

FIG. 3
Adsorption of Methylene Blue

Table IV and Fig. 2 for neutral violet, a basic dye of the formula $C_{14}H_{14}N_4HCl$ show curves that are the reverse of those for diamine blue 3B. A small amount of acid decreases the dye adsorption very appreciably except with the red sandy clay No. 6, which has but little colloidal matter present as shown by the small amount of adsorption with any of the dyes. After the decrease every soil increases again due to the adsorption of Cl ion partly overcoming the effect of the H ion.

Table V and Fig. 3 for methylene blue, which is also a basic dye of the formula $C_{16}H_{18}N_3S\,Cl$, show the same type of curves as did neutral violet although the effect is not so pronounced, possibly because the amount of dye adsorbed is less.

In Fig. 4 the values are plotted for four dye solutions with one of the soils (No. 1). In addition to the data already given in the tables a curve is shown for another dye, methylene violet, in an alkaline solution. This is a basic dye and should therefore be more adsorbed from a basic solution and this is what it is found to be. Also as the concentration of the base increases the Na ion apparently has a retarding effect as it should.

Base Exchange

When a paste was made with each one of the soils using distilled water the solution was found to be slightly alkaline to litmus. It was noticed that if an amount of methylene blue or neutral violet was added, which was insufficient to saturate the clay but left the solution still colorless, it was more alkaline than it had been with pure water. A qualitative examination of these solutions showed the presence of calcium, magnesium and potassium. Each soil was then tested to see if they showed any base exchange between the colored ion of the dye and the metal ions of the soil.

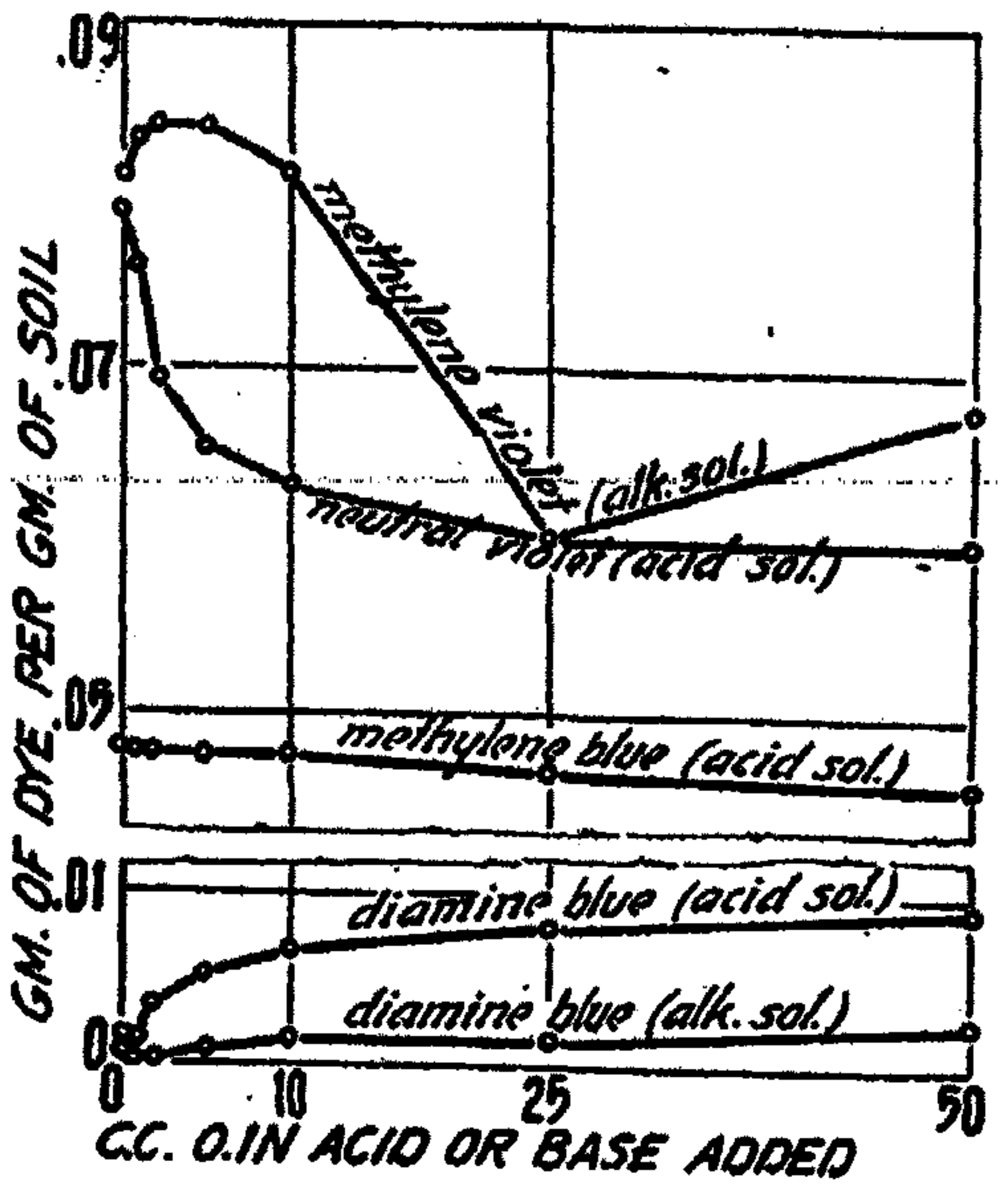

Fig. 4
Adsorption of Dyes by Soil No. 1

Two grams of the clay were treated with 50 cc of conductivity water and shaken for a period of several days and then allowed to stand until the supernatent liquid was clear. This in some cases required several weeks. Another sample was treated with insufficient amount of dye to quite saturate it so that the liquid remaining behind was clear. This was shaken in the same way and allowed to stand. After pipetting off the solutions they were analyzed for Ca, Mg and K and in every case more of all these were found in the solutions where the dye was used than in the water solutions.

A quantitative determination was made with Soil No. 1 and methylene blue for the amount of Ca and Mg replaced. With water alone 2 grams of the soil gave 0.0346 grams of Ca while with the dye it gave 0.0570 grams. The amount of Mg found was but a trace, being 0.0002 grams, but none at all was found in the pure water solution. A further quantitative study is being made of the effect of base exchange.

Conclusions

(1) The adsorption of dyes by soils and clays is of the same nature as the dyeing of fibers.

(2) The amount of dye taken up may be increased or decreased by varying the acidity or alkalidity of the solution.

(3) Ninety-five per cent of the total dye adsorbed will be taken up during an hour of steady shaking.

(4) There is some evidence of base exchange between the dyes and the basic elements in the soil.

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THE THIRD LAW OF THERMODYNAMICS AND CALCULATION OF ENTROPIES

BY T. J. WEBB

The evaluation, from thermal data, of the free energy change accompanying a reaction, has been of fundamental importance since 1888, when LeChatelier integrated the Gibbs-Helmholtz equation:[1]

$$\Delta F = \Delta H + T\left(\frac{\partial \Delta F}{\partial T}\right)_P \qquad (1)$$

$$\frac{\Delta F \partial T - T \partial \Delta F}{T^2} = \frac{\Delta H \partial T}{T^2}$$

$$\partial\left(\frac{-\Delta F}{T}\right) = \frac{\Delta H \partial T}{T^2}$$

$$\int \partial\left(\frac{-\Delta F}{T}\right) = \int \frac{\Delta H \partial T}{T^2} + I$$

$$-\Delta F = T\int \frac{\Delta H\, \partial T}{T^2} + I\,T \qquad (2)$$

I is a constant of integration, and upon its evaluation, as well as upon a knowledge of ΔH, depended the usefulness of the above equation. Nernst[2] in 1906 in a paper, "Uber die Berechnung chemischer Gleichgewichte aus thermischen Messungen", brought forth evidence to show that the integration constant in the above equation is zero for all reactions in which only pure solids and liquids are involved. The evidence for the assumption that the integration constant is zero arose from the fact that ΔF and ΔH rapidly approach a constant value, as the temperature is lowered. It was assumed that $\partial\Delta F/\partial T$ and $\partial\Delta H/\partial T$, which are always of opposite sign, approach zero as the absolute zero of temperature is approached. ΔH in the above equation may be expressed by a equation such as the following:

$$\Delta H = \Delta H_o + \Delta\Gamma_o T + \tfrac{1}{2}\,\Delta\Gamma_1 T^2 + \tfrac{1}{3}\,\Delta\Gamma_2 T^3 + \ldots\ldots \qquad (3)$$

where the ΔΓ's stand for the increments of heat capacity terms, and ΔH_o is therefore the heat of reaction at the absolute zero. Substituting this value of ΔH in equation (2), and integrating,—

$$\Delta F = \Delta H_o - \Delta\Gamma_o T \ln T - \tfrac{1}{2}\Delta\Gamma_1 T^2 - \tfrac{1}{6}\,\Delta\Gamma_2 T^3 + \ldots\ldots + IT$$

Then

$$\frac{\partial \Delta F}{\partial T} = -\,\Delta\Gamma_o(1+\ln T) - \Delta\Gamma_1 T - \tfrac{1}{2}\,\Delta\Gamma_2 T^2 + I \qquad (3a)$$

and

$$\frac{\partial \Delta H}{\partial T} = \Delta\Gamma_o + \Delta\Gamma_1 T + \Delta\Gamma_2 T^2 + \ldots\ldots$$

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[1] The symbols used are those considered standard. Cf. Lewis and Randall: "Thermodynamics", McGraw-Hill Book Co.

[2] Nernst: Nachr. kgl. Wiss. Gottingen. Math.-physik. Klasse, 1906, 1.

Introducing the assumption that:

$$\lim \frac{\partial \Delta H}{\partial T} = \lim \frac{\partial \Delta F}{\partial T} = 0 \qquad \text{for } T = 0$$

it follows that

$$\Delta\Gamma_0 + \Delta\Gamma_1 T + \Delta\Gamma_2 T^2 = 0$$

and

$$\Delta\Gamma_0 - \Delta\Gamma_0 \ln T - \Delta\Gamma_1 T - \tfrac{1}{2}\Delta\Gamma_2 T^2 + I = 0.$$

In order that the two expressions may be simultaneously equal to zero at $T = 0$, it is necessary that

$$I = 0$$

$$\text{and } \Delta\Gamma_0 = 0$$

This is the original way in which the third law was formulated by Nernst in 1906. Accurate specific heat data over the entire range of temperature were almost non-existent, and therefore accurate tests of the law were not readily forthcoming. A much more wieldy method of testing is furnished by entropy relations, directly deducible from the fundamental assumptions outlined above. From the definitions of free energy and entropy,

$$\frac{\partial \Delta F}{\partial T} = -\Delta S,$$

where ΔF and ΔS denote respectively free energy and entropy increases. From Kirchhoff's law, the following relation is obtained:

$$\frac{\partial \Delta H}{\partial T} = \Delta C_p$$

Consideration of the assumption that $\frac{\partial \Delta F}{\partial T}$ and $\frac{\partial \Delta H}{\partial T}$ approach zero at the absolute zero brings to light the relation that $-\Delta S$ approaches zero as well as ΔC_p. The fact that ΔS approaches zero means that in any reaction at the absolute zero the entropies are additive: at $T = 0$, the entropy of a compound is the sum of the entropies of its elements. The general principle of the additivity of entropies, however, necessitates that all elements and compounds have zero entropy at the absolute zero.

The methods of testing the third law have been varied. In all attempts the ultimate object of all investigators has been to show that the integration constant in the above equation is zero. In this paper, evidence will be brought forward to show that the inaccuracies attending measurement of temperature coefficients of reversible galvanic elements in many cases are of sufficient magnitude as to render them useless in many such calculations. A typical example is furnished by the silver-iodine combination, which will be taken up in considerable detail. Practically all experiments were in agreement to within 30 calories as regards the free energy change, while the value for the total energy change varied from 14,565 calories to 15,250 calories. The discordance of thermochemical measurements rendered the thermodynamic properties of this combination all the more uncertain.

The method of testing the third law, initiated herein by the silver-iodine combination, and illustrated subsequently by the calculation of the entropy of iodine, is as follows. An accurate knowledge of the free energy change accompanying the process must be obtained. This may be obtained in various ways: the most convenient one (where possible) is by setting up a reversible galvanic element employing the process under investigation. The free energy change of any element which is reversible and reproducible can be measured by potentiometric means with an accuracy of 50 calories (corresponding to an accuracy of 0.15 entropy unit at 298°). Instead of calculating the total energy change from the free energy change and its variation with temperature, it is proposed that an accurate calorimetric determination be substituted. An accuracy of 50 calories can be obtained without an excessively elaborate apparatus. The chief errors arise from heat capacity determinations and from stirring corrections. The former can be minimized by accurate measurement of the electrical energy (i. e., with potentiometer) and the latter by the choice of an efficient stirrer. A Beckmann thermometer is amply accurate for the temperature measurements. The difference between the total energy change and the free energy change gives $T\Delta S$, (or $T\frac{\partial(-\Delta F)}{\partial T}$). The entropy change thus obtained may then be compared with that obtained from specific heat measurements. The tables compiled by Miething (referred to later) facilitate the calculation of ΔS from specific heat data. The tables give the numerical value of the following functions:

$$E = \int C_p dT \qquad\qquad F = -T\int \frac{E}{T^2}\,dT$$

E is the total energy increase from $T = 0$ to $T = T$ and F is the free energy increase from $T = 0$ to $T = T$. It is obvious from the equations that E and F correspond respectively to ΔH and ΔF, previously used. Substitution in the fundamental equation, $\Delta F = \Delta H - T\Delta S$, gives immediately the value of ΔS between $T = 0$ and $T = T$, which is usually spoken of as simply the entropy of the substance at temperature T. The third law is involved in that an integration constant appears in the equation defining F. It is clear that if the third law is assumed, and if the entropies of all of the substances except one are known, the entropy of that substance may be calculated. This is the method used in the calculation of the entropy of iodine (vide infra).

The method of testing the third law by comparing observed temperature coefficient with that calculated from equation (3a) may prove most hazardous, as exemplified by the work of Jones and Hartman who found that the integration constant was 2.33 calories per degree in the silver-iodine combination. It seems that these unusual results may be attributed entirely to inaccurate calculations of the temperature coefficient of the liquid potential and osmotic work connections.

In most cases, however, where such corrections are unnecessary, the entropy relations may be obtained from the temperature coefficient of the cell with considerable accuracy. The third law may be tested by calculating in several ways the entropy of a compound from temperature coefficients of ΔF of several of its reaction processes. Obtaining the same value in various reactions is evidence of the validity of the third law.

II. Entropy Relations applied to Cadmium Chloride and Iodide

The absence of accurate specific heat data for these two salts prevented their employment in a purposed test of the third law (as originally put forward by Nernst). The principle of the additivity of entropies simplifies the calculations. In the case of cadmium chloride, the following reactions have been investigated:

$$^{*}\ Cd + 2AgCl + 2.5H_2O = CdCl_2 2.5H_2O(Solid) + 2Ag \qquad (4)$$

$$^{**}\ Cd + Hg_2Cl_2 + 2.5H_2O = CdCl_2 2.5H_2O(Solid) + 2Hg \qquad (5)$$

$$^{*}\ Cd + PbCl_2 + 2.5H_2O = CdCl_2 2.5H_2O(Solid) + Pb \qquad (6)$$

If the third law is assumed true, that is, if it is assumed that every cyrstalline substance has zero entropy at the absolute zero, the entropy of cadmium chloride hydrate may be calculated by three independent methods from the following equations:

$$S_{Cd} + S_{2AgCl} + S_{2.5H_2O} = S_{CdCl_2\ 2.5H_2O} + S_{2Ag} - (\Delta S_1) \qquad (7)$$

$$S_{Cd} + S_{Hg_2Cl_2} + S_{2.5H_2O} = S_{CdCl_2.2.5H_2O} + S_{2Hg} - (\Delta S_2) \qquad (8)$$

$$S_{Cd} + S_{PbCl_2} + S_{2.5H_2O} = S_{CdCl_2.2.5H_2O} + S_{Pb} - (\Delta S_3) \qquad (9)$$

ΔS_1, ΔS_2, and ΔS_3 are the entropy increases accompanying each reaction, and are measured by the cell temperature coefficients, i.e., $\frac{\partial(-\Delta F)}{\partial T} = \Delta S$, where ΔF is the increase in free energy accompanying the reaction process. In the cells mentioned above, cadmium amalgam was used instead of pure cadmium; electrolytic silver chloride instead of the precipitated form; and water from a saturated solution of the hydrate instead of pure water. The entropy differences between these various forms must be taken into account. For the difference in entropy between cadmium and cadmium amalgam, the data of Hulett[1] may be employed. If however his data are used in combination with the measured values, to calculate the electromotive force of the cell,

$$Cd \mid CdCl_2 . 2.5H_2O \mid AgCl_{(E)}, Ag,$$

at various temperatures, the temperature coefficient is found to be −0.00065 volt. The corresponding entropy change is −29.96 entropy units. The entropy of precipitated silver chloride at 298° is obtained by plotting the logarithm of the absolute temperature against the molecular heat of silver chloride

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* Taylor and Perrott: J. Am. Chem. Soc., 43, 484 (1921).

** Lipscomb and Hulett: J. Am. Chem. Soc., 39, 38 (1916).

[1] Hulett: Trans. Am. Electrochem. Soc., 7, 333 (1905).

and integrating graphically from T = 0 to T = 298. The entropy of the electrolytic variety is found by comparison of cells using the different forms. Gerke[1] found the entropy increase in the reaction—

$2Ag + Hg_2Cl_2 = 2AgCl_{(P)} + 2Hg$ — to be 15.6 entropy units.

Brönsted[2], investigating the same reaction, employing however electrolytic silver chloride, found an entropy increase of 16.6 entropy units. ΔS for the reaction, $2AgCl_{(E)} \longrightarrow 2AgCl_{(P)}$, is therefore $-.5$ entropy unit. From specific heat data, the entropy of two moles of precipitated silver chloride is found to be 46.8 entropy units, and therefore that for two moles of the electrolytic variety is 47.3. This seems to be in agreement with the observations that amorphous silver chloride has the higher specific heat, it being assumed that the very finely crystalline electrolytic variety is a closer approach to the amorphous condition.

The value for the entropy of water as calculated from the relation, $\Delta F = \Delta H - T\Delta S$, when applied to the reaction, $H_2 + 1/2O_2 = H_2O$, is 14.44 entropy units. The value obtained from specific heat data is 16.8. The mean of these two is employed, namely, 15.6 entropy units. It is to be noted that the uncertainty of this figure in no way invalidates the agreement of the values for the entropy of the hydrate of cadmium chloride about to be set forth. Substitution of the values just obtained, along with the values 11.8 for cadmium and 10.25 for silver (both obtained from specific heat measurements), in equation (7) gives for the entropy[3] of $CdCl_2 . 2.5H_2O$:

$$11.8 + 47.3 + 39 = S_{CdCl_2 . 2.5H_2O} + 20.50 + 29.96$$

$$S_{CdCl_2 . 2.5H_2O} = \underline{47.64}$$

$$H_2O_{(pure)} \longrightarrow H_2O_{(CdCl_2 . 2.5H_2O \text{ sat. soln.})}$$

The temperature coefficient of the cell, $Cd \mid CdCl_2.2.5H_2O \mid Hg_2Cl_2, Hg$, was found by Lipscomb and Hulett[4] to be -0.00032 volt. The entropy increase corresponding is 14.65 entropy units. The cell measured contained cadmium amalgam, and the same correction was again employed as before. The entropy of one mole of Hg_2Cl_2 at 25° is 46.5; that of two gram-atomic weights of mercury is 35.6. Employing these data along with those previously employed for cadmium and water in equation (8) gives for the entropy of the hydrate 46.95 entropy units.

$$11.8 + 46.4 + 39 = S_{CdCl_2 . 2.5H_2O} + 35.6 + 14.65$$

$$S_{CdCl_2 . 2.5H_2O} = 46.95$$

The temperature coefficient of the cell, $Cd \mid CdCl_2.2.5H_2O \mid PbCl_2, Pb_{(E)}$, was found to be $-.00048$ volt. The entropy difference corresponding is

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[1] Gerke: J. Am. Chem. Soc., 44, 1703 (1922).

[2] Brönsted; Z. physik. Chem., 56, 645 (1906).

[3] Before the absolute value of the entropy of the hydrate is established, the entropy change accompanying the following reaction must be determined:

[4] Lipscomb and Hulett: loc. cit.

−22.13. The cell actually measured contained cadmium amalgam as well as 0.72 percent lead amalgam. Corrections for these were applied. The data of Brönsted were used in the calculation lead — lead amalgam by means of the interpolation formula:

$$E = .0051 + .000233t.$$

The value thus obtained is valid only for electrolytic lead. Sufficient data are available from the work of Gerke[1] for the calculation of ΔS- value between the two forms of lead. In his summarizing table he indicated an entropy difference of .28 entropy unit. A re-inspection of his data shows that this value is slightly low. In his Table V the voltage of the cell, $Pb_{(E)} \mid Pb(Ac) \mid Pb\,Hg$, at 25° is .00586 (±.041). This is checked on two days and with two cells. The voltage of the cell at 15° is .00552 (± .041). This value is also checked. These are the only temperatures at which the voltage was sufficiently checked in order to give an accurate temperature coefficient. During the last measurements of this cell, the cell was presumably not given time for attainment of equilibrium, for the cell shows an impossibly large temperature coefficient of ΔS, $\frac{\partial \Delta S}{\partial T} = \frac{\Delta C_p}{T}$. The values accepted are those obtained at the first of each day (except the check of the 15° measurement)—presumably after the cell had remained at constant temperature over night. The entropy difference corresponding to the temperature coefficient indicated is 1.56 entropy units. The entropy difference between stick lead and the same lead amalgam was found to be .69 entropy unit. The difference, .89, represents the entropy change concomitant with the following reaction:

$$Pb_{(S)} \longrightarrow Pb_E \quad \Delta S = -.89$$

The entropy of electrolytic lead is therefore taken as 14.64. Substitution of these values in equation (9) gives for the entropy of cadmium chloride hydrate 47.2 entropy units.

The values thus obtained for the entropy of this salt hydrate for three independent experiments are 47.6, 47.0 and 47.2. The absolute value of the entropy of the hydrate may be obtained by finding ΔS for the reaction:

$$H_2O_{(sat.soln.CdCl_2\,.\,2.5H_2O} \longrightarrow H_2O_{pure}$$

Such is not necessary for the verification of the third law. The three values were arrived at by employment of the principle of additivity of entropies and of the postulate that the entropy of every crystalline substance at the absolute zero is zero. The degree of concordance revealed above is as good as could be anticipated, considering the inaccuracies attending the measurements. The assumption was also made that the forms of material used by one investigator were identical thermodynamically with the corresponding forms used by another, which, if true, constituted a most bizarre coincidence. However, such differences were assumed to be within the experimental error.

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[1] Gerke: loc. cit.

The thermodynamic data of cadmium iodide may also be employed in a test of the third law. Taylor and Perrott[1] found that the temperature coefficient of the cell employing the reaction, $Cd + 2AgI = CdI_2 + 2Ag$, is −.000136 volt. This corresponds with an entropy increase of −6.3 entropy units. The silver iodide employed was not the precipitated variety, but the electrolytic. The thermodynamic differences between these forms may be obtained from a consideration of the cell[2] $Ag, AgI_{(E)} \mid KI \mid AgI_{(P)}, Ag$. The electrolytic variety is the positive electrode of cell. The emf. at 25° is .00054 volt and its temperature coefficient at 25° is −.000011 volt. The electrolytic variety has therefore a higher entropy by .254 entropy unit, and a higher heat content by 88 calories. The entropy of precipitated silver iodide is 26.8; that of the electrolytic variety is 27.05. Substitution of these values in the equation

$$S_{2AgI(E)} + S_{Cd} = S_{CdI_2} + S_{2Ag} - \Delta S$$

gives the value of 39.1 for the entropy of cadmium iodide.

The entropy of cadmium iodide may be calculated in other ways. The reaction, $Cd + PbI_2 = CdI_2 + Pb$, is one for which the data are available:

Subtraction of equation (11) below from equation (10) gives the proposed reaction:

$$Cd + 2AgI_{(p)} = CdI_2 + 2Ag \qquad (10)$$

$$Pb + 2AgI_{(p)} = PbI_2 + 2Ag \qquad (11)$$

$$Cd + PbI_2 = CdI_2 + Pb \qquad (12)$$

ΔH for reaction (10) may be calculated from the voltage, and temperature coefficient of the cell employing the reaction involving electrolytic silver iodide, (provided this is coupled with the data of Gerth giving the difference in heat contents between the two varieties). ΔH for this reaction is thus found to be −18016 calories. ΔH for reaction (11) is calculated from the equations:

$$Pb + I_2 = PbI_2 \qquad (13)$$

$$2Ag + I_2 = 2AgI \qquad (14)$$

Subtraction gives

$$Pb + 2AgI = PbI_2 + 2Ag \qquad (15)$$

ΔH for reaction (13) has been found repeatedly to be equal to −41,850 calories. ΔH for reaction (14) has been found equal to −29,950 calories (vide infra). ΔH for reaction (11) is therefore −11,900 calories, and ΔH for reaction (12) becomes equal to −6116 calories.

ΔF for reaction (12) may be calculated by a similar process. ΔF for reaction (10) corresponds to a free energy decrease of 0.3540 volt, or 16,320 calories. ΔF for reaction (13) is given by Gerke as −41501 calories, and for reaction (14) it is −31,540 calories (vide infra). The difference (ΔF for reaction (15) or (11)) is 9,960 calories, and the difference between this and ΔF for reaction (10)

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[1] Taylor and Perrott: loc. cit.

[2] Gerth: Z. Elektrochem. 27, 291 (1921).

gives the free energy increase corresponding with the reaction to be investigated, viz. −6360 calories. Substitution of these values in the equation

$$\Delta F = \Delta H - T\Delta S$$

gives ΔS for reaction (12) to be .9 entropy unit. Substitution of this value in the equation

$$S_{Cd} + S_{PbI_2} = S_{CdI_2} + S_{Pb} - 0.9$$

$$S_{CdI_2} = 38.5 \text{ entropy units.}$$

It is to be noted that all of the values used in the preceding calculations were taken from cells involving lead in the ordinary form. The calculations may be made with data from cells involving electrolytically deposited lead. The entropy changes accompanying the reactions are given:

[1] $$Pb_{(E)} + 2AgI_{(E)} = PbI_2 + 2Ag \quad \Delta S = -6.4$$

$$Cd + 2AgI_{(E)} = CdI_2 + 2Ag \quad \Delta S = -6.3$$

$$Cd + PbI_2 = CdI_2 + Pb_{(E)} \quad \Delta S = 0.1$$

$$S_{Cd} + S_{PbI_2} = S_{CdI_2} + S_{Pb(E)} - .1$$

$$S_{CdI_2} = 38.6$$

The three values found for the entropy of CdI_2 are 39.1, 38.5, and 38.6; an average is taken, viz., 38.7. The maximum divergence from the mean corresponds to 120 calories.

The Heat of Formation of Silver Iodide

The heat of formation of silver iodide has been determined by various experimenters, but the degree of discordance between the results obtained, has by no means been compatible with the experimental accuracy. The methods that have been employed fall naturally into three classes: calorimetric determinations, electrometric determinations, and determinations involving the third law of thermodynamics.

Practically all of the calorimetric determinations recorded in the literature have been made with the employment of potassium cyanide solution as solvent. Finely divided silver was suspended in the solution; a known weight of iodine introduced; and the resulting rise of temperature noted. Silver iodide was then introduced into the same solution, and the heat effect noted. The difference between the two heat effects obviously gives the heat of formation of the solid salt—provided that only the following reactions take place:

$$Ag + 1/2 I_2 \xrightarrow{KCN} AgI \text{ (Dissolved)}$$

$$AgI \xrightarrow{KCN} AgI \text{ (Dissolved)}$$

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[1] Taylor: J. Am. Chem. Soc., 38, 2295 (1916); also Krahmer: Z. Elektrochem., 26, 97 (1920).

The calorimetric values obtained in this manner have been discredited however, owing to the possibility of vitiating side reactions, such as the following:

$$I_2 + KCN = KI + ICN$$

Such side reactions appear all the more probable, since, in an attempt to obtain the heat of formation of silver bromide using potassium cyanide solution as a solvent, little, or no, silver bromide was formed. It may be pointed out that other experimenters have been concerned with the same point: Taylor and Anderson[1] attempted to prove or disprove the existence of side reactions by use of a 3N potassium cyanide solution instead of a 1N solution as used by Braune and Koref[2], and by comparing the results obtained in the two cases. It was assumed that the side reaction would take place to a greater extent in one case than another and the existence of side reactions would thus manifest itself (if real) by a discordance of results under the different conditions. Braune and Koref obtained 15,100 calories for the heat of formation, while Taylor and Anderson obtained 15,150 calories. The agreement is well within the experimental error, but it must be remembered that the side reaction takes place only to a slight extent, and the difference in the heat effects produced by the difference in the small extents to which they take place, might well be attributed to the experimental error. (Neither set of experiments was carried out with excessive accuracy.) The other calorimetric experiments (notably those by Thomsen[3], Berthelot[4], and Fischer[5]) were all indirect, involving other uncertain values, and did not approximate the degree of accuracy of Braune and Koref or of Taylor and Anderson.

The results obtained by electrometric means have been even more discordant, ranging from 14,565 calories, obtained by Jones and Hartman[6] to 15,220 calories obtained by Gerth[7]. The chief methods of electrometric investigation involved reactions of the following types:

$$Pb + 2AgI = PbI_2 + 2Ag \qquad (13)$$

$$\text{and } Pb + I_2 = PbI_2 \qquad (14)$$

$$Ag + 1/2I_2 = AgI \qquad (15)$$

The inaccuracy of the electrometric method is due chiefly to two causes: (1) inaccurate measurement of the temperature coefficient; (2) improper calculation of liquid potentials. The validity of the first cause becomes obvious when it is remembered that in a process such as illustrated by reaction (13), (14), or (15), an error of .01 millivolt in the determination of the temperature coefficient produces an error of approximately 140 calories in the heat of the reaction. Two determinations of the electromotive force (accurate to .01

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[1] Taylor and Anderson: J. Am. Chem. Soc., 43, 2014 (1921).
[2] Braune and Koref: Z. anorg. Chem., 87, 175 (1914).
[3] Thomsen: "Thermochem. Untersuchungen", 3, 510.
[4] Berthelot: "Thermochimie", 2, 370.
[5] Fischer: Z. anorg. Chem. 78, 41 (1912).
[6] Jones and Hartman: J. Am. Chem. Soc., 37, 752 (1915).
[7] Gerth: loc. cit.

millivolt) at temperatures differing by ten degrees, gives quite sufficient accuracy (i. e., ± 14 calories), but experience proves that it is very difficult to obtain electromotive forces accurate to .01 millivolt, and also in many cases rapid change of the temperature coefficient with temperature, $\frac{\partial^2(-\Delta F)}{\partial T^2} = \frac{\Delta C_p}{T}$, makes it unwise to obtain temperature coefficients over ten-degree intervals. The second cause for difficulty in obtaining accurate electrometric measurements is well illustrated by the work of Jones and Hartman[1] and by that of Gerth[2]. The former attempted to calculate the liquid potential in the silver-iodine cell by the Planck-Henderson formula; the incorrectness of the results is evident from the value for the heat of formation obtained, viz., 14,565 calories, and also from the fact that the results were not in accord with the third law. Gerth attempted in a very ingenious manner to determine the value of the liquid potential, and the greater degree of accuracy is evinced by the results; however, they seem to be in error by at least 150 calories. Gerke[3] avoided the difficulty of liquid potential in the lead-iodine combination by making the cell reversible (throughout) to the lead ion instead of to the iodine. The difficulty of obtaining an accurate temperature coefficient in this theoretically sound cell was present however.

The heat of formation obtained by Nernst from calculations involving the third law, while more accurate than the values obtained by the two other methods, is inaccurate owing to slightly low values for the free energy of formation[4] and to the unreliability of the specific heat data for iodine.

An attempt has been made by the writer to make an accurate calorimetric determination of the heat of formation of silver iodide. This is important not only for its own value but also for the fact that it makes possible a calculation of the entropy of iodine. The principle of the method employed was essentially the same as that briefly outlined in connection with the work of Braune and Koref and of Taylor and Anderson, except that the solvent employed was a concentrated solution of potassium iodide in one series of experiments and a concentrated solution of sodium iodide in another. In both of these solutions silver iodide dissolves very rapidly and to a large extent. A repetition of the work of Braune and Koref and of Taylor and Anderson has also been made.

The calorimeter employed was a large Dewar vessel, provided with cover, through which there were holes for the admission of stirrer, heater, Beckmann thermometer, and reactant-container. The heat capacity of the calorimeter was determined by sending known amount of electrical energy through a constantan wire, wound on a glass tube and completely covered by paraffin, and observing the rise in temperature. Heavy copper leads were used, the resistance of which was negligible. These formed the ends of the coil surrounding

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[1] Jones and Hartman: loc. cit.

[2] Gerth: loc. cit.

[3] Gerth: loc. cit.

[4] The value used was that of Fisher, obtained from the cell involving free iodine, in which uncertainties are apparent regarding liquid potential and osmotic work corrections.

the glass tube, to insure any of the heat being liberated inside of the glass tube and subsequent conduction out of the calorimeter. In some experiments both current and voltage were measured by potentiometer; in others by calibrated voltmeter and ammeter. The heating usually lasted from ten to fifteen minutes and was so adjusted as to give a rise of 0.7 to 1.0 degree. The current was sent through an external resistance for at least two hours before the heating in order that constancy of current and voltage could be obtained while heating. The stirring was obtained by a motor-driven paddle, and was so regulated as not to give more than 0.003 degree rise in temperature per minute. In all cases finely divided silver, prepared by the reduction of silver nitrate by ammonium formate, was suspended in the solvent and a known weight of iodine introduced The reaction went to completion very quickly; in most cases constant heating due to stirring was obtained in five minutes (or less) after the introduction of the iodine. Silver iodide was prepared metathetically from silver nitrate and potassium iodide (excess). In the "solution" experiments, a known weight of silver iodide was introduced into the same solution, employed for the silver-iodine combination. The solution was extremely rapid; in most cases it was complete in one minute. The resulting rises in temperature were noted in all cases, and from a knowledge of the heat capacity and stirring correction the heat effect was calculated.

A repetition of the experiments in which potassium cyanide solution was used as solvent, was made in order to be certain that any discordance in the results obtained might not be attributable to systematic errors. The results obtained in the experiments in which potassium cyanide solution was used as solvent, are even higher than those of Braune and Koref and of Taylor and Anderson. Since these values are higher by over two hundred calories than those obtained in the experiments in which concentrated potassium and sodium iodide solutions were used, the former are discredited. The results are given in Table I.

An average is taken between the two former values, and the value thus found for the heat of formation of solid silver iodide from solid silver and solid iodine is 14,975 calories. The error is thought to be within 50 calories.

The Entropy of Iodine

Owing to very peculiar difficulties, the specific heat of iodine has never been measured sufficiently accurately at low temperatures to warrant a direct calculation of the entropy. Resort is therefore made to reactions involving free iodine; cell reactions involving free iodine are most untrustworthy because of the formation of polyiodides. These necessitate liquid potential and osmotic work correction, if a knowledge of the energetics of the simple cell-reaction is desired. The entropy change corresponding with such reactions must be obtained indirectly.

A knowledge of the heat of formation of silver iodide and the free energy of formation gives immediately on subtraction the value $T\Delta S$ for the reaction:

$$Ag + 1/2 I_2 = AgI \qquad (16)$$

TABLE I.

Solvent: Concentrated KI Solution

Heat Capacity	Gms. Reactant	Rise in Temp.	Heat
1046	5.777 (Iodine)	0.749	17230
1033	6.051 "	0.794	17210
1028	3.788 "	0.499	17200
758.9	2.740 "	0.488	17170
980.1	10.845 "	1.506	17285
		(*Average:*	17220)
814.7	16.686 (AgI)	0.203	2327
985.5	13.153 "	0.132	2320
757.	9.166 "	0.114	2210
747.5	8.854 "	0.116	2299
749.5	11.009 "	0.142	2266
		(*Average:*	2281)

Heat of Formation: 14941 calories

Solvent: Concentrated NaI Solution

Heat Capacity	Gms. Reactant	Rise in Temp.	Heat
1086	8.669 (Iodine)	1.054	16770
963	5.9938	0.815	16647
977	5.709	0.776	16867
963	7.320	1.008	16837
979.6	9.174	1.110	16890
		(*Average:*	16802)
973.6	13.882 (AgI)	0.109	1797
963.1	14.549 "	0.114	1771
		(*Average:*	1784)

Heat of Formation: 15018 calories

Solvent: 2N KCN Solution

Heat Capacity	Gms. Reactant	Rise in Temp.	Heat
1132	3.5012 (Iodine)	0.669	27470
1159	5.5800 "	1.042	27500
		(*Average:*	27485)
1159	6.634 (AgI)	0.303	12440
1091	13.854 "	.652	12120
		(*Average:*	12280)

Heat of Formation: 15200 calories

The entropies of silver and of silver iodide are known; hence the entropy of iodine is calculable. The free energy of formation is obtained by combining the values for the following reactions, investigated by Gerke:[1]

$$Pb + I_2 = PbI_2 \qquad (17)$$

$$Pb + 2AgI = PbI_2 + 2Ag \qquad (18)$$

The free energy of formation per equivalent of silver iodide formed is found to be 15,800 calories. The data of Braune and Koref[2] for the free energy of reaction (17) may be combined with those of Taylor[3] for the free energy of reaction (18). (The data of Taylor may be combined with those of Braune and Koref since they both used 0.72 per cent. lead amalgam and the interpolation formula of Brönsted. Differences due to the different varieties of lead would therefore be cancelled.) The free energy of formation per mole of silver iodide is from the work of these investigators, 15,745 calories. Gerth, measuring the cell involving reaction (16) directly and determining the liquid potential and osmotic work corrections finds 15,770 and 15,720 calories at concentrations of potassium iodide of N/20 and N/40 respectively. Jones and Hartman obtained the value, 15,800 calories. An average of the five values gives 15,767 calories; only one of the five values differs from the mean by more than 33 calories.

Since $\Delta F = \Delta H - T\Delta S$

$\Delta S = 2.6$ entropy units at 298°

$S_{Ag} + S_{1/2I_2} = S_{AgI} - \Delta S$

The entropy of silver is 10.25; that of silver iodide is 26.8. The entropy of iodine is therefore 13.95 entropy units.

The entropy of iodine may also be determined from an investigation of the following reaction:

$$Zn + I_2 = ZnI_2 \qquad (19)$$

Reaction (19) has been investigated by the author directly and also by means of the intermediate reaction, $Zn + 2AgI_{(P)} = ZnI_2 + 2Ag$, (21). A cell involving the above reaction was set up and its voltage at various temperatures measured. Zinc was used in the form of a 10 percent amalgam; this is a convenient strength amalgam since it shows no potential difference compared with pure zinc. The other electrode was a silver-silveriodide one; the silver iodide was the precipitated variety. The electrolyte was a saturated solution of zinc iodide. The voltage of the cell at 25° is 0.39872 and its temperature coefficient is −0.000094 volt per degree. This corresponds with an entropy difference of 4.3 entropy units. Substitution of the known values for the entropies of the reactants and products yields the value of 38.6 for the entropy of zinc iodide.

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[1] Gerke: loc. cit.

[2] Braune and Koref: loc. cit.

[3] Taylor: J. Am. Chem. Soc., 38, 2295 (1916).

Substitution of the above data in the Gibbs-Helmholtz equation gives for the heat of the reaction 19,660 calories. The heat of formation of two moles of silver iodide has been found to be 29,950 calories. Addition of this value to the heat of the reaction gives the heat of formation of solid zinc iodide at 49,610 calories. A direct calorimetric determination yielded the value 49,800 calories. This determination was made in precisely the same manner (except that water was the solvent) as the silver iodide determinations. The mean of the two values, viz., 49,700, was taken to be the most probable value for the heat of formation of zinc iodide. The free energy change for reaction (21) was found from the voltage of the cell to be 18,380 calories. The free energy of formation of two moles of silver iodide is 31,540 calories. Addition of this to 18380 gives the free energy of formation of zinc iodide—49,920 calories.

$$\begin{aligned} \Delta F &= \Delta H - T\Delta S \\ \Delta S &= .7 \text{ entropy unit} \\ S_{Zn} + 2S_{1/2I_2} &= 38.6 - .7 \\ S_{1/2I_2} &= 14.05 \end{aligned}$$

The entropy of iodine may also be calculated from the newer specific heat data of Miething[1]. Concordant experimental results for the specific heat of iodine at very low temperatures have so far not been obtained, the difficulty encountered being attributed[2] to a slow transition bear 25 K. Miething, in the work referred to above, has found a $\beta\nu$-value which reproduced the experimental results (in so far as they are concordant) when employed in the Debye equation for specific heats. It is to be noted that, even though a transition remains undiscovered, the entropy $\left(\int C d \ln T\right)$ is given correctly by a theoretical specific heat curve. Miething has found that the value, 111, reproduces the specific heat curve. With the use of this information, the entropy of iodine may be calculated by the following procedure:

$$E = \int_{T=0}^{T=298} C_p dT \qquad F = -T \int_{T=0}^{T=298} \frac{E}{T^2} dT$$

According to Debye these equations become:

$$E = \frac{9}{12} R \left(\frac{Cp}{C_\alpha} + \frac{3x}{e^x - 1}\right) T; \text{ where } x = \frac{\beta\nu}{T}, C_\alpha = 3R$$

$$-F = 9R \left(\frac{Cp}{C_\alpha (36)} + \frac{x}{(e^x - 1)12} - \tfrac{1}{3} \ln (1 - e^{-x})\right) T$$

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[1] Miething: "Tabellen zur Berechmung des gesamten und freien Wärmeinhalts fester Korper", Abhandlungen der deutschen Bunsen Gesellshaft.

[2] Gunther: Ann. Physik, (4) 51, 828 (1916).

E for iodine comes out to be 1548 calories at 290°; F, −2530 calories. Substitution of these values in the equation, $F = E - T\Delta S$, will yield ΔS for iodine between $T = 0$ and $T = 290$. This is in reality what we have been referring to previously as the entropy of iodine (at 290°). The value found from above is 14.06 entropy units. The entropy difference between 290° and 298° must now be calculated. The specific heat is constant over this range and is taken as 6.6 calories.

$$\Delta S = 6.6 \int_{T=290}^{T=298} \frac{dT}{T}$$

$$= 6.6\,(\ln 298 - \ln 290)$$

$$= .18 \text{ entropy units}$$

Addition of this value to the value at 290° gives for the entropy of iodine at 298°, the value, 14.24 entropy units. The value, thus arrived at, for the entropy of iodine at 298°, are 13.95, 14.24 and 14.05. The most probable value for the entropy of iodine from these results is therefore 14.1; the maximum error is assumed to be 0.3 entropy unit. The value previously given in the literature is 13.3 entropy units.

The Entropy of Silver Bromide

Lewis and Storch[1] found that the free energy decrease accompanying the reaction, $2AgBr + H_2 = 2Ag + 2HBr$ (.01 M), at 25°C corresponded to the value, 0.3141 volts, or 3622 calories per mole of hydrogen bromine formed. The potential of the bromine electrode as given by Lewis and Randall[2] is −1.0659 volts. This corresponds to a free energy decrease of 24595 calories for the electrode reaction, $\frac{1}{2}Br_2(l) + \epsilon = Br^-$. Since the free energy change accompanying the reaction, $\frac{1}{2}H_2(g) - \epsilon = H^+$, is arbitrarily zero, both facts are represented by the following equation:

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Br_2\,(1) = H^+ + Br^- \quad \Delta F_{298} = -24595$$

Before combining this equation with the one mentioned previously,

$$AgBr + \tfrac{1}{2}H_2 = 1\ HBr\ (.01\ M) + Ag,\ \Delta F_{298} = -3622$$

the value, −24595, for the free energy decrease must be corrected to the value that corresponds to the formation of HBr at .01 molality. The activity coefficient of .01 HBr solution is given as .93; the corresponding activity is .0093. The correction is made by means of the following equations:

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[1] Lewis and Storch: J. Am. Chem. Soc., 39, 2544 (1917).

[2] Lewis and Randall: "Thermodynamics," XXX, Table 7.

$$\Delta F - \Delta F_0 = RT \ln a_{HBr}$$
$$\Delta F + 24595 = RT \ln .0093$$
$$\Delta F = -24595 - 2755 = -27350$$
$$\Delta F_{AgBr} + \Delta F_{\frac{1}{2}H_2} = \Delta F_{Ag} + \Delta F_{HBr} + \Delta F_{\Delta}$$
$$\Delta F_{AgBr} + 0 = 0 - 27350 + 3620$$
$$\Delta F_{AgBr} = -23730 \text{ calories}$$

The entropy of silver bromide may now be found by employment of the heat of formation of silver bromide; the relation, $\Delta F = \Delta H - T\Delta S$; and the entropies of the elements of silver bromide. The heat of formation has been determined in two ways. The first is a direct calorimetric method. A bulb containing a weighed amount of bromine was broken in a concentrated solution of ammonium bromide, containing finely divided silver in suspension. Silver bromide was thus formed in solution. The heat of solution of silver bromide in the same solution was found and correction made (the heat of solution was found to be zero, however).

Expt.	Amt. Br_2 added	Rise due to Reaction
1	4.908 grms.	1.29
2	1.830	.487
3	2.720	.669
4	4.301	1.045

Expt.	Heat Capacity of Calorimeter	Heat of Reaction
1	1126	23,710
2	1124	23,910
3	1210	23,810
4	1210	23,520

The average was taken between the first three values and found to be 23,810 calories.

The heat of solution was found by measuring the heats of the following reactions:

$$AgNO_3 + NH_4Br_{(conc.)} \longrightarrow AgBr_{(Dissolved)} + NH_4NO_3 + Q_1$$
$$AgNO_3 + NH_4Br_{(conc.)} \longrightarrow AgBr_{(Ppt.)} + NH_4NO_3 + Q_2$$
(sat. with AgBr)

Subtraction gives the heat of solution — $AgBr_{(Ppt.)} \longrightarrow AgBr_{(Dissolved)} + (Q_1 - Q_2)$

Expt.	$AgNO_3$ Added	Heat Capacity of Calorimeter	Rise due to reaction	Heat of Reaction
1	4.263	1141	.428	(Q_1) 19,460
2	4.022	1111	.413	(Q_1) 19,530
3	2.778	1102	.288	(Q_2) 19,430

The heat of solution was therefore taken to be zero. This was confirmed by dropping finely powdered silver bromide into a concentrated solution of ammonium bromide. No change of temperature, other than that due to stirring, was detected. The heat of formation of silver bromide as determined by this method was then compared with that determined electrometrically by Krahmer[1], employing the cell reaction, $Pb + 2AgBr = PbBr_2 + 2Ag$, and the heat of formation of lead bromide. The value obtained by him is 24,190 calories. The mean of the two values was taken, viz., 23,990 calories. Substituting this value for ΔH, along with the value of -23730 for ΔF, in the equation, $\Delta F = \Delta H - T\Delta S$, ΔS is found to be $-.87$ entropy unit. When this value is used in the following equation, the entropy of silver bromide is obtained:

$$Ag + \tfrac{1}{2}Br_2 = AgBr \qquad \Delta S\ -.87$$
$$10.25 + 16.3 + S_{AgBr} + .87$$
$$\Delta S_{AgBr} = 25.68 \text{ entropy units.}$$

It may be pointed out that the above calculation suggests a method for an accurate determination of the potential of the bromine electrode. A specific heat curve over the entire range of temperature would give an accurate and independent value for the entropy of silver bromide. The above calculations could then be reversed, and the value of the bromine potential calculated. This is important, owing to the difficulties attending any cell reversible with respect to Br-ion involving bromine, due to the formation of Br^3 and Br^5 ions.

Summary

The third law of thermodynamics has been subjected to a test by the application of the entropy relations of cadmium chloride hydrate and cadmium iodide. (The data were obtained from temperature coefficients of the free energy changes of their cell reactions.)

A slightly different method of testing the third law has been proposed, viz., obtaining ΔS of the reaction from an accurate calorimetric determination of the heat of reaction and the free energy change, and comparing this with ΔS obtained from specific heat measurements.

The heat of formation of silver iodide has been redetermined. The solvents used were concentrated sodium and potassium iodide solutions. A repetition of the experiments of the investigators, giving the most accurate values recorded, has also been made. The value, concluded correct, from these experiments is 14,975 calories. The maximum error is thought to be 50 calories. The previously accepted values are over 100 calories higher.

The entropy of iodine has been calculated (1) from the energetics of the silver-iodine combination, (2) from the energetics of the zinc-iodine combination, and (3) from the specific heat of iodine. The values obtained are 13.95, 14.05, and 14.24 entropy units.

The heat of formation of silver bromide has been determined. From the energetics of the reaction, $H_2 + 2AgBr = 2HBr + 2Ag$, and from the value

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[1] Krahmer: Z. Elektrochem. 26, 97 (1920).

of the potential of the bromine electrode, the entropy of silver bromide has been calculated. An accurate method for the determination of the potential of the bromine electrode has been indicated.

NOTE: Since the writing of the above paper, an article has appeared by Lange[1], giving a new and apparently satisfactory set of specific heat data for iodine. $E = \int_{0}^{290} C_p dT = 1527$ calories; $F = -T\int_{0}^{290} \frac{EdT}{T^2} = -2465$ calories; whence $S_{290} = 13.77$ and $S_{298} = 13.95$.

I wish to acknowledge my gratitude to Profs. G. A. Hulett and H. S. Taylor of this laboratory for their helpfulness and interest in connection with this problem.

Princeton, N. J.

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[1] Fritz Lange: Z. physik. Chem. **110**, 343 (1924).

STUDIES IN EMULSIONS

BY WILLIAM SEIFRIZ

VI. THE EFFECT OF ACIDITY ON TYPE AND REVERSIBILITY OF EMULSIONS

Introductory

The author's observations on the effect of acidity on the behavior of emulsions are limited to emulsions of olive oil.

The fact that sodium hydroxide causes reversal of certain emulsions in one direction while sodium chloride does not, suggests, as do numerous other behavior phenomena, that acidity might be a factor in phase reversal. Accordingly, H-ion concentration determinations were made of ten of the emulsifiers used in these studies[1] on olive oil emulsions, both before and after the addition of electrolytes to the emulsions.

Experimental

The colorimetric method of measuring H-ion concentration was employed, except in those few instances where the value was over 10. Since this method is not adapted to measuring acidity of such turbid systems as oil emulsions and could not possibly be employed to determine the pH of water-in-oil emulsions, the pH values of the aqueous phase were measured separately, i.e., apart from the emulsions. The actual acidity values of the emulsifiers when in the emulsions undoubtedly differ from that of the emulsifiers alone, owing to the acidity of the olive oil, but for comparative purposes the values obtained are suitable.

The pH values and concentrations of the ten emulsifiers are given in Table V. There is also given the type of emulsion which each emulsifier produces with olive oil, and whether or not the emulsion is reversible with NaOH, if of the water-in-oil type, and with $BaCl_2$ if of the oil-in-water type.

TABLE V

Emulsifier	Concentration	pH Value	Type of emulsion	Electrolyte added.	Reversibility with electrolyte added.
Sodium Stearate $(NaC_{18}H_{35}O_2)$	M/1000	9.6	oil-in-water	NaOH	reversible
Gelatose	10%	5.4	" " "	"	partially rev.
Saponin	0.2%	6.0	" " "	"	irreversible
Gum arabic	10%	4.6	" " "	"	"
Lecithin	1%	4.6	" " "	"	"
Albumin	0.5%	6.6	" " "	"	"
Cholesterin	0.02%	6.6	water-in-oil	$BaCl_2$	reversible
Casein	0.2%	5.2	" " "	"	"
Gliadin	0.1%	7.4	" " "	"	"
Cephalin	0.2%	4.8	" " "	"	"
Olive oil	——	5.4	——	——	——

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[1] W. Seifriz: Am. J. Physiol. 66, 124 (1923).

From the above table no relation between acidity, reversibility, and type of emulsion, with one possible exception, is evident. Soap, with the maximum pH value, and lecithin with the minimum value, both form oil-in-water systems. Cephalin, with a pH value of 4.8, is reversible, while lecithin with approximately the same pH value is not reversible. The only conceivable relationship between type of emuslion and acidity which can be derived from the above data is the following. If we select an arbitrary intermediate pH value, say 8.0, then all those emulsions which are reversible and which have a pH value below this selected one (cholesterin, gliadin, casein and cephalin), are water-in-oil systems, while the one reversible emulsion with a pH value above 8.0 (soap), is an oil-in-water system. That there is more to this relation will be seen from what follows.

All of the water-in-oil emulsions are reversible with $BaCl_2$ and also with HCl. A second reversal in the opposite direction is accomplished by the hydroxide of Na but not by the chloride. A further fact which still more strongly indicates a relationship between acidity and phase reversal is the following. If two samples of emulsion with sodium stearate as the stabilizer are reversed, one by $BaCl_2$ and one by HCl, the pH value of the aqueous phase is the same in each case at the same point of reversal. For example: the pH value of freshly made M/1000 sodium stearate is 9.6. The emulsion formed with it as stabilizer is an oil-in-water one. If to such an emulsion 0.3 c.c. of M/100 $BaCl_2$ is added, two-thirds of the total volume of the emulsion is converted into an emulsion of the water-in-oil type. The pH value of the aqueous phase plus this amount of $BaCl_2$ (measured separately) is 8.8. If now, enough dilute acid (0.1 c.c. of M/4 HCl) is added to a similar emulsion until the same proportion, i.e. two-thirds of the total volume, is reversed, the pH value of the aqueous phase plus this amount of acid will be found to be 8.6. In other words, the pH value of the aqueous phase of an olive oil emulsion with a sodium stearate emulsifier, is the same when the emulsion is brought to the same point of reversal by either $BaCl_2$ or HCl. If the two experiments are carried further until reversal of the entire volume of the two emulsions is complete, which requires 0.7 c.c. of M/100 $BaCl_2$ in the first case and 0.15 c.c. of M/4 HCl in the second case, and the pH of the two respective aqueous phases then determined, it will be found to be 7.2 in both cases: that is, in order to cause complete reversal, whether with $BaCl_2$ or HCl, the pH of the soap emulsifier must be brought down to the same value in each case. It will be noticed also that this value of 7.2 is below the arbitrary value of 8.0 selected as that below which all reversible emulsions are of the water-in-oil type.

Interesting in connection with the apparent fact that a pH value below 8.0 means that the emulsion is of the water-in-oil type, is the fact that a soap ($NaC_{18}H_{35}O_2$) solution several days old always forms a water-in-oil emulsion. The pH of such a soap solution is near or below 8.0.* Further, when a freshly prepared soap solution has a pH of over 10.0 (the sooner the pH readings are

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* The cause of the drop in pH with age of the soap solution is probably due to solubility of CO_2 from the air.

taken after preparing the solution the higher are the values), the more readily is the oil emulsified, the higher is the electrical conductivity, and the more finely dispersed is the oil. When the soap solution, after standing for a day, has a pH value of about 9.0, the oil emulsifies with difficulty and the milliamperage is low (i.e. the electrical resistance is high and the less perfect is the continuity of the aqueous phase). The emulsion is near the reversal point and unstable.

Were we to look no farther than the behavior of one type of emulsifier, (soap) and the effect of but two electrolytes ($BaCl_2$ and HCl), a very nice theory of the relationship between acidity, type of emulsion, and reversibility could be formulated. We could say that acidity is a determining factor in phase reversal, that there is a definite pH value at which phase reversal takes place, and that above this value the emulsions are of the oil-in-water type and below it they are of the water-in-oil type. When, however, we investigate the behavior of emulsions with other stabilizers, and the effects of other electrolytes, these apparent facts all collapse.

$Ba(OH)_2$ will reverse the olive oil emulsions which can also be reversed with $BaCl_2$; yet, while $BaCl_2$ increases the acidity of the emulsifier, $Ba(OH)_2$ increases the alkalinity.

All of the reversible olive oil emulsions enumerated in the table can be repeatedly reversed by alternate additions of $BaCl_2$ and NaOH. In this process the pH value steadily climbs. Four reversals with M/10 $BaCl_2$ and M/10 NaOH of an emulsion with a Na stearate stabilizer, raises the original pH value of 9.6 to 12.19. Even more rapid is the steady increase in alkalinity when this process of repeated reversal is carried out by alternate additions of $Ba(OH)_2$ and NaOH. It is not conceivable that acidity plays an important part in these repeated reversals. In the case of the emulsion with gelatose as the stabilizer, the same electrolyte (NaOH or $Ba(OH)_2$) produces reversal first in one direction and then in the other. (See Part III of these studies). What rôle acidity might play here it is difficult to surmise.

One fact bearing on the possible influence of H-ion concentration on phase reversal holds in the case of all emulsions, namely, when reversal is produced by HCl, whether of an emulsion which has not previously been reversed and is of low pH value, or of one which has been frequently reversed and is of high pH value, the pH must in every case be brought to a definite minimum in order to cause reversal. An olive oil emulsion with an aqueous phase of M/10 NaOH and therefore of high pH value (sodium oleate is the emulsifier in this case), can be reversed with 3 c.c. of M/10 $BaCl_2$. The pH value of the reversed emulsion is still above 10.0. Three times the quantity of $BaCl_2$ necessary to cause reversal will not bring the pH value below 10.0. In order to reverse the same kind of emulsion with HCl, the pH must be brought down to 7.4. The same is true of the water-in-oil emulsions with cholesterin as stabilizer. The pH value of the cholesterin solution is 6.6. If two samples of such an emulsion are both first reversed by NaOH (0.25 c.c. M/10) into oil-in-water systems and the two emulsions then brought back to the reversal point, in the one case by $BaCl_2$

(0.4 c.c. M/10), and in the other case by HCl (0.3 c.c. M/4), the pH value of the aqueous phase in the first ($BaCl_2$) case is still above 10.0, while in the second (HCl) case it is 7.4. It will be noticed that this pH value of 7.4 or 7.2 is obtained in several instances where the emulsions are brought to or near the reversal point.

Conclusion

The fact that olive oil emulsions, with one of a variety of stabilizers, which are reversible with $BaCl_2$, are also reversible with HCl, and the further fact that a pH value of 7.2 is always that at which reversal of olive oil emulsions takes place with HCl, and frequently that at which reversal with $BaCl_2$ takes place, goes to indicate that H-ion concentration is a factor in phase reversal in emulsions; but the further facts that two hydroxides, each adding to the alkalinity of an emulsion, may cause reversal in *opposite* directions, and that highly alkaline emulsions of the oil-in-water type may be reversed by $BaCl_2$ without bringing the pH value down to 7.2 or even to approach that value, precludes ascribing to acidity any prime rôle in determining type or reversibility in emulsions.

It is likely that the key to alternate reversal in olive oil emulsions lies in the presence of free fatty acids in the olive oil which form Ba and Na soaps. Possibly a closer relation between pH and emulsion type and reversibility can be obtained if an acid-free mineral oil of known simplicity is used.

VII. THE EFFECT OF PHASE RATIO AND OF METHOD IN HANDLING ON EMULSION TYPE

A. Inversion by alteration of phase-volume ratio

Introductory

Pure oil and water can be emulsified only when the oil phase is very dilute, (1 part in 1,000). When a third substance is used as a stabilizer the proportion of oil and water may vary within wide limits.

Inversion of oil emulsions by the alteration of volume concentration has been studied by Robertson[1] who finds that 91 c.c. of olive oil with 8 c.c. of water and 1 c.c. of 5N.NaOH, yields an emulsion of the *water-in-oil* type, as do all higher proportions of oil to water; while 90 c.c. of oil with 9 c.c. of water and 1 c.c. of 5N.NaOH forms an *oil-in-water* emulsion, as do all ratios below this proportion. Robertson obtains from these data what he terms the critical ratio, which is $\frac{9.5}{90.5} = 0.105$.

The writer's observations on the effect of phase ratio on emulsion type are restricted to refined petroleum oils and pure aqueous casein, without the addition of any electrolyte.

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[1] Kolloid-Z. 7, 7 (1910).

Experimental

Alteration of the phase-volume ratio has no effect on the type of emulsion of petroleum oils of *light* weight stabilized with casein. Such emulsions in equal proportions of oil and water are fine stable oil-in-water systems. In decreasing the proportion of water to oil a point is reached where the oil cannot be emulsified in the minimum amount of water.

Those petroleum oils which are in or near the zone of instability are readily influenced as to type by change in ratio of the oil and water phases.

In Part 1 of these studies is described the change in type of casein stabilized emulsions from oil-in-water of the light oils to water-in-oil of the heavy oils, which take place with increase in specific gravity of the petroleum distillates. Those oils whose specific gravity values lie about midway (sp. gr. 0.82 to 0.857) in a series of distillates from 0.664 (hexane) to 0.895 (heavy lubricating oil) represent a zone of instability. All hydrocarbon distillates lying within this zone of instability, either do not emulsify at all or form poorly stable systems which may contain emulsions of both types. The forming of emulsions of both types without the addition of any electrolyte, is especially characteristic of the less pure commercial petroleum oils, such as "Diamond Paraffin" oil, (Standard Oil Co.) which lie within or near the zone of instability. This peculiarity is undoubtedly due to their wide boiling range, and resulting heterogeneity which make them an admixture of relatively light and of relatively heavy hydrocarbons.

It is these oils which lie near the critical point (point of type reversal) within the zone of instability, which can be readily thrown one way or the other, as to type, by change in volume ratio.

In the following table are given the types of emulsions which the high grade commercial "Diamond Paraffin" oil (specific gravity 0.886, boiling range 305° - 400°C) forms when emulsified with different proportions of an aqueous phase of casein.

TABLE VI

Volume of oil (in c.c.)	Volume of aqueous phase (in c.c.)	Nature of emulsion. Type[1]	Texture[2]	Stability[3]
25	10	WO	fine	stable
25	15	WO[4] OW	fine coarse	stable unstable
25	25	WO OW	fine medium	stable stable
25	35	OW	fine	stable

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[1] WO = water-in-oil, OW = oil-in-water.

[2] Fine = droplets average 0.02 mm., medium = droplets from 0.02 to 0.5 mm., coarse = droplets over 0.5 mm.

[3] Stability a relative term: stable = emulsion maintained for 15 minutes or more, unstable = phases separate quickly.

[4] Both types exist.

It is difficult to understand the behavior of the above emulsions on the basis of either of the two existing theories on the mechanism of emulsion type, namely, that of surface tension[1] and that of orientation of molecules[2]. (The theories are discussed in Part I of these studies). There is no reason to believe that change in phase-volume ratio in any way alters the surface tension value between the oil and the aqueous casein, or that it alters the chemical constitution of the molecules at the interface. Nor does the suggestion of Robertson[3], made in explanation of the behavior of olive oil with alteration of phase ratio, seem to hold here. While it might be argued that the amount of casein in the 25 : 10 ratio—which yields a WO emulsion—would be insufficient to surround the greater number of oil globules of an oil-in-water emulsion while it is sufficient to envelop the fewer water globules of the water-in-oil emulsion obtained, the speculation collapses on realizing that *a good stable oil-in-water emulsion can be formed at this same ratio of 25 : 10 if the oil is a light hydrocarbon distillate*, (e.g. hexane).

B. The effect of methods in handling on emulsion types.

Much excellent work has been done pertaining to the influence of methods of handling emulsions on the rate of emulsification and on stability. Less reference has been made to the effect of methods in handling on emulsion type.

One of the most common cases of inversion of type due to difference in handling is that which results from standing. Practically all emulsions studied by the writer were made up in volumes of 100 c.c. which were divided into 50 c.c. samples, one of which was experimented with immediately while the other stood for from 15 to 30 minutes awaiting treatment.

It not frequently happens that a second sample of one and the same emulsion forms, on reshaking after a rest of half an hour, the opposite type of emulsion as did the first sample. This is especially true of petroleum oils which lie in the zone of instability (see Part I of these studies). It is such idiosyncrasies of emulsions which try the patience of the investigator!

Another interesting case of the effect of resting on emulsion type, is the following. Four samples of "Diamond Paraffin" oil (Standard Oil Co.) were prepared in the proportion of 25 c.c. of oil to 15 c.c. of aqueous casein. All quickly formed good stable water-in-oil emulsions. Ten c.c. of water was then added to each sample. The emulsions remained fine stable water-in-oil systems. Three of the samples were allowed to stand while the fourth was treated with NaOH. Ordinarily an emulsion of equal parts of a "Diamond Paraffin" oil (specific gravity 0.886) and water is of both types (see Table V) and is readily reversed into a fine oil-in-water emulsion by a few drops of M/5 NaOH. In the case of the water-in-oil samples above mentioned the one first treated was so stable as to resist 30 c.c. of M/5 NaOH. Not until 40 c.c. had been added could the emulsion be in-

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[1] J. Phys. Chem. **17**, 501 (1913).

[2] J. Am. Chem. Soc. **45**, 2780 (1923).

[3] Kolloid-Z. **7**, 7 (1910).

verted into a pure oil-in-water system. In the meantime, samples 1, 2 and 3, all identical at the outset with sample 4 just discussed, had been standing for some 20 minutes. On reshaking these three emulsions, each one became a fine stable *oil-in-water* system, the reverse of the original condition. Mere resting without the addition of a hydroxide had caused these three emulsions to reverse while their sister sample which had not rested, could not be reversed with less than 40 c.c. of M/5 NaOH.

While reversal in type due to resting, is usually from the water-in-oil to the oil-in-water state, the opposite is often to be observed. An emulsion of "Straw" oil (specific gravity 0.882) is ordinarily of both types, and therefore so near the reversal point as to be readily thrown into a fine stable oil-in-water emulsion by 1 c.c. of M/5 NaOH. If, however, an original emulsion of this kind is allowed to stand some 20 minutes and is then reshaken it may be a pure water-in-oil emulsion and so stable as to be reversible with not less than 60 c.c. of M/5 $Ba(OH)_2$. (Where such large volumes of electrolytes are necessary to cause reversal much of the effect of the added solution is to be attributed to increase in the volume of the water phase; but not all, since the same volume of water added without electrolyte will not reverse the emulsion).

Any number of instances such as those given above could be cited. Needless to say, there is as yet no actual physical theory which will account for these behavior phenomena of emulsions.

VIII. A COMPARISON OF THE BEHAVIOR OF VEGETABLE OILS WITH THAT OF PETROLEUM OILS

Introductory

Emulsions of any one oil stabilized with different substances may be of either the oil-in-water or the water-in-oil type, depending upon specific but as yet unknown properties of the emulsifying agent. That this is true has been shown, among others by Bhatnagar[1] and Seifriz[2]. The former finds that kerosene emulsions stabilized with sodium oleate, casein, alkaline zinc hydroxide, lecithin, or univalent soaps, are of the oil-in-water type; while the same oil stabilized with carbon, zinc hydroxide, aluminum hydroxide, lead oxide, or rosin forms water-in-oil emulsions. Seifriz found that olive oil stabilized with sodium oleate, sodium stearate, gelatose, gum arabic, albumin, lecithin, saponin, senegin, smilacin, or plant juices (cell sap and protoplasm) form oil-in-water emulsions, while the same oil stabilized with casein, gliadin, cholesterin, or cephalin forms water-in-oil emulsions.

A comparison of the data of Bhatnagar and Seifriz shows that two different oils, kerosene and olive oil, stabilized with the same substances may form like or opposite types of emulsions. Thus, kerosene and olive oil both form oil-in-water emulsions when stabilized with either sodium oleate or lecithin, while

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[1] J. Chem. Soc. 119, 1760 (1921).

[2] Am. J. Physiol. 66, 124 (1923).

when stabilized with casein an oil-in-water emulsion is formed by kerosene and a water-in-oil one by olive oil.

That this difference in the type of emulsion which casein forms exists not only between oils as widely different as a vegetable oil and a mineral oil, but even between oils of the same origin. is evident from the experimental data presented in Part I of these studies where it is shown that light petroleum distillates form oil-in-water emulsions with aqueous casein, while heavy petroleum distillates form water-in-oil emulsions with the same stabilizing agent.

With the idea of determining how far other vegetable oils duplicate the behavior of olive oil, the following preliminary experiments have been carried out.

Experimental

The vegetable oils used were olive, sperm, castor bean, poppy seed, linseed and cod-liver. All form, with aqueous casein, fine stable water-in-oil emulsions except linseed oil which forms a dual emulsion with the water-in-oil type the more stable and predominating.

All of the water-in-oil emulsions of the six vegetable oils stabilized with casein, are readily reversible by NaOH into stable oil-in-water systems, and may be reversed back again to their original type by $BaCl_2$ or $Ba(OH)_2$. The linseed oil emulsion, which is dual in nature, is readily thrown into a fine stable oil-in-water emulsion by NaOH, or into a fine water-in-oil emulsion by $BaCl_2$ or $Ba(OH)_2$.

The vegetable oils, therefore, are all in the same category, as regards type and reversibility. They are unlike light petroleum oils as to type, and unlike all petroleum oils as to reversibility. As set forth in Part II of these studies, oil-in-water emulsions of *light* petroleum oils are irreversible with NaOH, NaCl, $Ba(OH)_2$, $BaCl_2$, $Al_2(SO_4)_3$, or $Th(NO_3)_4$; while water-in-oil emulsions of *heavy* petroleum oils can be reversed by NaOH, $Ba(OH)_2$, $Al_2(SO_4)_3$, or $Th(NO_3)_4$ but not by NaCl or $BaCl_2$. (NaCl has no pronounced influence on *any* of the emulsions studied. At best, it has a relatively slight stabilizing effect on petroleum oil emulsions of the oil-in-water type).

Conclusion

Vegetable oils, so far as six different kinds go to prove, are all of one class, both as regards type of emulsion originally formed (with one partial exception), and as regards reaction to electrolytes. As to type they are like the *light* petroleum oils. In respect to behavior in the presence of electrolytes the vegetable oils are in quite a different class from that of the petroleum oils.

MECHANISM OF THE PHOTOCHEMICAL REACTION BETWEEN HYDROGEN AND CHLORINE*

BY ABRAHAM LINCOLN MARSHALL

The object of this work was to try to establish experimentally one of the steps in the Nernst[1] mechanism for the photochemical combination of hydrogen and chlorine. This theory was an attempt to reconcile the Einstein photochemical equivalence law with the experimental results of Bodenstein and Dux[2]. Bodenstein calculated a yield of a million molecules of hydrogen chloride per quantum of light absorbed. Nernst assumed that the primary action of the light was to dissociate a chlorine molecule according to the equation

$$Cl_2 \longrightarrow Cl + Cl$$

and that the following sequence of reaction was initiated by the chlorine atoms.

$$Cl + H_2 \longrightarrow HCl + H$$
$$H + Cl_2 \longrightarrow HCl + Cl$$

Since, for every chlorine atom used up, another was produced, the reaction could continue indefinitely except for the reaction

$$H + Cl \longrightarrow HCl$$

which would gradually tend to decrease the concentration of the chlorine atoms. Oxygen also when present is able to slow down the rate of the reaction. Nernst showed that both of his secondary reactions were thermodynamically possible and since the explanation seemed inherently plausible it met with general acceptance. Weigert and Kellerman[3] have demonstrated experimentally that secondary reactions are important in the photochemical combination of hydrogen and chlorine.

Bowen[4] has attempted to account for all the observed phenomena in the photochemistry of the halogen halides by means of the "dissociation" theory of the primary light reaction. His prediction concerning the effect of traces of water vapor on the hydrogen and chlorine reaction are at variance with more recently published facts.

Bodenstein[5] has put forward a quite different type of mechanism. He assumed the primary action of the light to be

$$Cl_2 \longrightarrow Cl_2'$$

where Cl_2' means chlorine in some energy-rich state.

$$\text{then}\quad Cl_2' + H_2 = 2HCl'$$
$$\text{and}\quad HCl' + Cl_2 = Cl_2' + HCl$$

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* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Z. Elektrochem. **24**, 335 (1918).

[2] Z. physik. Chem. **85**, 297, 329 (1913).

[3] Z. physik. Chem. **107**, 1 (1924).

[4] J. Chem. Soc. **125**, 1233 (1924).

[5] Z. Elektrochem. **22**, 53 (1916).

The activated chlorine can either reradiate its energy or use it to react with hydrogen. At low pressures, the probability that chlorine will lose its excess energy by radiation before making an impact with a hydrogen molecule is increased. Stern and Volmer[1] have put forward a similar idea for the primary photochemical reaction to account for the observed results in a number of reactions. Chapman and Chapman[2] have developed a mechanism to account for the kinetics of the hydrogen chlorine combination assuming the primary light action to be the formation of an excited chlorine molecule.

It seemed desirable if possible to test the reactions postulated by Nernst under different conditions and see if they gave the predicted results. The method used consisted in introducing hydrogen atoms into a mixture of hydrogen and chlorine and determining if the yield of hydrogen chloride was in excess of the known concentration of hydrogen atoms[3]. An attempt was first made to deposit hydrogen atoms on a glass surface by the "clean up" method described by Langmuir[4]. An active mixture of hydrogen and chlorine was then admitted to this vessel. The results obtained were entirely negative. The next method employed was to generate atomic hydrogen in the manner described by Wood[5]. This was led into a stream of chlorine. Very satisfactory results were obtained and the exact experimental technique employed will now be described.

The discharge tube (A) was of pyrex glass about one metre long and twelve millimeters in diameter. The aluminum electrodes (B,B′) were sealed in with tungsten leads which in turn were covered on the outside with Khotinsky cement to make a vacuum-tight seal. Hydrogen was led in at one end, the rate of flow being controlled by the glass stopcock (M). The outlet tube was of five millimeters diameter and joined to the middle of the discharge tube. About two centimeters from the joint a side tube was sealed on and two centimeters from this joint was placed the jet (E) the tip of which had a diameter of one millimeter. The chlorine or bromine to be used was introduced on the far side of this jet. At this point a large bulb (G) was joined after which came four liquid air traps (H,H′,H″,H‴) connected in series with two two-stage Langmuir diffusion pumps and a Hyvac pump. Two McLeod gauges were used for pressure measurements, one (D) connected to the discharge tube through a liquid air trap (C) and the other (K) in the line close to the Langmuir pumps. Bromine and chlorine were introduced through the capillary traps (F) and (F′), the rate of flow being controlled by constrictions in the capillaries and by regulation of the temperature of the liquid bromine and chlorine.

The hydrogen was generated electrolytically using nickel electrodes and sodium hydroxide solution of maximum conductivity. The generator was water-cooled and capable of delivering eight liters of hydrogen per hour. The

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[1] Z. wiss. Phot. 19, 275 (1920).
[2] J. Chem. Soc. 123, 3079 (1923).
[3] Nature, 112, 937 (1923).
[4] J. Am. Chem. Soc. 37, 1161 (1915).
[5] Proc. Roy. Soc. 102 A, 1 (1922).

hydrogen passed through a tower packed with solid potassium hydroxide to remove most of the water vapor but no attempt was made to remove traces of oxygen as they were converted to water in the discharge tube. A small amount of water is necessary to poison the walls of the tube[1] which otherwise catalyse the recombination of the hydrogen atoms. Bromine was prepared by washing c.p. bromine with concentrated sulphuric acid and redistilling. It gave a blank test for free acid. All air was removed from the bromine container by freezing the bromine in liquid air and evacuating the whole apparatus until no pressure registered on the McLeod gauge which was sensitive to a pressure of 10^{-6}mm. This process was repeated several times allowing the bromine to liquefy between each to remove dissolved air. Chlorine was prepared by the method described by Tramm[2] and about two hundred cubic centimeters of the liquid were collected. Bromine and chlorine were excluded from the rest of the apparatus by keeping (F) and (F′) in liquid air. A five kilowatt 100-25,000 volt transformer was used as a source of power. The current and voltage applied to the tube will be indicated by giving the current flowing in the primary circuit of the transformer.

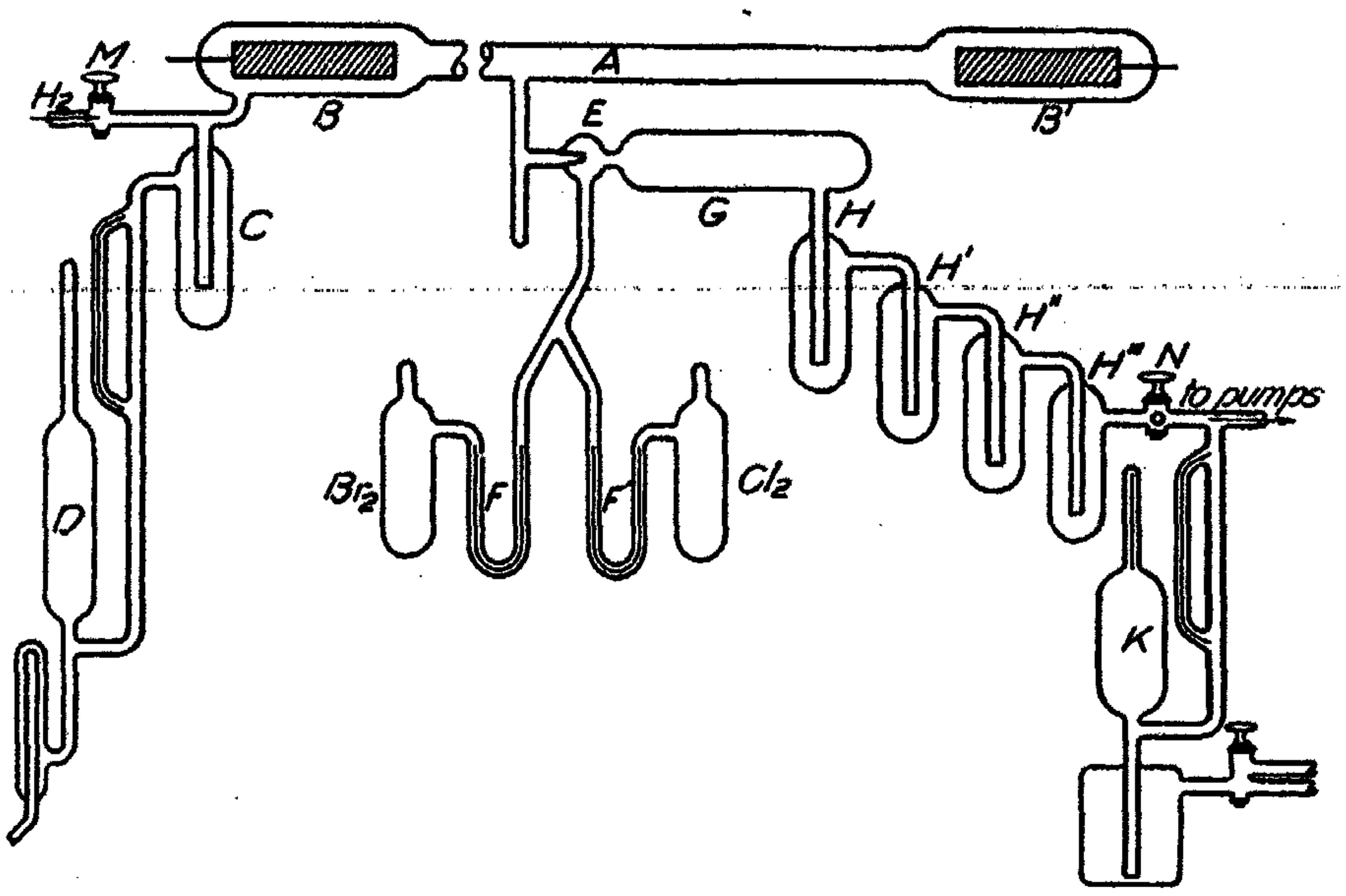

FIG. 1

Method of Procedure

The jet (E) was introduced into the apparatus in order to give the hydrogen a high velocity relative to the chlorine or bromine at the point where they met and thus to prevent their diffusing back into the discharge tube. At the

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[1] Bonhoeffer: Z. physik. Chem. 113, 199 (1924).

[2] Z. physik. Chem. 105, 356 (1923).

pressure of chlorine used, it was possible to operate the discharge tube at a pressure of hydrogen as low as 0.050cm. With this pressure in the tube, gauge (K) registered 0.0010cm. At the start of a series of experiments the tube was operated overnight with a current of thirty-five amperes to season it thoroughly and to remove most of the adsorbed gases from the walls. The purity of the gas used was tested by means of a small direct vision spectroscope. A faint trace of the band spectrum of nitrogen always showed up along with the brilliant lines of the Balmer series. In any particular set of experiments a run was first made with bromine, then chlorine, another bromine and finally a chlorine. The condensible gases were caught in liquid air traps. After a run, the whole apparatus was filled with hydrogen from the generator, the traps warmed up in turn and blown out through the tap (N) to a bubbler containing potassium iodide solution. The iodine and acid were titrated with standard thiosulphate and alkali. It was found that very steady pressures could be obtained by regulating the stopcock (M). The results obtained in any series of experiments were in good agreement with one another.

The experiments with bromine were used to indicate the amount of atomic hydrogen in the gas issuing from the jet. Nernst[1] has shown that the reaction

$$H + Br_2 = HBr + Br$$

goes with a large free energy decrease but that the reaction

$$Br + H_2 = HBr + H$$

goes with a free energy increase and so is successful at only a very few impacts. Hence one molecule of hydrogen bromide is obtained per atom of hydrogen.

Results of Experiments

The results will now be tabulated. In column (1) is given the primary current in the transformer; column (2) the pressure registered by gauge (K); column (3) the ratio HCl/HBr found at the pressure indicated and the final columns give the amounts of chlorine, bromine, hydrogen chloride and hydrogen bromide for the particular experiment. These amounts are expressed as c.c. of 0.756N solution in case of chlorine and bromine and c.c. of 0.496N solution in case of the acids. Individual experiments lasted one hour. At 0.01cm. pressure about 750cc. hydrogen passed through in this time and at 0.60cm. about 8000cc. measured at N.T.P. The amount of chlorine or bromine averaged about 250cc. per hour.

Besides the results reported here a large number were obtained in the preliminary experiments to determine the best working conditions. These were mostly at low pressures and within experimental error the ratio HCl/HBr was unity.

In the first part of experiment (f) dealing with bromine the temperature of the bromine reservoir was about 10°C. higher than normal and about four times as much bromine came through the capillary compared to the check experiment. The amounts of hydrogen bromide formed in the two experiments

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[1] Grundlage des neuen Wärmesatzes, 1918.

1	2	3	Cl_2	HCl	Br_2	HBr	
10 amps.	0.15cm.	2 to 1	3.5	45.5			
			1.5	48.3	9.2	24.0	(a)
			4.3	53.8			
10 amps.	0.01cm.	3 to 2	13.9	5.6	9.2	3.8	
			13.5	7.1	10.3	4.6	(b)
6 amps.	0.13cm.	5 to 2	1.26	23.8	7.2	9.26	(c)
5.2 amps.	0.007cm.	3 to 2	15.1	9.71	8.0	6.88	(d)
			10.5	9.23	6.7	6.62	
4 amps.	0.26cm.	4 to 1	0.6	24.57	8.6	5.57	
			0.25	25.6	10.8	7.6	(e)
4 amps.	0.30cm.	9 to 2	7.6	21.7	40.7	7.05	(f)
			5.8	26.0	11.0	5.26	
3.5 amps.	0.40cm.	11 to 2	5.34	19.11	12.9	3.10	
			5.10	20.62	12.7	3.63	(g)
3.5 amps.	0.60cm.	7 to 1	6.70	13.7	10.1	2.08	
			7.1	14.9			(h)
	0.004cm.	1 to 1	48.7	12.2	16.4	19.2	
			60.1	9.5			(i)

are, however, strictly comparable which is further evidence for the validity of the analytical method employed. The current in the discharge tube was progressively decreased as the pressure increased in order to have a considerable amount of chlorine present at the end of each experiment. This was necessary if the results on the length of the "chains" at the various pressures in the experiments with hydrogen and chlorine were to be comparable with one another.

In the discussion of the tube characteristics it was mentioned that the band spectrum of nitrogen showed up faintly in the discharge. This trace of nitrogen was converted to ammonia by the discharge and a faint white sublimate of ammonium chloride or bromide was always observed after a day's work at a point just beyond the jet. Chapman and Burgess[1] have shown that a trace of ammonia cuts down enormously the yield of hydrogen chloride per quantum. The reproducibility of the results seems to indicate that the amount present was roughly constant. While the yield of hydrogen chloride per atom of hydrogen was undoubtedly decreased many-fold by the presence of the ammonia, the fact still remains that it increased with increasing pressure.

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[1] J. Chem. Soc. 89, 1402 (1906).

It was very important to be certain that none of the chlorine or bromine diffused back into the discharge tube. It has been previously stated that it was possible to work with a pressure as low as 0.050cm. in the discharge tube. At lower pressures than this, with the rate of flow of chlorine employed, the characteristics of the tube commenced to alter. When observed with a spectroscope, a light field showed up with many bright lines present. Under these conditions no hydrogen chloride or bromide was formed. If the discharge tube was run for several hours under these conditions a black deposit slowly formed on the walls around the electrodes. When the pressure was still further reduced the discharge became blue-green colored and the electrodes were attacked leaving a black deposit on the tube walls.

The presence of a small concentration of mercury vapor in the discharge tube cut down immensely the concentration of hydrogen atoms reaching the chlorine. In one case a considerable amount of mercury was present in the tube with the hydrogen. The green mercury line showed up brilliantly but the yellow line was extremely faint. In general it was found that, if the pressure in the tube became very low (around 0.0001mm.) and a high current was allowed to flow, the tube would quickly heat up locally and puncture. Just before breaking, the yellow line of sodium showed up brilliantly. When the discharge tube was functioning normally, the yellow sodium line could be made to appear in the discharge along with the Balmer lines of hydrogen by heating it slightly externally with a gas flame. In the early experiments, the apparatus was made from G702P glass and it was observed that in a short time the tube became brown colored on the inside and that the ring of the jet was colored deep brown.

It will be seen from the ensuing discussion that the results obtained seem to support the mechanism put forward by Bodenstein[1] for the photochemical combination of hydrogen and chlorine and to be contrary to predictions from the Nernst mechanism.

Objections to the Nernst Mechanism

Recent thermochemical measurements giving more exact data on the heat of dissociation of chlorine seem to throw doubt on the probability of the reaction

$$Cl + H_2 = HCl + H$$

occurring at every impact of a chlorine atom with a hydrogen molecule. Wohl[2] has obtained values for the heat of dissociation of hydrogen and chlorine.

$$\begin{aligned} H_2 &= 2H & \Delta H &= 95{,}000 \pm 2{,}000 \text{ cals.} \\ Cl_2 &= 2Cl & \Delta H &= 56{,}000 \pm 2{,}000 \\ \text{For } 1/2H_2 + 1/2Cl_2 &= HCl & \Delta H &= -22{,}000 \\ \text{hence } H + Cl &= HCl & \Delta H &= -97{,}500 \pm 2{,}000 \\ \text{and } Cl + H_2 &= HCl + H & \Delta H &= -2{,}500 \pm 3{,}000 \end{aligned}$$

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[1] Z. Elektrochem. 22, 53 (1916).

[2] Z. Electrochem, 30, 36 (1924).

Lewis and Randall[1] give

$$S_{H_2} = 29.44$$
$$S_{Cl_2} = 52.6$$
$$S_H = 25.70$$
$$S_{Cl} = 36.35$$

also for the reaction

$$1/2\ H_2(g) + 1/2\ Cl_2(g) = HCl(g) \quad \Delta F = -22{,}692 \text{ cals.}$$
$$\Delta F - \Delta H = -T\Delta S$$
$$-22{,}692 + 22{,}000 = 298\ (41.0 - S_{HCl})$$
$$S_{HCl} = 43.4$$

For the reaction $Cl + H_2 = HCl + H$

$$\begin{aligned}\Delta F &= -2.500 \pm 3{,}000 - 298\ (36.35 + 29.44 - 25.70 - 43.3)\\ &= -1{,}450 \pm 3{,}000\\ &= -\ RT \ln K\end{aligned}$$

so that

$$K = 11.5 \pm 159$$

where $K = \dfrac{(p_{HCl})\ (p_H)}{(p_{Cl})\ \ (p_{H_2})}$

If the value of Wartenberg and Henglein[2] for the heat of dissociation of chlorine is used log K becomes negative and K is less than unity.

Nernst and Noddack[3] have put forward another type of objection to the original Nernst mechanism. There are a number of other reactions in which the yield per quantum absorbed is excessive which *cannot* be formulated by a similar scheme of reactions involving chlorine atoms.

$$Cl_2 + CH_4 \longrightarrow CCl_4 + HCl$$
$$Cl_2 + CO \longrightarrow COCl_2$$

which take place in visible light and hence with the chlorine as the photosensitive constituent. Also the reaction

$$H_2O_2 \longrightarrow H_2O + \tfrac{1}{2} O_2.$$

They postulate an alternative mechanism for the reaction between hydrogen and chlorine involving excited molecules similar to that advanced by Bodenstein in 1916.

The results of Bodenstein and Lütkemeyer[4] show that atomic bromine is a comparatively stable substance. Only about one per thousand of the impacts which bromine atoms make with one another are fruitful in causing combination. Bonhoeffer[5] has shown that atomic hydrogen behaves analogously. It seems legitimate to assume, therefore, that atomic chlorine would have similar properties. When two chlorine atoms collide they form an energy-rich complex which is unstable and decomposes again if it cannot get rid of its excess energy. It may do this either by collision with another molecule or by impact

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[1] "Thermodynamics," 1923.

[2] Z. anorg. Chem. **123**, 137 (1922).

[3] Sitzungsber. preuss. Akad. **1923**, 110.

[4] Z. physik. Chem. **114**, 208 (1924).

[5] Z. physik. Chem. **113**, 199 (1924).

with the vessel walls. Bodenstein and Taylor[1] have attempted to make measurements on the rate at which chlorine loses its activity after being excited by light. They illuminated a stream of chlorine, and passed it through a bent capillary into a stream of hydrogen. The capillary was blackened and prevented light from reaching the mixed gases. In one series of experiments they were able to mix the chlorine with the hydrogen 0.00065 sec. after illumination, but observed no detectable reaction. Warburg[2] has calculated on the basis of the Nernst mechanism, assuming every absorbed quantum gives two chlorine atoms and that every impact between atoms leads to combination to form molecular chlorine, that there is a high enough concentration of atoms in the chlorine when it meets the hydrogen to give a marked amount of hydrogen chloride and states that the experimental results of Bodenstein and Taylor are not compatible with this conclusion. Gohring[3] has also treated the results of Bodenstein and Taylor and reaches an opposite conclusion to Warburg. The chlorine used contained a small amount of oxygen which he assumes to be 0.1 percent. He assumes that it is possible to remove chlorine atoms by means of the reaction

$$Cl + O_2 \longrightarrow ClO_2$$

From the experimental results of Bodenstein and Dux on the rate of the photochemical reaction between hydrogen and chlorine he calculates that one in seven hundred of the impacts between atomic chlorine and oxygen are fruitful. Using this value he shows that one would not expect a detectable amount of reaction when the chlorine meets the hydrogen. The results obtained on the optical sensitization of ozone by means of chlorine discussed by Weigert[4] throw great doubt on the reaction postulated by Gohring for deactivating the chlorine. It is possible to obtain chlorine with a very low oxygen content and experiments are contemplated similar to those of Bodenstein and Taylor which will be free from Gohring's objection and should enable a definite decision to be reached on the possibility of the Nernst mechanism.

In the experiments described in this paper the concentration of atomic hydrogen and molecular chlorine was roughly constant. The only variable was the hydrogen concentration. It seems difficult to account for the marked increase in hydrogen chloride formed at the higher pressures (i.e., increased hydrogen concentration) on the basis of the Nernst mechanism.

Evidence for a Mechanism employing Excited Molecules

In the past few years a considerable amount of material has been collected regarding the average life of atoms and molecules in excited or upper quantum states. Tolman[5] has developed a theoretical equation for the mean free life of excited atoms based on a consideration of the width of absorption lines, the probability that a molecule will absorb a quantum of energy and Einstein's

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[1] Z. Elektrochem. **22**, 202 (1916).
[2] Z. Elektrochem. **27**, 133 (1921).
[3] Z. Elektrochem. **27**, 511 (1921).
[4] Z. physik. Chem. **106**, 422 (1923).
[5] Phys. Rev. (2) **23**, 693 (1924).

views on the mechanism of light absorption and emission. For mercury he calculates 10^{-7} secs.; iodine $3\ (10)^{-8}$ secs. These are the only two that can be compared with observed values. The agreement for mercury is good but for iodine Stern and Volmer[1] give $(10)^{-6}$ secs. and Pringsheim considers the value may be as small as $(10)^{-8}$ secs. Wien[2] has made a number of determinations of the rate at which the light intensity falls off in a beam of positive rays. He worked at low pressures to decrease as much as possible the probability of new excitation of the atoms by collision and obtained values of the order of $(10)^{-8}$ secs. for the line and band spectra of hydrogen, oxygen and nitrogen. Turner[3] from a consideration of Cario and Franck's work on the rate of dissociation of hydrogen by excited mercury atoms has calculated an average life for these between $(10)^{-7}$ and $(10)^{-8}$ secs. Saha and Sur[4] give an interpretation of all the experimental observations on active nitrogen in terms of excited nitrogen molecules and calculate an average life of $(10)^{-3}$ seconds. Weigert and Kellerman[5] have studied the course of the reaction in a sensitive mixture of hydrogen and chlorine after its illumination by a spark discharge. They employed the Töpler "Schliermethode" which makes use of the change in refractive index accompanying change in gas pressure. The results obtained showed a maximum effect in times ranging from 1-300 to 1-40 sec. after illumination. An experiment made 1-5 sec. after illumination showed no effect. The whole reaction involving the formation of a million molecules of hydrogen chloride per quantum of light absorbed has been shown in these experiments to take place in less than a tenth of a second. This would involve a time of $(10)^{-7}$ secs. for each step in the chain of reactions.

From kinetic theory it is possible to calculate the mean free time between impacts of the reactive form of chlorine with hydrogen molecules. Meyer[6] gives a formula for the number of collisions a single molecule of gas A makes with the molecules of B in a mixture of A and B. The reciprocal of this value is the mean free time desired, if we consider A to be chlorine and B hydrogen.

$$n_A = \pi\sigma^2 N_B \sqrt{\Omega^2_A + \Omega_B^2}$$

where n_A = number of impacts per second that one molecule of A makes with the molecules of B.

σ = sum of molecular radii of A and B.

N_B = number of molecules of B per cubic centimetre.

Ω_A = mean value of molecular velocity of A in cm.-sec.

Ω_B = " " " " " " B " " "

$\Omega = 14{,}500 \sqrt{T/M}$ where M is the molecular weight.

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[1] Physik. Z. **20**, 183 (1919).

[2] Ann. Physik., (4) **60**, 597 (1919).

[3] Phys. Rev. (2) **23**, 464 (1924).

[4] Phil. Mag. (6) **48**, 421 (1924).

[5] Z. phys. Chem. **107**, 1 (1923).

[6] "Die kinetische Theorie der Gase."

Taking 2 $(10)^{-8}$ as the sum of the radii of hydrogen and chlorine and making a calculation for a hydrogen pressure of 0.010cm.

$$N_B = \frac{6.06\ (10)^{23}}{22,400 \times 7600}$$

$$n_A = \pi \times 4\ (10)^{-16} \times \frac{6.06\ (10)^{23}}{22,400 \times 7600} \times 14,500\sqrt{\frac{300}{2} + \frac{300}{35}}$$

$$= 8.17\ (10)^{5}$$

so that $\tau = 1.22\ (10)^{-6}$ secs. which is the desired value.

From the values given above for the mean free life of excited molecules a value of from $(10)^{-6}$ to $(10)^{-8}$ secs. for excited chlorine seems reasonable. At a pressure of hydrogen of 0.010cm. the mean free time between impacts is $(10)^{-6}$ secs. and decreases with increased hydrogen pressure. When the time between impacts is short compared to the time the chlorine would be in an upper quantum state before spontaneous re-emission of its energy one would expect the chains in the reaction between hydrogen and chlorine to be long while at very low pressures where the kinetic impact time is long compared to that for spontaneous re-emission the chains should be short. These conclusions are in agreement with the results obtained.

The most satisfactory mechanism for the experimental observations recorded herein seems to be

$$H + Cl_2 \longrightarrow HCl' + Cl$$
$$HCl' + Cl_2 \longrightarrow Cl_2' + HCl$$
$$Cl_2' + H_2 \longrightarrow 2HCl'$$
$$Cl + Cl \longrightarrow Cl_2$$

The experiments of Coehn and Jung[1] dealing with the effect of water vapor on the photochemical reaction between hydrogen and chlorine can also be accounted for by the mechanism adopted here. They observed with a partial pressure of water vapor less than $(10)^{-5}$mm. that hydrogen and chlorine did not react in visible light and that at $(10)^{-6}$mm. pressure of water vapor light of 300$\mu\mu$ was necessary to bring about combination. With water vapor pressures greater than $(10)^{-5}$mm. the reaction went in visible light up to a wave length of 540$\mu\mu$ and no reaction was observed above this wave length.

The quantum absorbed by chlorine from visible light may be insufficient to cause it to react with hydrogen and it may receive some of its energy of activation from the polar water molecules present in the gas. That is, it may be a molecular complex of water and chlorine which initiates the primary reaction with hydrogen. In support of the idea that chlorine can take up a larger amount of energy than that necessary for dissociation, experiments on iodine can be cited. Mohler and Foote[2] have observed inelastic impacts in iodine at 2.3 volts with no evidence of dissociation although it would require only 1.6 volts for dissociation.

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[1] Z. physik. Chem. **110**, 705 (1924).

[2] Phys. Rev. (2) **21**, 382 (1923).

Summary

1. Experiments have been described on the reaction between atomic hydrogen and chlorine at low pressures.

2. Values ranging from one molecule of hydrogen chloride per hydrogen atom at 0.004cm. pressure to seven molecules per atom at 0.60cm. pressure have been obtained.

3. A discussion of possible objections to the Nernst mechanism for the photochemical reaction between hydrogen and chlorine has been given and a method suggested for a direct experimental test.

4. The results obtained have been interpreted by a mechanism involving excited chlorine molecules.

The writer wishes to thank Professor Hugh S. Taylor for suggesting this piece of work and for his kindly interest during its progress.

THE ABSORPTION OF ULTRA-VIOLET LIGHT BY INORGANIC HALIDES

BY FREDERICK H. GETMAN

The first systematic investigation of the absorption of ultra-violet light by inorganic compounds was undertaken by Hartley[1] in 1902. He studied the behavior of a series of aqueous solutions of metallic nitrates and found, in every case, a characteristic absorption band in the ultra-violet, the position of which was shifted toward the less refrangible end of the spectrum as the atomic weight of the combined metal increased.

Subsequently, Drossbach[2] showed that ultra-violet light is strongly absorbed by solutions of the heavy metals, and emphasized the fact that atomic weight is a factor of relatively small importance in connection with the absorption of ultra-violet radiation by solutions of metallic salts. Thus, he pointed out that while the atomic weight of thorium is more than four times that of iron, the former is non-absorptive while the latter absorbs strongly. In 1912, Crymble[3], in an interesting paper, directed attention to the fact that, although the selective absorption of solutions of certain metallic salts had been made the subject of extensive investigations, comparatively little attention had been paid to the phenomenon of general absorption. As the result of his studies he concluded that the metallic elements may be divided into two groups as follows:

(a) those of constant valence whose salts in aqueous solution transmit ultra-violet radiation and, (b) those of variable valence whose salts in aqueous solution absorb ultra-violet radiation. Furthermore, he pointed out that if the metals are arranged in the order of their electrode potentials, the more electropositive metals are found to be of constant valence and non-absorptive. It is of interest to note that Crymble states that "the metals which yield *non-absorptive* salts are: Li, Na, K, Rb, Cs, Gl, Mg, Ca, Ba, Sr, Zn, Cd, Th, Al and Zr," and in another place he points out, that he chose the chlorides of the metals for his investigation because of the fact that the chloride radicle is "*non-absorptive.*"

A quantitative study of the absorption of ultra-violet radiation by salts was undertaken by Brannigan and Macbeth[4] with a view to establishing, if possible, a relation between the extinction coefficients and the atomic weights of the constituent elements of salts of the same family. In this investigation, a Hilger rotating sector photometer was used in conjunction with a quartz spectrograph, in order to detect and measure minute differences between the absorbing power of solution and solvent. The extinction coefficients of very concentrated aqueous solutions of HCl, LiCl, NaCl, RbCl, NaBr, KBr, NH_4Br

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[1] Hartley: J. Chem. Soc. **81**, 556 (1902); **83**, 221 (1903).

[2] Drossbach: Ber. **35**, 91 (1902).

[3] Crymble: J. Chem. Soc., **101**, 266 (1912).

[4] Brannigan and Macbeth: J. Chem. Soc. **109**, 1277 (1916).

LiI, NaI, KI, RbI and CsI were determined and, contrary to the statements hitherto published, that these compounds are diactinic, each was found to exert well-defined absorbing power. It was further shown, that the frequency of the absorption bands decreases with increase of atomic weight of the halogen, and that the extinction coefficient of the alkali chlorides and iodides increases with increase of the atomic weight of the combined metal.

In a later communication by Macbeth and Maxwell[1], the results of similar studies on the chlorides of arsenic, antimony and bismuth are reported. While the values of the molecular extinction coefficients of the alkali halides were found to lie between 0.05 and 0.5, the corresponding values of the molecular extinction coefficients of the chlorides of arsenic, antimony and bismuth were found to range from 5 to 12,000. The optimum concentration for the measurement of the absorption of the alkali halides was 4-molal, while in the case of the chlorides of the arsenic group, the concentration ranged from 0.0001- to 0.01-molal. Furthermore, bismuth chloride was the only one of the three to exhibit selective absorption, the head of the absorption band corresponding to a wave-length of 323 $\mu\mu$ instead of 273 $\mu\mu$ as in the case of the alkali halides. The authors point out that the values of the molecular extinction coefficients in the arsenic group increase with increase in the atomic weight of the combined metal.

Recent quantitative measurements of the absorption of ultra-violet radiation by salts have been made by H. von Halban[2] and his pupils, employing a photoelectric cell. The method, it is claimed, is capable of a very high degree of accuracy, even for solutions of extremely low absorptive power. The results of these investigations are in accord with the theory that the ionic properties of solutions of strong electrolytes are to be explained in terms of the electrostatic forces between the ions and, since these forces exert a varying influence on the properties of the ions, it follows that there is not, of necessity, a parallelism between light absorption, electrical conductance or ionic activity.

The present investigation was undertaken with a view to extending our knowledge of the quantitative absorption of ultra-violet radiation by simple inorganic salts in the hope that, with the accumulation of sufficient reliable data, it may be possible to establish some relationship between absorbing power and other physical properties of the elements.

Apparatus

In order to determine extinction coefficients with a high degree of accuracy, a new type of sector photometer developed by Judd Lewis was employed in conjunction with a Hilger quartz spectrograph (Size E 3) fitted with a wave-length scale and giving a spectrum approximately 200 mm. in length, ranging from 800 $\mu\mu$ to 210 $\mu\mu$. The outstanding features of this sector photometer, which has already been described in detail by its inventor[3], are shown diagram-

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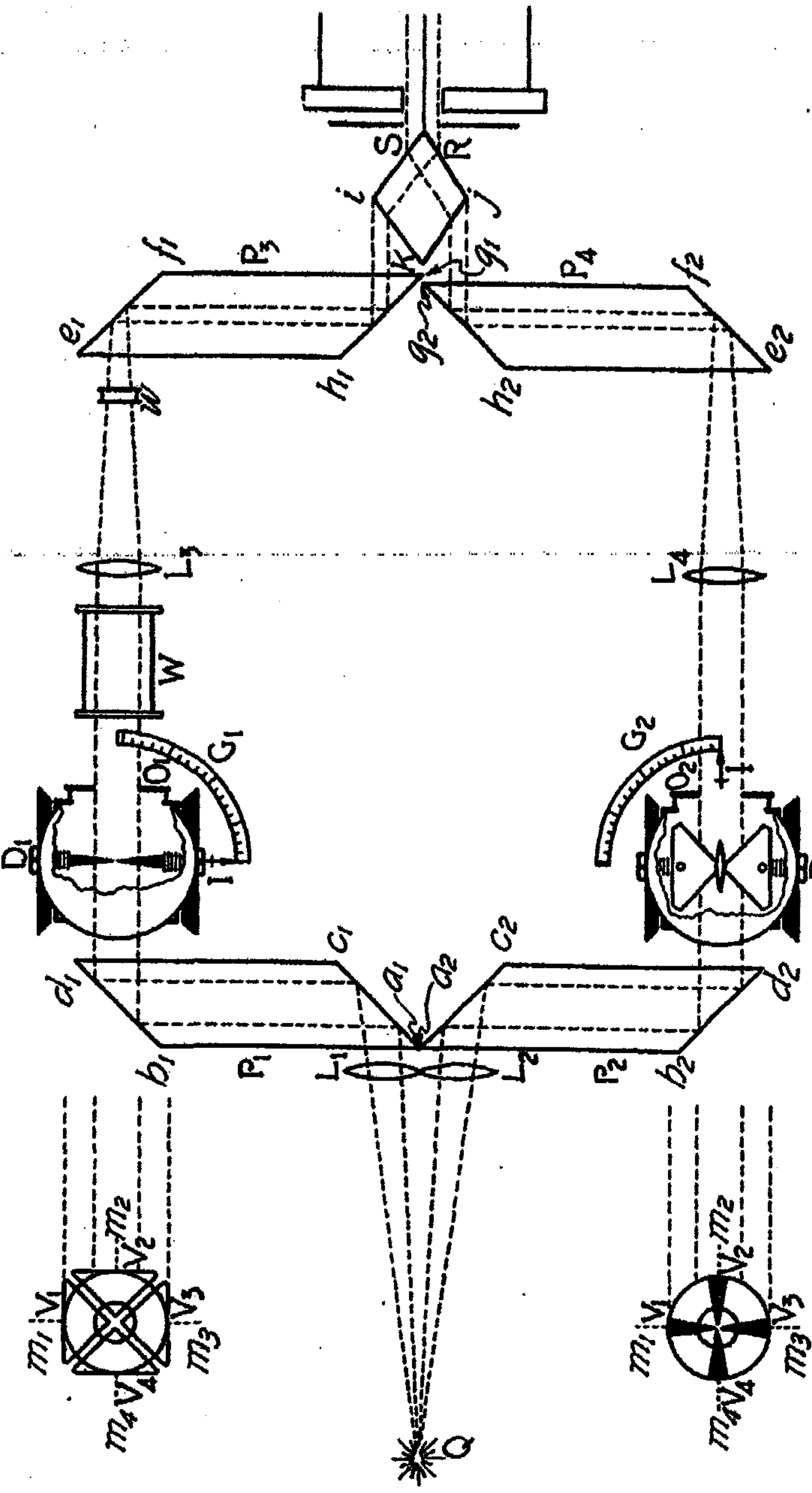
[1] Macbeth and Maxwell: J. Chem. Soc., 123, 370 (1923).

[2] H. v. Halban and Geigel: Z. physik. Chem., 96, 214 (1920); H. v. Halban and Siedentopf: 100, 208 (1922); H. v. Halban and Ebert: 112, 321 (1924).

[3] Judd Lewis: J. Chem. Soc., 115, 312 (1919).


S
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O_2
D_1
D_2
I
I
c_1
c_2
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L_2
m_1 V_1
m_2 V_2
m_3 V_3
m_4 V_4
m_1 V_1
m_2 V_2
m_3 V_3
m_4 V_4
Q

FIG. 1

matically in Fig. 1. Light from the source Q is rendered parallel by the two quartz lenses L_1, L_2, and then enters the two fluorite rhombs P_1, P_2. The upper beam is reflected from the face, a_1c_1, to the opposite face, b_1d_1, whence it is reflected as a parallel beam through the sector D_1, and the observation cell, W, to the lens L_3, which brings the light to a focus on the slit of the spectroscope, after it has traversed the reflecting rhomb, P_3, and the Albrecht rhomb, R. The lower beam of light traverses an exactly similar path and is brought to a focus in close juxtaposition to the first beam on the slit of the spectroscope. The cell, W, contains the solution and a similar cell, not shown in the diagram, similarly placed in the path of the lower beam contains the solvent. In this manner the effect of the solvent is eliminated and we measure only such differences as may be caused by the solute alone. By adjustment of the lower sector, D_2, the intensity of the light in the path containing the solvent may be diminished by successive steps and the resulting series of spectra compared directly with the absorption spectrum produced by the solute. The general method of procedure in making a quantitative determination of the absorbing power of a solution is briefly as follows: Several pairs of spectra are photographed on the same plate after which the plate is developed and then measured. In each of these pairs of spectra, the intensity of the lower spectrum, measured in terms of the intensity of the incident light, is indicated by the position of the index on the graduated quadrant, G_2. In each pair of spectra, the upper spectrum is that produced by the absorbing medium and, therefore, the aperture remains fixed throughout the entire experiment at 0° on the quadrant, G_1. The wave-length at which the two members of each pair of spectra have equal densities is then noted under a magnifying lens, whence the unknown intensity in the absorption spectrum is measured in terms of the known intensity of the normal spectrum. One of the most distinctive features of the Judd Lewis photometer is the unique construction of the sectors, but for these details reference must be made to the original description given by the inventor. The outstanding advantages of this type of sector photometer are, (a) uniformity of illumination, (b) utilization of the entire aperture, (c) avoidance of the necessity of calibrating photographic plates, and (d) avoidance of the necessity of supplementary rotating mechanism and (e) increase in precision in setting for small apertures.

As a source of light, a condensed spark between nickel-steel electrodes was employed, the apparatus being arranged as shown in Fig. 2. By means of a 0.25 K.W. transformer, T, the primary of which was fed by a 110 volt, 60 cycle alternating current, a secondary voltage of 6000 volts was obtained. The current from the secondary charged the condenser, C, (capacity 0.03 m.f.) which in turn discharged across the spark gap between the nickel-steel electrodes at E. A supplementary spark gap, G, was also included in the circuit. Special attention was given to the form of the terminals of the electrodes. The end of each electrode was first ground to a chisel-shaped edge and then the sharp corners were rounded with a file. The electrodes were mounted in a stand which was so arranged that the position of the spark-gap could be adjusted both vertically and horizontally. Special precautions were taken in the final adjustment of the source of light to insure that the prolongation of the optical axis of the photometer should lie in the plane of the two parallel chisel-shaped edges of the electrodes. The time of exposure was determined by means of the formula,

$$\text{Exposure} = A\,\frac{t_1}{t}$$

where the ratio, t_1/t, is the number corresponding to the sector reading, $\log t_1/t$, and where A is a constant. In the majority of cases, satisfactory results were obtained with A = 10 seconds. All spectrograms were made on special Wratten and Wainwright, 10″ × 4″ panchromatic plates.

Preparation of Solutions

All of the salts used in this investigation were prepared by recrystallization of the purest samples obtainable from reliable manufacturers, and conductivity water was used as a solvent in making up the solutions. The concentration of each mother solution was determined analytically, and dilution to the desired strength was effected by means of calibrated volumetric apparatus.

Method of Experiment

Having adjusted the position of the source of light so that the upper and lower halves of its spectrum were uniform, and having ascertained that the tilt of the slide-holder of the camera of the spectrograph was such as to insure correct registration of the wave-length scale, a series of preliminary exposures with varying concentrations of the solution under examination were made, in order to determine the proper thickness and concentration to be used in subsequent experiments. When the most suitable concentration and tube-length had been found, a series of exposures was then made. Having set the indices of the two quadrants at 0°, an exposure, known as the "test-band," was first made in order to verify the results of the previous experiment as to the uniformity of the juxtaposed spectra. The two tubes containing the solution and solvent were now placed in their respective troughs, and a second exposure,

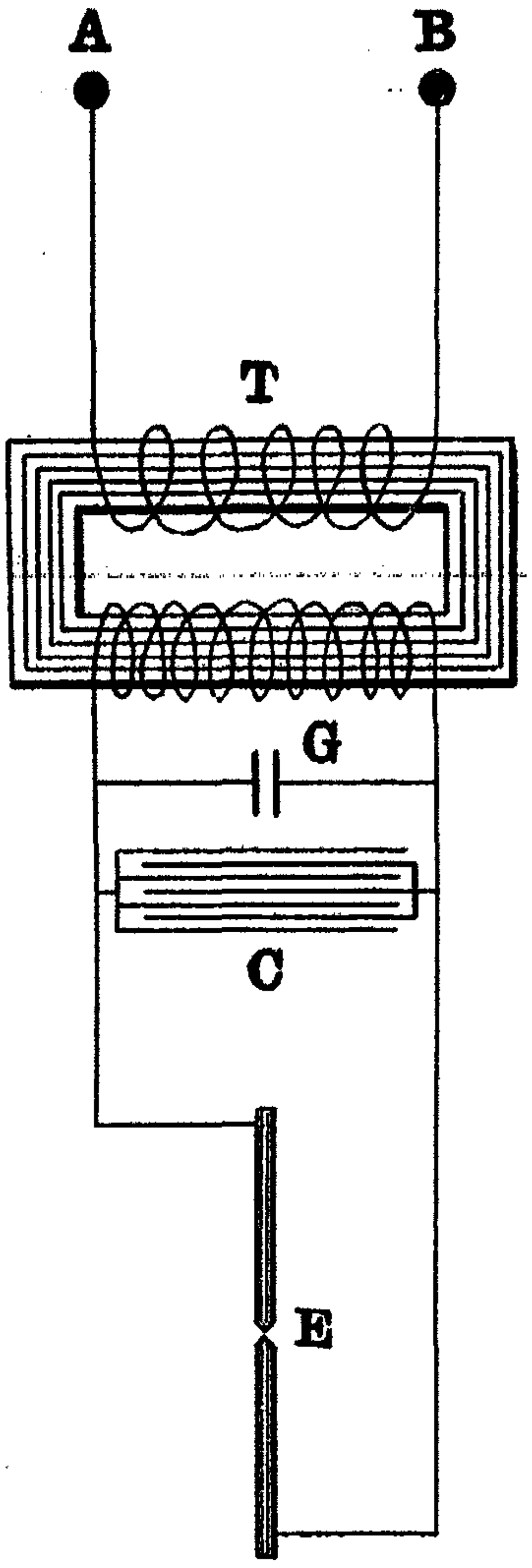

FIG. 2

with the indices still at 0°, was made. This pair of spectra, known as the "comparison band," shows the relative absorbing powers of solution and solvent. A series of exposures was now made with the sector in the path of the solvent set at successively smaller apertures, while the sector in the path of the solution remained fixed at 0°. In this manner, a series of from twelve to fifteen spectra, 5 mm. apart, were obtained on a single plate. In every case the last exposure was similar to the first, a second test-band being made to detect any slight change in adjustment of the apparatus during the experiment. After development, the plate was examined with a magnifying lens and the wavelengths at which the two members of each pair of spectra were found to have equal densities was noted, and plotted as abscissas against the corresponding values of the molecular extinction coefficients as ordinates. The value of the molecular extinction coefficient is calculated by means of the formula,

$$M = \frac{\log I/I_0}{lm}$$

where I and I_0 denote the intensities of the transmitted and incident radiation respectively, and where l and m represent the thickness and concentration of the absorbing medium respectively. As has already been stated, the values of the ratio, log I/I_0, are read directly from the graduated quadrant attached to the sectors.

Experimental Data

The data of the following tables is compiled from a series of measurements of the absorption coefficients of a number of simple inorganic salts. The wavelength, expressed in millimicrons, is denoted by λ and the value of the molecular extinction coefficient by M.

TABLE I

Calcium Chloride

Concentration 3.613m, 10 cm. tube

M	λ		
0.003	318		
0.006	310		
0.008	305		
0.011	299		
0.014	295		246
0.017	292	250	242
0.019	289	254	420
0.022	288	256	239
0.025	287	257	236
0.028	283	259	233
0.030	279	266	229

TABLE II

Strontium Chloride

Concentration 2.486m, 4cm. tube

M	λ		
0.01	315		
0.02	300		
0.03	290	257	
0.04	280	261	235
0.05	278	270	234

Table III

Barium Chloride

Concentration 1.171m, 10cm. tube

M	λ
0.021	313
0.043	295
0.064	284
0.085	277
0.107	270
0.128	265

Table IV

Magnesium Chloride

Concentration 2.955m, 4cm. tube

M	λ		
0.01	288	256	233
0.02	283	262	229
0.03	281	265	226
0.04	279	268	225
0.05	277	271	223

Table V

Zinc Chloride

Concentration 2.254m, 2cm, tube

M	λ		
0.04	310		
0.06	303		
0.08	298		
0.09	296	248	238
0.10	293	254	232
0.11	290	258	229
0.12	287	260	228
0.13	281	265	227

Table VI

Cadmium Chloride

Concentration 0.421m, 4cm. tube

M	λ
0.06	365
0.12	318
0.18	273
0.24	264
0.30	260
0.36	259

Table VII

Mercuric Chloride

Concentration 0.01m, 10cm. tube

M	λ
1	270
2	268
3	267
4	266
5	265
6	264

Table VIII

Cupric Chloride

Concentration 0.145m, 4cm. tube

M	λ
0.17	372
0.35	365
0.52	360
0.69	355
0.86	359
1.04	350

Table IX

Aluminium Chloride

Concentration 0.9m, 4cm. tube

M	λ		
0.139	283		
0.167	280		
0.195	279		
0.232	278	241	
0.250	278	247	231
0.278	277	248	228
0.306	276	249	227
0.333	276	251	226
0.361	275	252	225
0.389	274	253	

The foregoing experimental data, together with that of Brannigan and Macbeth[1] for HCl, NaCl, LiCl and RbCl, is represented graphically in Figs. 3, 4 and 5.

Discussion of Results

An examination of the curves reveals well-defined selective absorption in solutions of the chlorides of hydrogen, sodium, lithium, rubidium, calcium, strontium, magnesium, zinc and aluminium, while solutions of the chlorides of barium, cadmium, copper and mercury show marked general absorption. The wave-length corresponding to the head of the absorption band of each salt exhibiting selective action is found to be approximately 273$\mu\mu$. The persistence of this characteristic band at approximately the same wave-length throughout the series suggests that it may be attributed to the one constituent which is common to all of the salts, viz. the chlorine ion. If the chlorine ion is responsible for this characteristic band, it is apparent that the depth of the band should increase as the number of chlorine ions is increased

In order to decide this question, a nearly saturated solution of calcium chloride was prepared, and a portion diluted to one-third the concentration of the original solution; the concentrations of these solutions were determined and found to be respectively, 5.592m and 1.864m. Spectrograms of these two solutions were then made, a 2 cm. tube being filled with the concentrated and a 6 cm. tube with the dilute solution. In this manner, the same total mass of absorbent was interposed in the path of the beam of light, the only difference in the condition of the solute in the two cases being a difference in degree of ionization. If absorption is due to the chlorine ion, the effect should be more pronounced in the more dilute solution. An examination of the results obtained, as shown by the experimental data of Table X and the curves of Fig. 6, proves that the more concentrated solution exerts the greater absorbing action.

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[1] loc. cit.

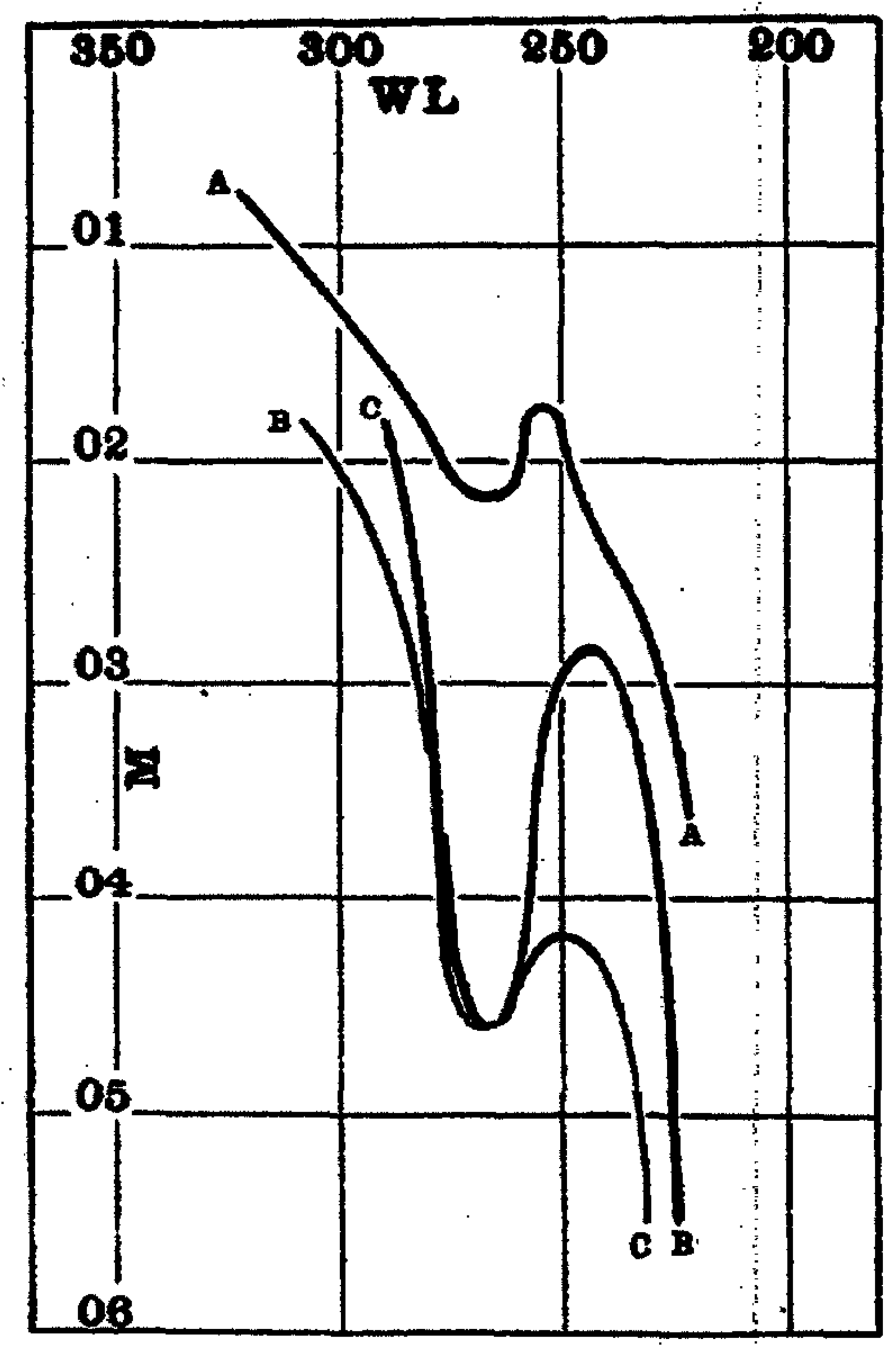

Fig. 3

A Hydrogen chloride
B Sodium chloride
C Lithium chloride

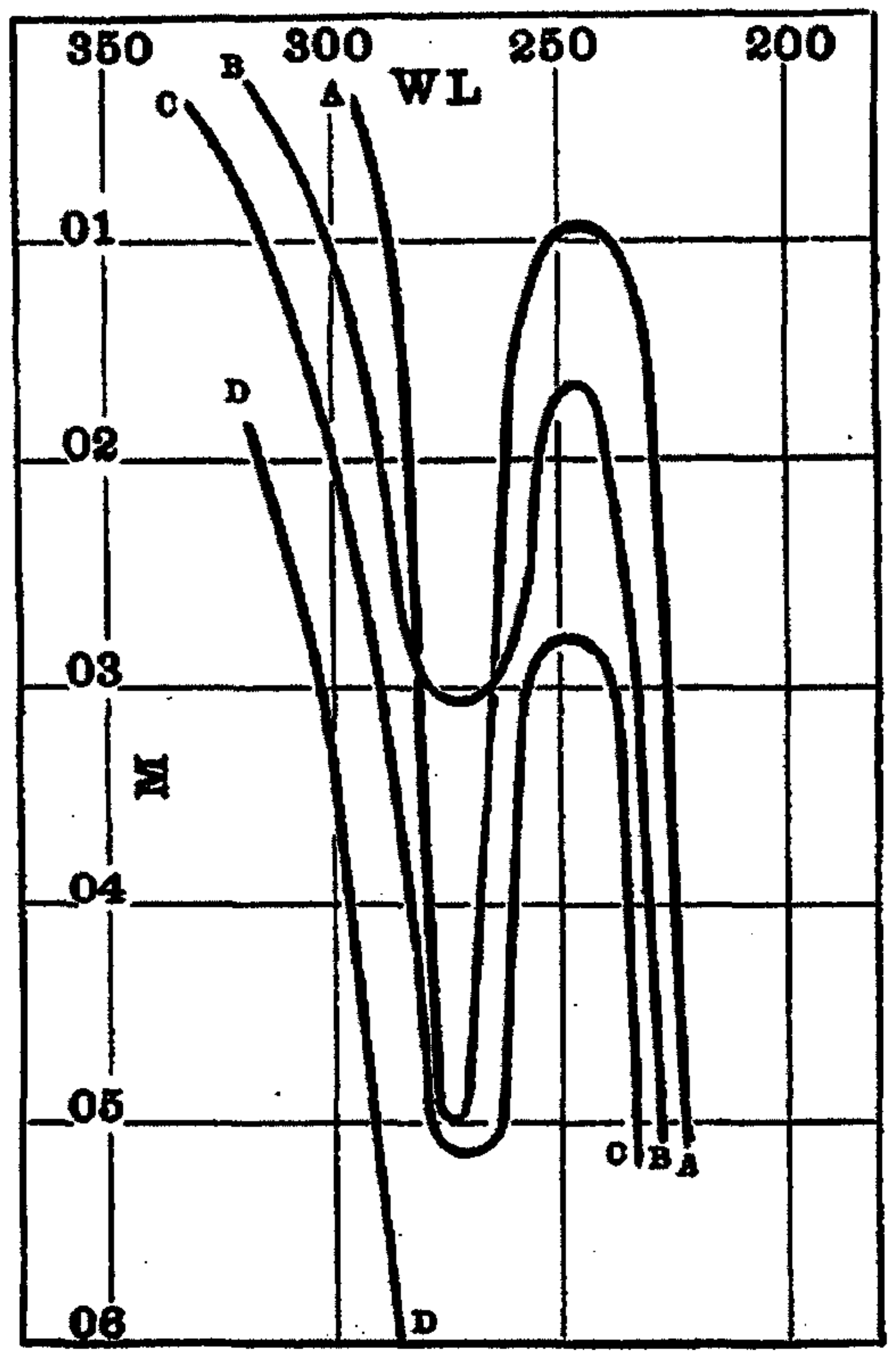

Fig. 4

A Magnesium chloride
B Calcium chloride
C Strontium chloride
D Barium chloride

TABLE X

Calcium Chloride

Concentration 5.592m, 2 cm. tube

M	λ		
0.018	305		
0.022	291		
0.027	287		
0.031	283		
0.036	280	263	242
0.040	279	265	232
0.045	277	275	225

Concentration 1.864m, 6 cm. tube

M	λ		
0.009	300		
0.013	291		
0.018	284		
0.022	281		
0.027	278	260	235
0.031	275	265	233
0.036	273	273	230

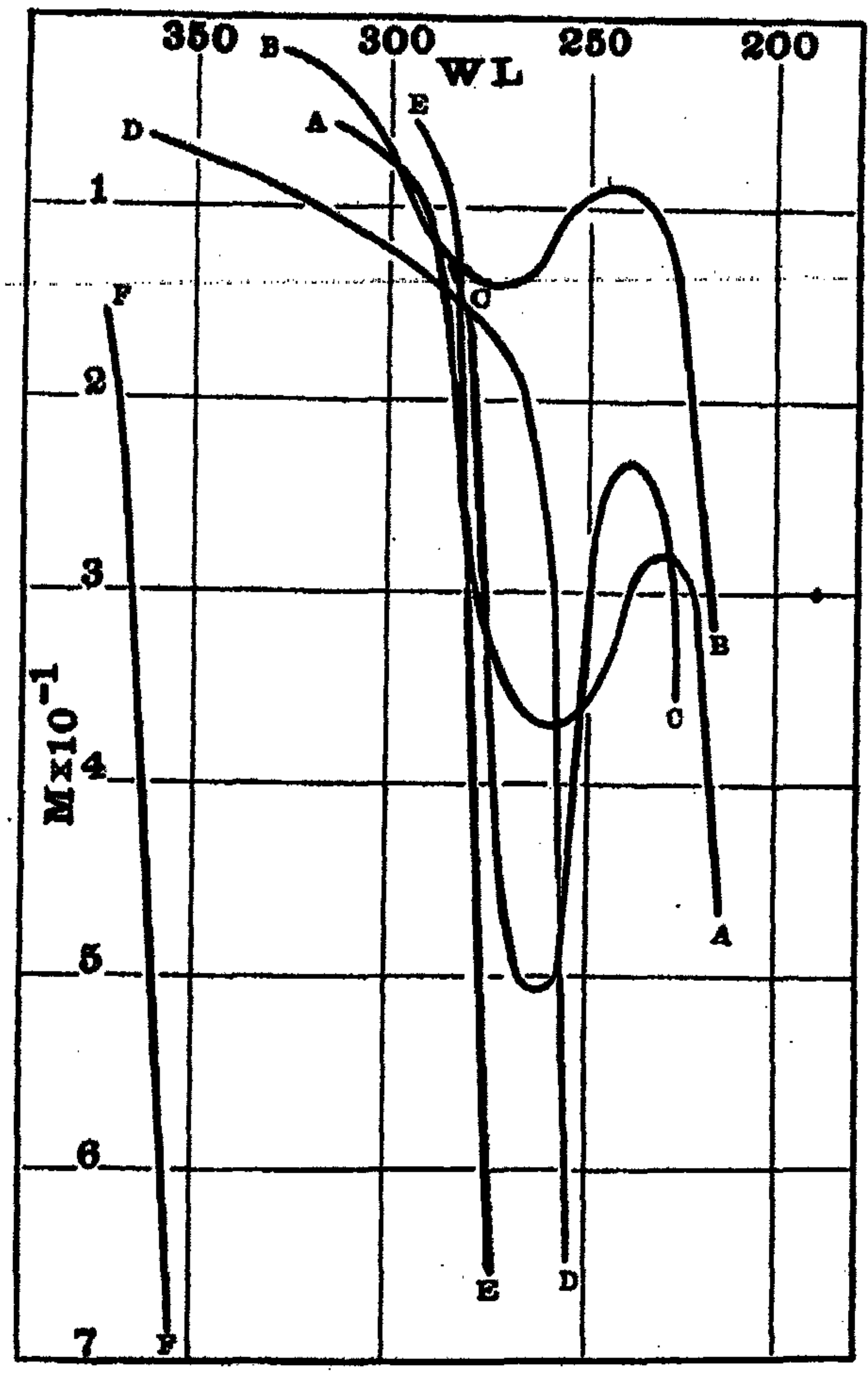

FIG. 5

A Rubidium chloride
B Zinc chloride
C Aluminium chloride
D Cadmium chloride
E Mercuric chloride
F Cupric chloride

Not only does this experiment make it appear unlikely that the absorption bands are to be ascribed to free chlorine ions, but also it shows conclusively that calcium chloride does not conform to Beer's law. According to this law, the absorption exerted by a solute is independent of the concentration, provided that the tube-length be altered in such a manner as to maintain the product of the two factors, concentration and tube-length, invariant.

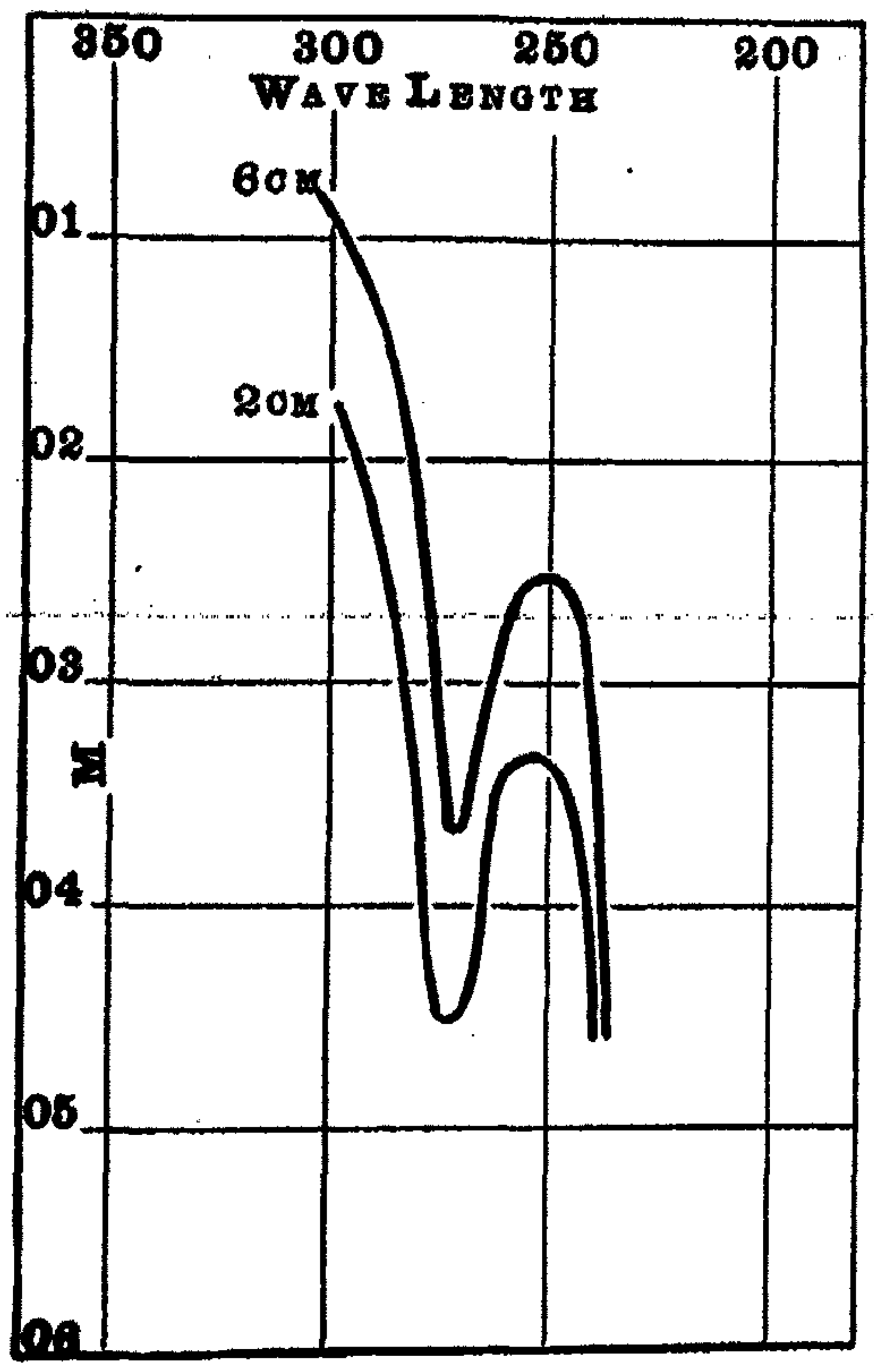

Fig. 6

5.592m $CaCl_2$ in 2 cm. tube
1.864m $CaCl_2$ in 6 cm. tube

After having determined the absorption of ultra-violet radiation by azobenzene over a wide range of concentration in tubes of different lengths, Macbeth and Maxwell[1] concluded that "the molecular extinction coefficient remains the same for a particular wave-length, whether a concentrated or a dilute solution is employed."

Having found that solutions of azobenzene conform to Beer's law, they then assume that the law is equally valid for solutions of metallic chlorides. The foregoing experiment with calcium chloride, however, proves this assumption to be wholly unwarranted and leads us to suspect that Beer's law does not apply to solutions of strongly polar compounds.

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[1] J. Chem. Soc. 123, 370 (1923).

The molecular extinction coefficient of the metallic chlorides apparently increases with increase in the atomic weight of the metal. Those chlorides which do not absorb ultra-violet radiation selectively nevertheless exhibit marked general absorption. While barium chloride failed to reveal any tendency toward selective absorption within the range of concentration studied, it is possible that in more dilute solutions it may be found to conform to the behavior of its congeners, calcium and strontium.

From the foregoing statements it is apparent that the generalization put forward by Crymble[1], that only the salts of metals of variable valence absorb ultra-violet light, has been disproven. Without exception, every metallic chloride thus far examined exhibits either selective or general absorption. The degree of absorbing power varies greatly among the chlorides investigated; for example it is difficult to understand why 4m NaCl should absorb nearly four times more strongly than 12m HCl. At this time it would be premature to venture any explanation of this and other anomalies presented by the experimental data thus far accumulated. It is hoped, however, that ultimately it may be possible, after other groups of salts have been examined, to establish some connection between absorption and atomic or molecular constitution.

Summary

The results of this investigation may be briefly summarized as follows:

(1) The chlorides of calcium, strontium, magnesium, zinc and aluminium have been found to absorb ultra-violet radiation selectively, the wave-length corresponding to the head of the absorption band of each salt being approximately $273\mu\mu$. This is in conformity with the results previously obtained by Brannigan and Macbeth in their investigation of the absorption of ultra-violet radiation by the chlorides of hydrogen, sodium, lithium and rubidium.

(2) It has been shown that the persistence of this characteristic absorption band throughout a series of chlorides cannot be attributed to the presence of the common ion, chlorine.

(3) It has been proven that solutions of calcium chloride do not follow Beer's law. From this fact it appears doubtful whether the law applies strictly to any strongly polar compounds.

(4) The molecular extinction coefficients of the metallic chlorides increase with the atomic weight of the combined metal.

(5) While certain metallic chlorides do not exert selective absorption, they, nevertheless, exert marked general absorption.

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[1] J. Chem. Soc. **101**, 266 (1912).

SOME OBSERVATIONS ON THE COLLOIDAL CHARACTER OF ASPHALTS

BY R. E. KIRK AND L. H. REYERSON

Certain data are here presented which are thought to have significance concerning the colloidal character of asphalts. This significance can best be shown when the facts are viewed in the light of the generally accepted ideas about the subject in question.

It has long been recognized that asphalts are colloidal in character. Ideas as to the character and kind of colloidal particles present in asphalts have been numerous. Much difference of opinion and much discussion has arisen from an endeavor to correlate the colloidal character of asphalts with the wearing properties of pavements made therefrom. Such a correlation is made more difficult by the fact that asphalt undoubtedly may change somewhat its colloidal character during the time that it is being applied to a pavement. It seems also to be true that some of the finer portions of mineral aggregates used in asphaltic pavements may become more or less dispersed in the asphalt. The degree of dispersion, while it may not always be so great as to give a particle which exhibits the Brownian movement, is great enuf to cause significant alterations in the surface energy of the asphaltic mixture.

Proponents and opponents of certain kinds of asphalts or of certain patented processes for the building of asphaltic pavements have been prone to emphasize only those of the known facts or current ideas which favored their side of a commercial controversy.

For these and other reasons some engineers with whom the writer has come in contact have come to regard the colloidal character of asphalt as something in which the practical builder of roads has no immediate interest. This is doubly unfortunate since these men may not only profit by using what knowledge has now accumulated about the colloidal character of asphalt but may also contribute greatly to the correlation of that knowledge with the success of a pavement.

Certain general statements of fact may be made.

1. Asphalts may have inorganic matter dispersed in them. This has been shown for the Trinidad deposits by Richardson[1].

"The crude asphalt appears from the preceding observations to consist of a suspension of relatively large size mineral particles in an extremely viscous medium, together with highly dispersed mineral matter in colloid form, intimately mixed with an emulsion of a thermal water with the bitumen present." "In addition to the scientific interest in the presence of solid disperse matter to such an extent in the Trinidad Lake asphalt, it is of great importance from an industrial point of view, since the presence of such a large amount of

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[1] J. Phys. Chem. 19, 241 (1915).

material in a suspensoid and dispersoid state adds enormously to the surface energy developed by the material, and this has been shown to be of great importance in the construction of asphalt surfaces."

2. Asphalts are themselves mixtures of substances in a state of both molecular and colloidal dispersion. This has been established by several different modes of attack. A recent review of the evidence is that by Errera[1]. He concludes that raw asphalt is a mixture of substances in a state of molecular and colloidal dispersion. "Asphalt is a poly dispersoid," says Errera, and the experimental work cited leads to the view that there exist "intermediate stages between molecular and colloidal asphalt." This consideration, it should be noted, is complicated by the fact that asphalts may possibly exhibit, to some extent at least the properties of colloidal solutions and still exist in molecular dispersion. This is due to the size of the molecules as evidenced by the high molecular weight. The change in the colloidal character of asphalts after various physical and chemical treatments has been noted by Rosinger[2]. He notes primarily the increased sensitiveness to light as the colloidal character of the asphalt is increased. Errera comes to a similar conclusion.

3. Asphalts may have their colloidal character changed by adding under various conditions either clay or certain inorganic salts. This was directly established by E. C. E. Lord[3]. He dispersed certain asphalts, so prepared, in benzol and estimated directly with the ultra microscope the colloidal particles present. The increase in number of colloidal particles was immediately apparent. He found a larger number of colloidal particles visible with the ultra microscope when the original asphalt had been mixed with copper carbonate salts than in any other case. Mr. Lord did not, however, test the effect of these salts on the colloidal mineral matter present in certain native asphalts.

He states that he removed the colloidal matter in the original Trinidad asphalt, for example, checking by dispersion in benzol, and then recovering the bitumen. This was treated with the various inorganic salts and tested, as before, after dispersion in benzol. He concludes that the colloidal particles are due primarily to a chemical action between the bitumen and the salt employed. "These bitumens have been separated into groups containing clay as colloidal material (Nos. 1-19) and into others in which this mineral matter was replaced by carbonates, sulfates and acetates of copper, iron, zinc, and lead (Nos. 20-47). The samples included in the first class, except untreated refined Trinidad asphalt (Nos. 1-5), were prepared by incorporating 33 per cent sandy clay in each type of bitumen by Richardson's method of heating an aqueous emulsion of clay and bitumen until all moisture and gas had been expelled. In the case of refined Trinidad asphalt and clay (Nos. 6-10) all insoluble mineral and organic matter originally present in the bitumen was removed before emulsifying by dissolving in benzol and adding about two per cent shellac dissolved in alcohol and evaporating to constant weight, redissolving in benzol

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[1] Trans. Faraday Soc. 19, 314 (1923).

[2] Kolloid-Z. 15, 177-9 (1914).

[3] J. Agri. Research 27, 167-176 (1919).

and filtering through an alundum tube until the solution was essentially void of colloidal particles.

"In the second group of bitumens (Nos. 20-47) the salts were introduced in an anhydrous condition and the mixtures were heated to about 170°C. under constant stirring until all evolution of gas had ceased. On examining solutions of this kind under the ultra-microscope it was found that the copper carbonate salts had been largely reduced to red cuprous oxid, accompanied by an enormous colloidal dispersion (Nos. 20-30), while with the remaining salts the reduction had been much less complete (Nos. 31-39) or entirely lacking (Nos. 40-47), and the development of colloids correspondingly less. It may be stated, therefore, that the colloidal capacity of the second group of materials taken as a whole was dependent largely upon the degree of chemical reaction between the bitumen and the salts employed, while in the first group this supporting value was related more directly to the physical character of the bitumen."

4. When asphalt is mixed with finely divided mineral matter it seems to undergo some alteration of surface energy relations even though the particles are not so small or so completely dispersed as to show the Brownian movement. This is best evidenced by the many successful pavements based on various methods of mixing finely divided mineral matter with asphalt. Evidently we are passing thru a transition stage in which the particles, while for the most part too large to show the Brownian movement, are small enough, in part at least, to give to the mixture some of the properties of colloidal solutions.

We must then recognize that in asphalts and in asphalt pavements we are dealing with complex mixtures of materials for each of which the state of molecular arrangement may range from the extreme randomness of true solution to the definiteness of crystals. We must also note the probability that at least part of the asphalt molecules are very large in size and that even when molecularly dispersed they show some of the properties characteristic of colloidal dispersions.

Certain ideas concerning the relationship between the colloidal character of asphalts and the properties of an asphalt pavement surface have been presented in a series of papers by Richardson[1].

Certain experimental work has been started by the writers designed to aid in the correlation of the known facts about the colloidal character of asphalts and their behavior under various conditions[2]. At this time they desire to report on three series of observations.

1. The effect of copper sulfate on the colloidal character of certain Trinidad asphalts.

Through the courtesy of the Department of Civil Engineering of this University and the Minnesota Highway Department, the attention of one of the

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[1] J. Ind. Eng. Chem. 7, 463 (1915); Met. and Chem. Eng. 17, 650 (1917); Third Report on Colloidal Chemistry (British Association for the Advancement of Science), 98-102 (1920).

[2] Project No. 27 Minnesota Engineering Experiment Station.

writers was called to the results of certain cooperative tests made on asphalts which had been treated with copper sulfate. The asphalts had been heated to such a temperature that finely divided copper sulfate ($CuSO_4 . H_2O$) could be stirred in. A series of physical tests had been made. The deviations so noted were such that they could all be reasonably explained on the assumption that there had been an increase in the colloidal character of the asphalt and a consequent alteration of surface energy. This was, of course, what would have been predicted from the observations of Lord[1].

During the routine laboratory examination of these asphalts certain deviations were noted in the so-called inorganic insoluble portions of the treated and untreated Trinidad asphalts. In this test (made according to the directions on page 52, Bulletin 691, Bureau of Public Roads) a portion of the asphalt is treated with carbon disulfide, shaken, allowed to settle for a short time and filtered thru an asbestos filter in a tared gooch. The crucible is ignited and weighed. The increase in weight is called "inorganic insoluble matter."[2]

This may better be called, "inorganic matter retained on an asbestos filter." The values so obtained with two samples fluxed Trinidad asphalt treated with 3.25 % of $CuSO_4.H_2O$ are as follows:

	"Inorganic Insol."
Untreated "Trinidad 45'"	27.6 %
Treated "Trinidad 45'"	22.8 %
Untreated "Trinidad 65"	25.7 %
Treated "Trinidad 65"	19.86 %

(Tests by M. A. Peterson, Chemist, Minnesota Highway Department). Evidently more of the inorganic material passes thru the asbestos after treatment than before.

The determinations on these asphalts were repeated by one of the writers save that the carbon disulfide insoluble tests were made according to page 53 of Bulletin 59. In this method 120 hours settling is allowed.

	"Inorganic Insoluble"
Untreated "Trinidad 45"	27.59 %
Treated "Trinidad 45"	28.78 %
Untreated "Trinidad 65"	27.00 %
Treated "Trinidad 65"	27.50 %

(Tests by R. E. Kirk).

The results are noticeably different from the preceding ones. This is evidently due to the longer time of settling allowed.

These results were so interesting that direct evidence of the changed colloidal character of the asphalts were sought.

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[1] J. Agri. Research, 27, 167-176 (1919).

[2] It should be noted that the inaccuracy of this method as regards asphalts containing colloidal mineral matter has long been recognized and adequate tests devised to estimate mineral matter in such asphalts. The data containing these tests is presented only because it offers indirect evidence concerning a change in the colloidal character of these asphalts.

The filtrates from the determinations of CS_2 insoluble (120 hrs. settling) were examined by the aid of the ultra microscope, as follows. Definite portions of each filtrate were diluted with optically inactive carbon disulfide until they ceased to be opaque when used with the dark field illuminator. The microscope, used in observing the colloidal character of the solutions, was a Bausch and Lomb fitted with a dark field illuminator. The observations were made by means of the dry 16 mm. and 4 mm. objectives. Glass cells were used of the proper depth for dark field observation and the light source was a thousand watt lamp mounted in the conventional manner for ultra-microscopic work[1]. A tremendous diminution in apparent size and a great increase in the number of particles was at once observed in the cases of the treated asphalts as compared to the untreated ones. Direct observations of the colors of the Tyndall beam in the treated and untreated asphalts were then made. A very distinct shift from light yellow to golden yellow was noted.

The same Trinidad asphalts were then treated with $CuSO_4 . 5H_2O$ and portions treated with carbon disulfide as before. Portions of the filtrates (after 120 hrs. settling) were diluted and examined with the ultra microscope. The same lessening in apparent size of the particles and the same marked increase in numbers of particles were noted.

Next observations were made on filtrates where only a short time was allowed for settling. The increase in number of particles and decrease in apparent size of particles in the treated as compared to the untreated was even more noticeable than when longer settling time was allowed.

The remaining portions of the filtrates were allowed to stand and at various intervals were examined with the ultra-microscope as described. After standing four months the solutions showed definitely that clustering together of colloidal particles had started. At seven months the process was well under way, and at nine months no distinction could be made between the filtrates from the treated and untreated asphalts.

The evidence, seems to justify the conclusion that when asphalts containing mineral matter are treated with copper sulfate the mineral matter itself is more highly dispersed than previously. This action is very probably accompanied by the formation of colloidal particles due to the action between the salt and the organic material present, as observed by Lord.

It should be recognized that the dispersions in carbon disulfide give only suggestions as to the state of aggregation in the asphalts. For reasons to be later developed it is our feeling that carbon disulfide is a better dispersion agent for asphalts containing mineral matter than is benzene.

II. The effect of copper sulfate on asphalts having little mineral matter present.

Samples of fluxed "Stanolind" asphalt were examined in a similar manner. Here the carbon disulfide dispersions of the untreated asphalts showed no colloidal particles when examined with the ultra microscope. The carbon disul-

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[1] The microscopic equipment for this work was made available thru aid from the Graduate School Research Fund of the University of Minnesota.

fide dispersions of the treated asphalts showed a large number of colloidal particles. This is in exact agreement with the observations of Lord previously noted.

III. The dispersion of various asphalts in certain organic liquids.

Certain preliminary observations have been made on the dispersion of asphalts in certain organic liquids. The liquids used were carbon disulfide, carbon tetrachloride and acetone. These were selected as covering a wide range of solubility; asphalts, in general, being very soluble in carbon disulfide and rather sparingly soluble in acetone while carbon tetrachloride occupies an intermediate position. The liquids were carefully purified and tested for colloidal particles with the ultra-microscope.

An oil asphalt was first selected, since such an asphalt is very low in inorganic material. The asphalt used was a sample of "Stanolind" furnished by the State Highway Laboratory.

A portion of the asphalt was thoroly shaken with the liquid in question and allowed to stand several days, before testing with the ultra-microscope. The method and equipment has been previously described.

The asphalt disappeared completely in the carbon disulfide and no colloidal particles could be detected with the ultra-microscope. The illuminated field was clear and colorless.

With carbon tetrachloride the asphalt disappeared completely. The ultra microscope revealed no colloidal particles when the diluted liquid was examined but the illuminated field was colored a light blue. The color was very distinct and was attributed to minute particles of greater than molecular size.

Only a rather small portion of the asphalt dissolved in the acetone. The "solution" had a very marked greenish fluorescence. When the diluted liquid was viewed through the ultramicroscope, a brilliant green field was observed. A very few extremely small particles were revealed.

On standing several months the carbon disulfide solutions showed a very few colloidal particles. A test of the carbon disulfide check flask disclosed, however, that the same thing had happened where no asphalt was present; i.e. that the particles were formed by a gradual change in the carbon disulfide. The carbon tetrachloride solution of asphalt showed some colloidal particles and a definite deepening of the color of the field. The pure carbon tetrachloride showed no colloidal particles. Therefore, the effect noted in the asphalt solution was due to an agglomeration of particles which previously were only evidenced by the blue color.

The acetone solutions of asphalt showed an increase in both the size and number of colloidal particles, while the pure acetone remained unchanged. The color of the field appeared to be the same as before. Similar tests were made with Trinidad asphalts. This is an asphalt known to be high in inorganic material. This inorganic material is usually considered to be partly colloidal in character. The solutions showed many colloidal particles, but the colored fields were again observed in those cases where carbon tetrachloride and acetone were used as dispersion media. Tests with samples of fluxed Bermudez asphalts showed similar colored fields. Only a few colloidal particles were seen in the carbon disulfide dispersion. In the carbon tetrachloride dispersion the colloidal particles were fairly numerous but rather small. The same was true in the acetone dispersion.

The results seem to justify the view that the dispersion of asphalts in organic solvents involves two distinct factors. The first is the dispersion of the inorganic material which may be present in the asphalt in all stages of aggregation. The second is the dispersion of some part of the organic portion of the asphalt. It would seem probable from these experiments that the solvent used is at least as important a factor as the character of the asphalt.

Any attempt to explain completely the physical characteristics of asphalts solely on the basis of the colloidal character of the inorganic materials present would therefore seem doomed to failure.

Summary

1. Copper sulfate acts on the mineral matter present in Trinidad asphalt, increasing the number and decreasing the apparent size of the colloidal particles. The change is one involving the mineral matter present as well as an action between the bitumen and the copper sulfate.

2. The dispersion of asphalts in organic liquids involves both the dispersion of inorganic matter and possible dispersion of some of the organic matter present.

It is desired to acknowledge the aid of Professor F. H. Lang of the Department of Civil Engineering and of Messrs. R. E. Bergford and M. A. Peterson of the Minnesota State Highway Department.

The School of Chemistry,
The University of Minnesota,
Minneapolis, Minn.
February 18, 1925.

A NEW PATTERN FORMED BY COLORED SALTS IN SOLID GELS

BY E. RAYMOND RIEGEL AND LEO WIDGOFF

When a cake of gelatine containing potassium ferrocyanide, uniformly distributed, is submerged in a solution of copper sulphate, the copper ferrocyanide does not form evenly throughout the cake, but is concentrated in zones which are dark red, and which we have called the dark zones; these border cleared gelatine, which forms the center of the cake and extends to the edges; these clear areas we have called the light zones. Without cutting the cake, the zones may be seen by holding it against the light; they are exhibited better by cutting a vertical slice 3 or 4 mm. thick from the center of the cylindrical cake while it lies on its base. The light zones form against the dark zones the pattern shown in Fig. 1.

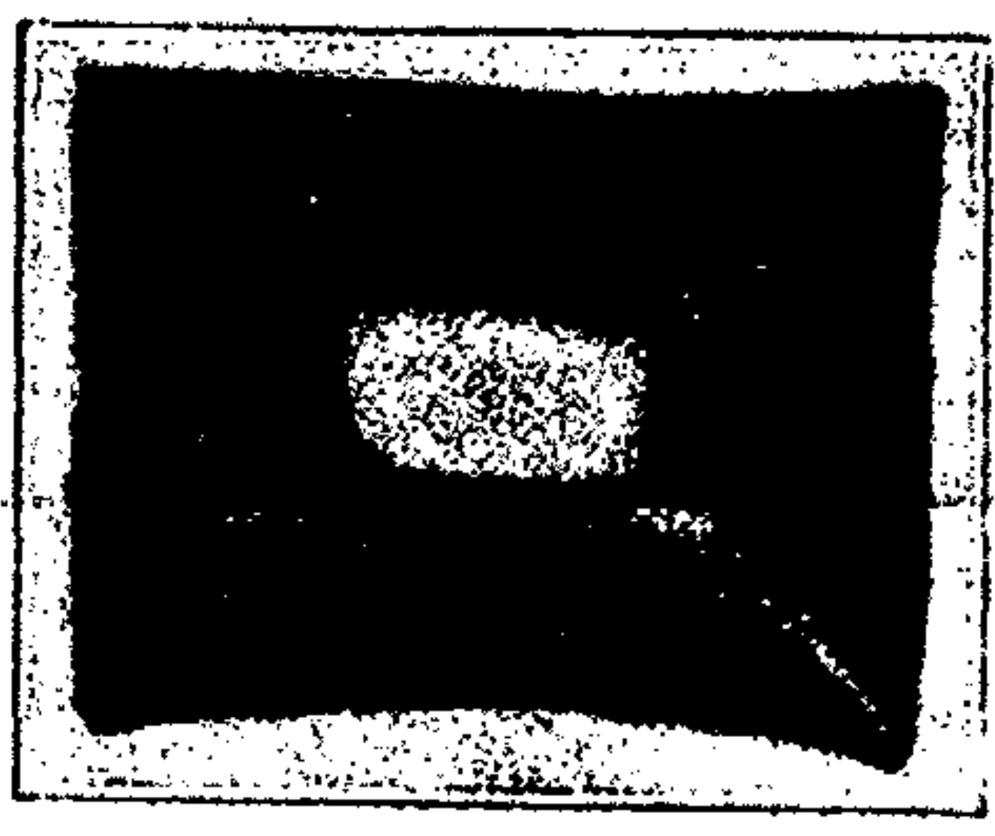

Fig. 1

Zone pattern formed by copper ferrocyanide in a gelatine cake. Photograph (positive) of a flat slice 3 mm thick cut from center of cake.

The 5% gelatine cake contained 0.05% potassium ferrocyanide and weighed 100 grams; it was submerged for two days in 100cc of 1% blue vitriol solution. The central portion is as clear as the original gelatine, except for the blue tinge due to excess copper sulphate solution; the light zone extends to the corners, reaching the very edge. During submergence this and all similar cakes were kept in an ice-chest.

The light zone extends to the corners because the cake was given sharp edges by trimming it with a knife; early in the work it was found that a rounded edge caused the zone to reach only halfway or so to the corners.

Several other concentrations were tried, ranging between those given above, and 0.2% potassium ferrocyanide in the cake, 5% blue vitriol in the solution; the latter concentrations gave a dense dark zone, well marked, but it is doubtful if higher concentrations would still form the pattern. No evidence of banding could be noticed, and no particles were visible under the microscope. One cake was kept in excess copper solution for fourteen months; the pattern remained unchanged. The effect of the number of edges on the pattern is well shown in Fig. 2, a photograph of three flat slices taken from a triangular column.

The gelatine cake contained 0.2% ferrocyanide; it was submerged for one day in 2% blue vitriol solution; horizontal slices were taken from the center of the column as it stood on its triangular base.

We were anxious to find a pair of salts which would give both the zone pattern and the rhythmic banding usually called the Liesegang phenomenon. The classic example, dichromate in the gel, silver nitrate in the solution, gave only the faintest indication of a pattern, although rings were formed. In lead nitrate and potassium chromate, we found the combination sought. Fig. 3 shows the pattern for lead chromate; the 5% gelatine (100 grams) contained 0.1% potassium chromate and was submerged two days in a 5% lead nitrate solution. The cuts were: two vertical ones from the center as the cake stood on its base, and one horizontal one, of which only half is shown.

The center is clear gelatine, all the chromate there originally has moved out to the sides; the branches of the light zone extending to the corners are frequently absolutely clear, and always well marked.[1] To the naked eye the details of the deposit are not visible; under a pocket lens some of the lines may barely be detected; but under a low power microscope the lines are plain.[2]

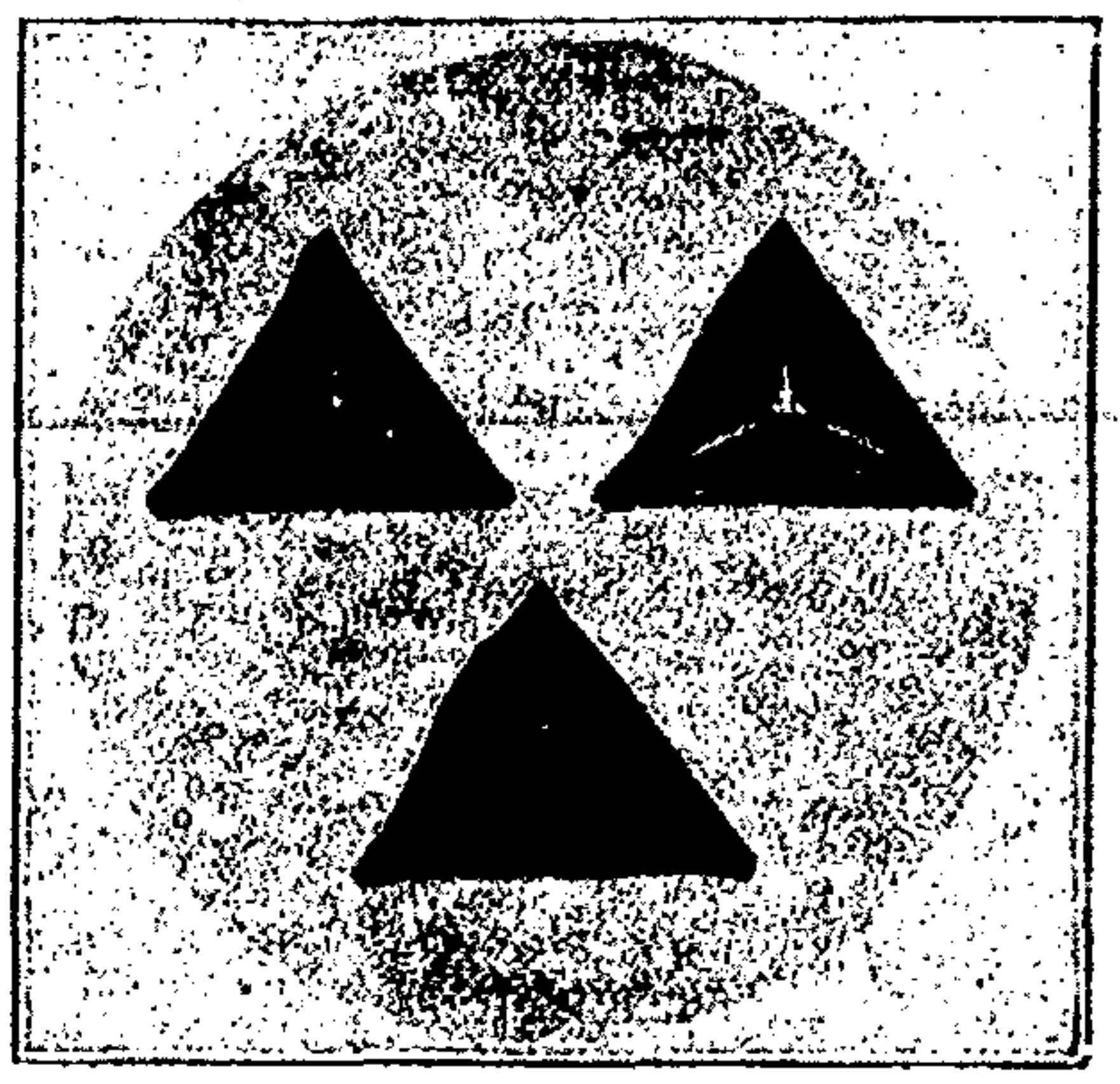

Fig. 2

Flat slices from a triangular gelatine column. The dark zones are copper ferrocyanide; the light ones clear gelatine, tinged blue by excess copper sulphate.

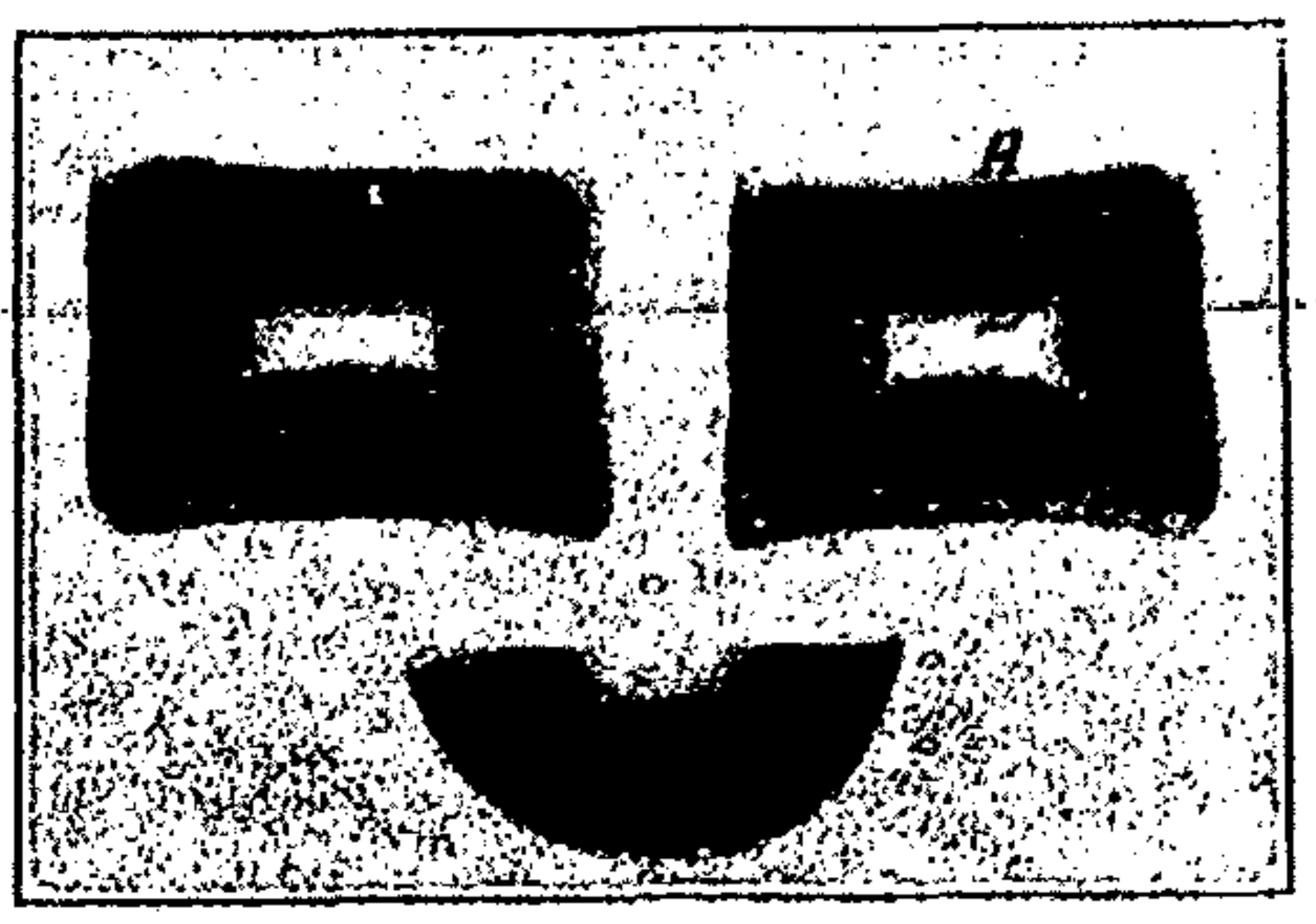

Fig. 3

Flat slices of a cylindrical cake. The upper slices are cut in the perpendicular plane; the lower picture shows half of a slice cut in the horizontal plane. The dark zones are yellow lead chromate; the light zones are thinner deposits, with clear gelatine in the center.

Moving from A toward B in Fig. 3, three places were selected and the photomicrographs in Fig. 4 taken.

Visual observation with the microscope shows that there are particles between the lines; few, when the lines are close together; many, when the lines are further apart and begin to be poorly defined; finally the lines are lost altogether in a mass of particles scattered without order.

When the slice is held up against the light, the scattered particles around the clear central zone act as a grating and resolve the light. With the circular slice, made by a horizontal cut, the effect is rather fine.

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[1] It is more difficult to photograph the lemon yellow deposit of this example than the dark red of the ferrocyanide of copper.

[2] In disagreement with a statement on p. 259 of "Applied Colloid Chemistry" by W. D. Bancroft.

With silica gels made into cakes the pattern for copper ferrocyanide was also obtained, but such a cake crumbles too easily to be handled, even when supported by wire netting. We confined ourselves therefore to gelatine solid gels. 2% and 3% concentrations of gelatine gave good results; we chose the 5% concentration because the stiffer cake could be cut more readily.

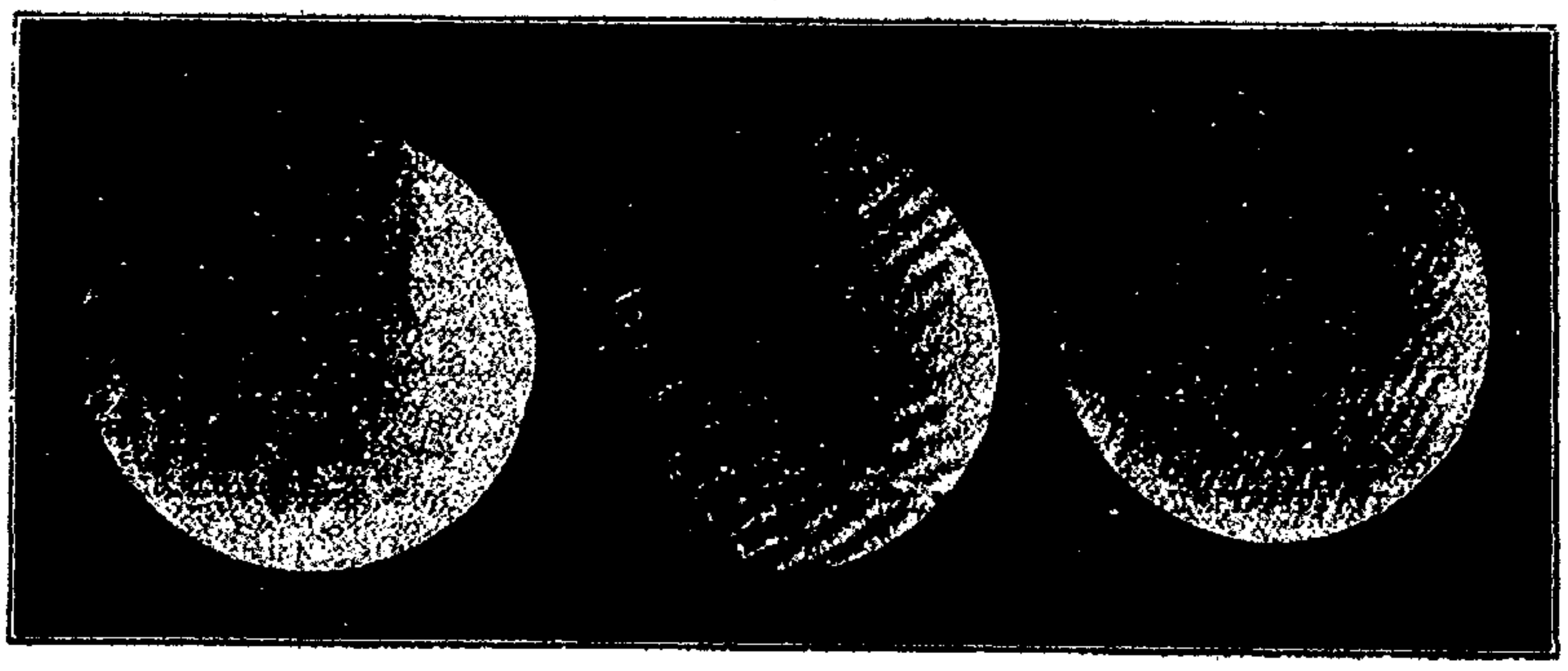

FIG. 4

Photomicrographs of lead chromate lines from a gelatine cake showing also the zone pattern. Taken at three places moving from A to B in Fig. 3. The fine lines were at A; the broadest and faintest at B. Magnification: 40 diameters.

More facts must be accumulated before a sound interpretation of our observations is presented. Without more delay, we thought it might be of interest to fellow workers in this field to give notice of the formation of the zone pattern. This much may be said: the formation of well marked clear zones reaching to the corners when the edges are sharp indicates that the entering soluble salt travels in straight lines perpendicular to the walls of the cake.

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POTASSIUM BICHROMATE AS DEPOLARIZER

BY G. P. VINCENT

Bengough and Stuart[1] stated that "the action of bichromate solutions in passivifying metals is not readily understood on electrochemical lines, since bichromate is a powerful depolarizer, and would be expected greatly to enhance any electrochemical action that took place in distilled water. Miss Souders[2] showed that copper, iron, and zinc become passive when made anodes in a dilute potassium bichromate solution with a low current density. She also showed qualitatively that hydrogen was given off at a platinum cathode in a dilute bichromate solution which means that the solution is not acting as an effective depolarizer. The present investigation was undertaken under the direction of Professor Bancroft to determine under what conditions and to what extent a potassium bichromate solution functions as a depolarizer to nascent hydrogen.

Two gas coulometers were set up in series, with molecular sulphuric acid in one and the potassium bichromate solution in the other; the reaction was followed gas analytically by comparing the relative amounts of hydrogen set free in the two coulometers. The electrodes were of platinum and the cathodes were so arranged that an inverted burette could be placed over each. It was expected that there would be little or no reduction in the dilute bichromate solutions and that the amount of reduction would increase with increasing concentration of the bichromate solution. This expectation was not fulfilled.

With M/40 potassium bichromate and an impressed voltage of 13.5 volts, 9.0 cc of hydrogen were obtained from the sulphuric acid coulometer and 9.1 cc from the bichromate coulometer, readings which are identical within the experimental error. There is therefore no depolarizing action at a platinum cathode under these conditions. The next runs were made with a saturated bichromate solution containing, approximately 135 grams potassium bichromate per liter at 25°. With an impressed voltage of 15 volts the hydrogen from the sulphuric acid was 37.8 cc and from the bichromate also 37.8 cc, showing that no depolarization occurred. When the voltage was dropped to 10.5 volts, the two values were 35.7 cc and 35.6 cc respectively. With an impressed voltage of 5 volts, gas was of course evolved very slowly; but the results were 5.1 cc and 5.1 cc. The bichromate solution was then heated to 63.5° and a run made at 10 volts; but 37 cc of gas were obtained from each coulometer. There is therefore no depolarization with a saturated solution of potassium bichromate using a platinum cathode and it seems desirable to abandon the myth that such a solution is a powerful oxidizing agent.

There was of course the possibility that the solution in contact with the electrode might be potassium chromate after the first few moments of electroly-

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[1] J. Inst. Metals, 28, 52, (1922).

[2] Bancroft: J. Phys. Chem. 28, 831 (1924).

sis, so a special coulometer was constructed with the anode and cathode in the same compartment and only two centimeters apart. The first run with saturated potassium bichromate and six volts gave 23.2 cc hydrogen from the sulphuric acid coulometer and 35.2 cc of oxyhydrogen gas or about 23.5 cc hydrogen from the bichromate coulometer. In another run the values were 24.1 and 36.3 cc. (+24.2 ccH_2) respectively, which indicated no depolarization. When the voltage was made so low that 3.8 cc hydrogen were obtained in the sulphuric acid coulometer in one and a half hours, the amount of oxyhydrogen gas was 4.0 cc, corresponding theoretically to 2.7 cc hydrogen. This would indicate some depolarization; but it is more probable that the calculated result is wrong owing to some oxygen having dissolved in the solution. Some may also have diffused to the cathode, which would cut down the yield irrespective of any depolarizing action of the bichromate.

Some experiments were next made with other cathodes to see whether a higher over-voltage would make a difference. With a lead cathode, not prepared in any special way, and six volts, 23.8 cc hydrogen were obtained in the coulometer in a three-hour run and 22.4 cc from the saturated bichromate solution. In a longer run the values were 54.1 cc and 51.0 cc respectively. If there is any depolarization, it does not exceed six percent which is not enough to be interesting.

Quite different results were obtained with a mercury cathode. With an impressed voltage of 9 volts, the hydrogen in the sulphuric acid coulometer was 12.9 cc and in the bichromate coulometer about 1.8 cc, indicating about 86% depolarization. It was noticed, however, that 100% oxidation of the hydrogen seemed to occur at the start, and that the efficiency decreased with the time. It seemed probable that this was due to the formation of a protecting film over the surface of the mercury, consisting of some chromium compound, presumably hydrous chromic oxide. When the mercury cathode was so arranged as to make it possible to expose a fresh surface of mercury to the solution, one hundred percent efficiency was obtained, 4.2 cc hydrogen being evolved in the acid coulometer and none at the mercury cathode. The reduction potential of a potassium bichromate solution is therefore at such a point that the depolarizing efficiency is zero at a smooth platinum cathode and one hundred percent at a clean mercury cathode. This is a very interesting demonstration of the effect of overvoltage. As was to be expected, there was no depolarization when an iron cathode was used.

When M/40 potassium permanganate was electrolyzed with platinum electrodes, 29.6 cc hydrogen was obtained in the acid coulometer and 18.3 cc hydrogen in the permanganate coulometer, indicating about 38% depolarization. A neutral permanganate solution is therefore a much stronger hydrogen depolarizer than the corresponding potassium bichromate solution.

Since it was not possible to construct a curve varying from zero to complete depolarization with platinum electrodes by varying the concentration of the potassium bichromate, it was decided to get a similar result by adding varying amounts of acid. The first run was made with 400 cc saturated potassium bichromate solution plus 20 cc concentrated sulphuric acid and an impressed voltage of 6 volts. In the sulphuric acid coulometer there were evolved 30.4 cc hydrogen and only 0.3 cc in the chromic acid coulometer. In other words addition of five percent by volume of concentrated sulphuric acid to a saturated potassium bichromate solution increased the depolarization at a platinum cathode from zero to practically one hundred percent. In the next set of runs the voltage was kept always at 9 volts and 250 cc saturated bichromate solution were taken in each case. The data are given in Table I, the column entitled acid showing the amount of sulphuric acid added, the next two columns showing the hydrogen evolved from the acidified bichromate and from the sulphuric acid coulometer respectively, while the fourth column shows the percentage oxidation of hydrogen.

Table I

250 cc saturated $K_2Cr_2O_7$+sulphuric acid
Platinum electrodes; 9 volts

Acid added	Bichromate	Coulometer	Oxidation	Acid added	Bichromate	Coulometer	Oxidation
cc	cc H_2	cc H_2	%	cc	cc H_2	cc H_2	%
0.1	21.1	20.6	0	2.5	10.4	29.5	64.5
0.3	18.9	18.3	0	3.0	2.8	16.5	83.0
0.5	18.3	18.3	0	4.0	3.9	33.0	88.0
1.0	21.3	26.8	20.5	5.0	2.0	42.7	95.5
1.5	8.3	23.9	65.0	6.0	0.4	27.6	98.5
2.0	8.5	28.2	69.8				

It will be noticed that there is no oxidation until 1.0 cc of sulphuric acid has been added. This means that under these conditions, depolarization does not begin until some amount between 0.5 and 1.0 cc sulphuric acid has been added to 250 cc saturated potassium bichromate solution. In order to determine more closely where this point occurred, another set of runs was made which differed from the preceding one only in the amounts of concentrated sulphuric acid added. The data are given in Table II.

Table II

250 cc saturated $K_2Cr_2O_7$+sulphuric acid
Platinum electrodes; 9 volts

Acid added	Bichromate	Coulometer	Oxidation	Acid added	Bichromate	Coulometer	Oxidation
cc	cc H_2	ccH_2	%	cc	ccH_2	cc H_2	%
0.1	21.7	21.7	0	0.6	22.9	23.1	0.9
0.3	22.0	21.7	0	0.7	30.9	36.1	14.4
0.5	28.1	28.2	0	1.0	34.5	42.2	18.2

While there is apparently some depolarization when 0.6 cc sulphuric acid is added, the value is within the experimental error, so that the first significant oxidation occurs on the addition of 0.7 cc concentrated sulphuric acid.

In Table III are given data obtained for a single sample of 250 cc saturated potassium bichromate solution to which varying amounts of sulphuric acid were added.

TABLE III

250 cc saturated $K_2Cr_2O_7$+sulphuric acid
Platinum electrodes; 9 volts.

Acid added	Bichromate	Coulometer	Oxidation	Acid added	Bichromate	Coulometer	Oxidation
cc	ccH_2	ccH_2	%	cc	cc H_2	cc H_2	%
0.7	16.4	20.1	18.4	3.0	4.7	20.7	77.3
1.0	13.8	20.8	33.6	4.0	1.6	20.2	92.0
1.5	8.9	30.0	70.3	5.0	1.7	23.9	92.9
2.0	8.5	20.1	57.7	6.0	1.1	20.2	94.5
3.5	3.9	20.2	80.6	7.0	0.4	23.5	98.2

These results are so wobbly that only a qualitative curve can be drawn from them. Since the presence of reduction products at the electrodes might affect the results, another set of data was obtained, using a fresh sample of saturated bichromate solution each time. In order to minimize the time necessary, the voltage was increased to 20 volts which meant a large increase in current density. The data are given in Table IV.

TABLE IV

250 cc saturated $K_2Cr_2O_7$+sulphuric acid
Fresh sample of bichromate each run.
Platinum electrodes; 20 volts

Acid added	Bichromate	Coulometer	Oxidation	Acid added	Bichromate	Coulometer	Oxidation
cc	ccH_2	ccH_2	%	cc	ccH_2	cc H_2	%
0.0	20.4	20.1	0	3.5	22.4	37.5	40.3
0.2	31.9	31.7	0	5.	5.6	23.1	75.7
0.4	26.6	26.4	0	6.	4.7	29.5	84.0
0.5	48.0	48.2	0	7.	3.8	31.2	87.8
0.7	28.8	29.4	2.0	10	2.5	28.2	91.1
0.8	25.9	27.4	5.5	15	3.9	43.0	90.9
1.0	17.0	18.7	9.2	20	3.6	33.0	89.0
1.5	14.9	17.3	13.9	25	7.3	44.5	83.6
2.5	14.8	20.7	28.5	40	8.8	46.1	90.1

These results give a fairly smooth curve and are plotted in Fig. 1, in which there is also given a smoothed curve for the data from Table III. We get much higher efficiencies with 10 volts than with 20 volts and the 20-volt curve passes through a maximum about 10 cc sulphuric acid. This is a question of current density. For a constant-voltage drop across the terminals of the two coulometers, the current increases with the amount of acid added. This may easily cause an apparent maximum in the curve. To show this another run was made with 10 cc sulphuric acid added and 20 volts. The hydrogen values were 2.1 cc and 20.2 cc, indicating 89.6% oxidation as against 91.1% in Table IV. The current was about 5.5 amperes. A run was made with 40 cc acid added and the voltage adjusted so that the current was 5.5 amperes. The hydrogen values were 2.1 cc and 20.6 cc, indicating 89.8% oxidation as against 80.1% in Table IV. In other words the current efficiency depends on the current density after a certain amount of sulphuric acid has been added and can undoubtedly be varied at least over the range 80-100% for the case of 40 cc concentrated sulphuric acid added to 250 cc saturated potassium bichromate solution. Since no immediate use could be made of the figures, it did not seem worth while to make a set of runs at a very low and constant current density.

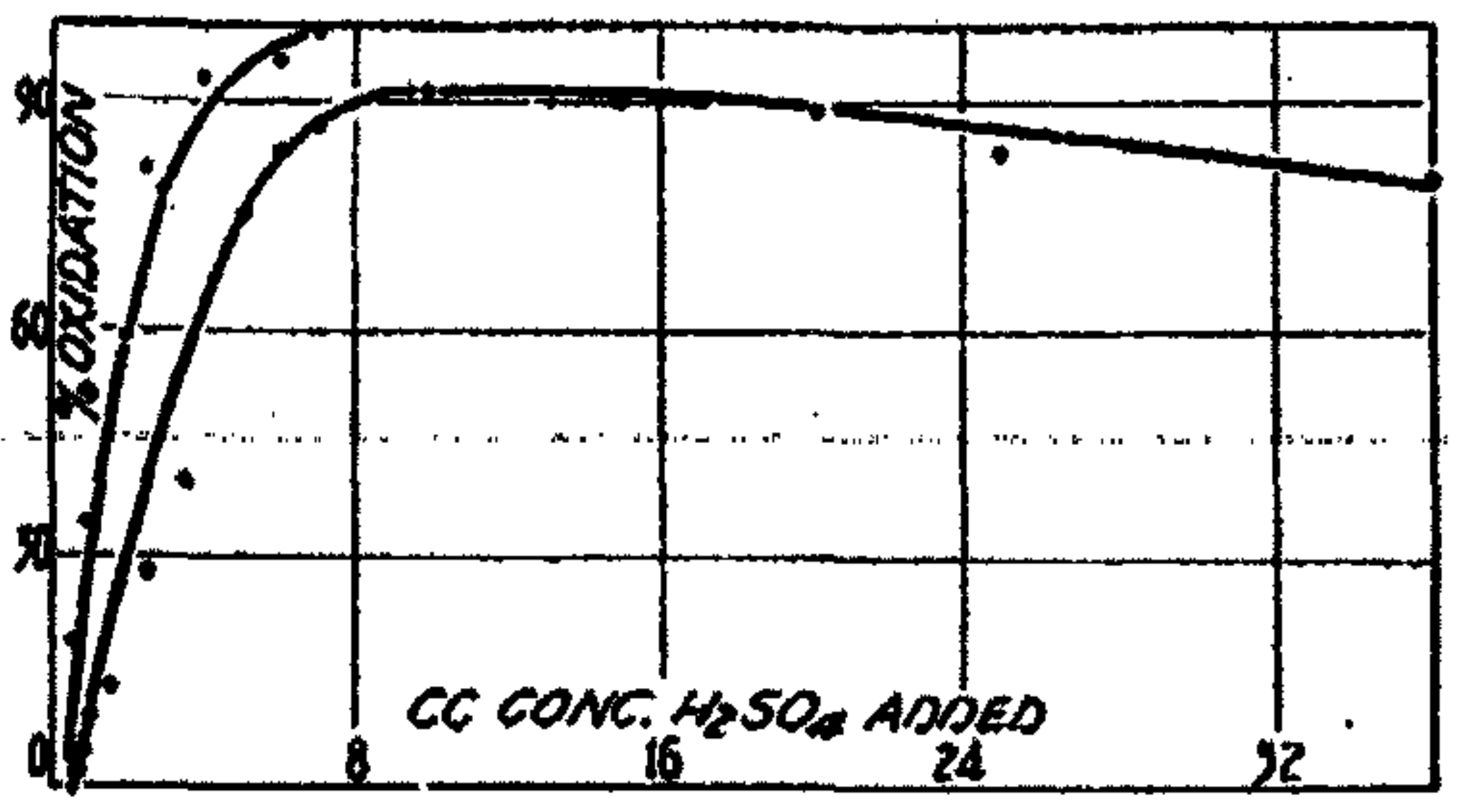

Fig. 1

250 c.c. saturated $K_2Cr_2O_7$ and sulphuric acid; platinum electrodes. Left curve 10 volts, right curve 20 volts.

A few experiments were now made on the actual corrosion of zinc, iron, and copper in saturated potassium bichromate solutions under various conditions at room temperature. A strip of zinc in a saturated bichromate solution showed no signs of corrosion in two months exposure. A strip of iron showed no corrosion in the solution; but there was corrosion in the portion exposed to the air. The strip of copper lost its original bright luster but did not waste away. This means that the protecting film is visible to the eye.

In order to show that heterogeneity is not necessarily sufficient to cause corrosion, a piece of platinum wire was wound tightly round a strip of copper and the whole immersed in a saturated bichromate solution. Although this is a short-circuited cell, there was no action on the copper beyond what was noted in the previous experiment with copper alone.

Zinc, iron, and copper strips were short-circuited with mercury cathodes in saturated bichromate solutions. With iron and copper the presence of the mercury cathode had no visible effect. With zinc there was a very slight corrosion, the surface ceasing to be highly lustrous and becoming slightly whitish. The change was so slight that it might easily have been overlooked by anybody making a hasty examination.

With zinc and iron strips in M/40 potassium permanganate solution there was distinct, though limited, corrosion, which is what one would expect because neutral permanganate is a better hydrogen depolarizer than potassium bichromate.

Some experiments were also made to determine the amounts of concentrated sulphuric acid that one must add to a saturated potassium bichromate solution in order to cause appreciable corrosion of zinc, and copper. In each case 100 cc of potassium bichromate solution were taken.

With zinc addition of 0.2 cc acid and exposure for 44 hours caused a slight brownish tinge on one face. There was no marked corrosion and the film may have been protecting the metal to some extent from further attack. Addition of 0.3 cc acid and exposure for 44 hours gave about the same results. With addition of 0.5 cc acid the effect was more marked and the exposure was therefore continued for six days. Corrosion was very apparent and the solution had turned dark brown. Addition of 0.5 cc acid is therefore sufficient to cause very appreciable corrosion of zinc.

With iron addition of 0.3 cc acid caused no visible corrosion in 44 hours and addition of 2.0 cc of 3.0 cc acid caused no appreciable corrosion in six days. With addition of 5.0 cc acid and exposure for six days, the iron was found to have corroded completely and the solution was black. It evidently takes a good deal more acid to cause the corrosion of iron than of zinc. These experiments do not show whether the difference is due primarily to the difference of chemical potentials or to the difference in the protecting films.

With copper there was perceptible corrosion on addition of 0.1 cc acid and the copper corroded completely on addition of 0.3 cc acid. This makes it probable that the important factor in these cases is the nature of the protecting film and not the electromotive force of the pure metal.

Bengough and Stuart[1] have called attention to the fact that dilute acetic acid corrodes zinc more rapidly than does dilute sulphuric acid. To test this, strips of zinc were immersed in solutions of 1:5000 acetic acid and 1:5000 sulphuric acid. The zinc in the acetic acid showed quite appreciable corrosion in two months, the corrosion products precipitating all over the surface of the zinc. In the sulphuric acid solution the zinc showed a slight amount of corrosion, the edges of the strip having turned black; but the amount of corroded metal was not at all equal to that in the acetic acid solution. It seemed possible that this was due to the fact that zinc acetate hydrolyzes much more completely than zinc sulphate and that the hydrogen ion concentration does not decrease as rapidly in the acetic solution as in the sulphuric acid solution. To test this hypothesis a weighed piece of extremely pure zinc was placed in a 1:5000 acetic acid solution. Another weighed piece of the same zinc was placed in a 1:10000 sulphuric acid because sulphuric acid is bivalent; but the sulphuric acid solution was renewed periodically. Under

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[1] J. Inst. Metals, 28, 89 (1922).

these conditions there was no appreciable difference in the action of the two acids and it seems justifiable to conclude that zinc corrodes as badly in extremely dilute sulphuric acid as in extremely dilute acetic acid if the corrosion products in the sulphate solution are removed.

The general conclusions of this paper are as follows:—

1. A saturated potassium bichromate solution has practically no depolarizing action on hydrogen set free at a smooth platinum cathode.

2. A saturated potassium bichromate solution shows 100 percent depolarization for hydrogen set free at a clean mercury cathode.

3. Addition of about 0.7 cc concentrated sulphuric acid to 250 cc saturated potassium bichromate solution is necessary before there is appreciable depolarization of hydrogen at a smooth platinum cathode.

4. Zinc, iron, and copper do not corrode appreciably in a saturated potassium bichromate solution.

5. Copper does not corrode appreciably when short-circuited with platinum in a saturated bichromate solution.

6. Iron and copper do not corrode appreciably when short-circuited with mercury in a saturated potassium bichromate solution; but zinc corrodes slightly.

7. Different amounts of concentrated sulphuric acid must be added to a saturated potassium bichromate solution in order to cause marked corrosion of zinc, iron, and copper. It seems probable that the important factor is the nature of the protecting film rather than the electromotive force of the pure metal.

8. Neutral M/40 potassium permanganate has a distinct depolarizing action on hydrogen at a platinum cathode and causes appreciable corrosion of zinc, iron, and copper.

9. Zinc corrodes more rapidly in an extremely dilute acetic acid solution than in an extremely dilute sulphuric acid solution; but this difference in rate disappears if the sulphate corrosion products are removed.

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SOLUBILITY RELATIONS OF ISOMERIC ORGANIC COMPOUNDS.
I. INTRODUCTION

BY JOHN JOHNSTON

The starting point of the investigations, begun about five years ago, to be described in a series of papers under the general title as above, was the belief that one of the outstanding problems of chemistry is the mechanism of organic reactions, and that any reliable observations which might aid in reconnoitering this field would be useful. In particular, we desired to learn more as to the factors which determine the position in the benzene ring of a second substituent group relative to that of the first substituent—the factors, namely, which favor the formation of the *ortho*, *meta* and *para* isomers; this case being chosen partly by reason of its large importance, partly because the substances are definite and easily available in a substantially pure state. Now if one will study the effect, say of temperature or concentration, upon the relative yield of the three isomers, one must have a means of determining how much of each is present in the reaction mixture; but the compounds, being isomeric, cannot usually be determined by a chemical method[1], and so recourse must be had to some other mode of analysis. Of these, the most promising appeared to be that based upon measurements of mutual solubility, that is upon the freezing or equilibrium diagram of the three isomeric substances. This method is, of course, not new, it has been used by Holleman and even as a control in the industry; but the published results on this type of system are in effect little more than random scratches upon the surface of the field.

Such determinations of mutual solubility have, of course, been made in large number, though not in any very systematic way[2]. For instance, they have been made at only one or two temperatures, instead of covering adequately the range of the solubility curve; or the substances used have been those readily available, the result being that the observations commonly do not extend to all three isomers. Moreover, many of the data are less reliable than one would wish to have them, because the experiments were clearly not carried out, or interpreted, with sufficient precision, or because insufficient attention was paid to the purity of the samples of material. Nevertheless the data available, though they are in these respects unsatisfactory and incomplete, indicate that more systematic work should yield useful generalizations with respect to the solubility, and related properties, of organic compounds.

We were therefore encouraged to hope that, apart from the initial object of securing a method of analyzing mixtures of certain isomers, we might un-

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[1] A recent example of the use of a chemical method, applicable to certain types of case, may be found in the paper of Francis and Hill: J. Am. Chem. Soc., 46, 2498 (1924).

[2] The long series of papers by Kremann and collaborators, in the Monatshefte during the last fifteen years, have been concerned more with systems (e. g. of phenols and amines) in which compounds appear. A similar remark applies to the papers of Kendall and his collaborators: J. Am. Chem. Soc., 43, 691 (1921) et seq.

cover some regularities of behavior which could be correlated with the chemical constitution of the substances. Indeed, organic systems offer a very promising field—as compared with inorganic systems—for learning something of the factors which determine solubility; for in them one can readily secure an almost continuous gradation of both solute and solvent by successive substitution of similar groups, a fine gradation of constitution and structure which is not possible in the characteristic inorganic systems. This remark applies to many properties other than solubility, heat of fusion or specific heat; and there is a wide field, the systematic cultivation of which—though, at the moment, somewhat laborious—is certain to yield information which will advance the whole science of chemistry.

Some slight progress in this direction is being made. For instance in many systems of the *ortho*, *meta* and *para* isomers of a given composition, the solubility of any one component in mixture with either of the others, or with both, is in accordance with the law of the ideal solution, and is therefore at any point readily calculable from a small number of constants pertaining to the pure components. Indeed Narbutt[1] showed that the mutual solutions of *ortho*, *meta*, *para* nitrobromobenzene are nearly ideal; and Holleman, Hartogs and van der Linden[2] observed the coincidence of melting curves of binary systems of the three nitroanilines and state that these are therefore "so-called ideal" melting curves. In order to learn in how far this is true for other similar systems, the available data were plotted, with the result that in most cases the solutions seemed to be substantially ideal. As to the proportion of this type of system to which this conclusion is applicable, we must be uncertain until the work has been extended to a far larger number of substances, and in particular to those which may be regarded as extreme examples; but the present evidence indicates that the assumption of ideal solubility would in any case of this kind be a safe first approximation.

Another provisional conclusion is that pairs of *ortho* compounds (or of *meta*, or *para*) form solid solutions; whereas, as we have just seen, an *ortho* compound separates in the pure state, and forms no solid solution with the corresponding (i. e. containing the same two substituent groups) *meta* or *para* isomers. This is of practical importance in connection with the purification[3] of such substances; and it indicates that the influence of the *relative position* of two substituents upon the crystal structure of the compound outweighs that of the chemical nature of the two. Nevertheless it is to be expected that if the two substituent groups are in one compound very different (e. g. much larger) from those in the other, incomplete solution would be the result; and it will be interesting to learn just how different the pairs of groups would have to be in order to cause the two crystalline compounds to be incompatible.

The measurement of a solubility is in essence the determination of the concentration of the solution in equilibrium with the crystals of the substance

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[1] Narbutt: Z. physik. Chem., 53, 697 (1905).

[2] Hollemann, Hartogs and von der Linden: Ber. 44, 704 (1911).

[3] In some cases we have found that a long series of fractional crystallizations was necessary to ensure adequate purity of the material.

at a definite temperature. This is done in two main ways. The more usual way is to leave the excess of the crystals in contact with solvent (strictly speaking, with solution) at a definite temperature until saturation has been attained; and then to determine by some appropriate method, the proportion of solute to solvent in the solution. This method is used in ascertaining the solubility curve of a salt or the freezing temperature of an aqueous solution, the latter being a point on the solubility curve of ice in the solution. In cases where the method of analysis is cumbrous or inexact (as it is in many organic systems) the other way is followed; one ascertains the temperature at which the first crystal of the solid separates from a slowly cooled solution of known composition, or sometimes, that at which the last crystal disappears when the system is heated slowly. This may be done by direct visual observation; more commonly, however, it is deduced from the appearance of a break on the cooling (or heating) curve which brings out the mode of temperature change of the system under definite conditions of environment. The uncertainty of the method is not in the temperature measurement itself, but in the difficulty of ensuring that this temperature really corresponds to equilibrium in the solution of the gross composition taken; for if some of the solid has already crystallized at the temperature noted, the concentration of the solution will be correspondingly different. By the use of proper methods of experimentation and interpretation, these difficulties can however be surmounted, and results of adequate accuracy secured.

In the course of the earlier determinations of solubility in the binary systems of the nitroanilines and nitrochlorobenzenes, it was observed that the results were more closely in accordance with the law of the ideal solution, the more carefully the experiment had been interpreted. This led us, on the one hand, to consider anew the theoretical form of the cooling curve, on the basis of Newton's law of cooling; on the other hand, to undertake the direct measurement of those properties of a substance (namely, its heat of melting, and secondarily, its specific heat as solid and as liquid) which determine the course of its solubility curve when the solution is ideal. For it was found that the heat of melting, as derived from the slope of the solubility curve, in some cases agreed well with the calorimetric value recorded in the literature, whereas in other cases it did not; these discrepancies disappear when these heats were redetermined and therefore are due to inaccuracies in the published calorimetric data. The results of the two distinct lines of experiment are now in very satisfactory agreement; for instance, the heat of fusion (which is of the order of 3700-6600 calories per mol) as derived from the initial slope of the solubility curve, differs from that directly determined in this laboratory, by only about 80 calories, which is about the error involved in reading this slope from a graph on a fairly large scale. This concordance may be stated in another way, namely, that the divergence between the solubility curve as calculated from the calorimetric data and that observed, amounts only to a few tenths of a degree. It may be mentioned that the heat of fusion of many of these substances, as given in the literature, may be too small by as much as 1000 calories; this error is probably due to lack of purity of the material[1], and to neglect of the fact that the heat diffusivity is low and hence, unless small amounts only are used, all of the heat in the sample will not flow into the calorimeter in the ordinary period of such experiment.

In the ideal solution there is no change in heat content or in volume when the components mix to form a solution; in other words, the components do not affect one another appreciably and the properties of the solution are linear functions of its composition. For instance, the partial vapor pressure, or the activity, of each component is, in accordance with Raoult's law, proportional to its mol fraction; if this relation is combined with what is often referred to as the van't Hoff reaction isochore, we get the equation

$$\frac{d \ln N_A}{d T} = \frac{\Delta H_A}{RT^2} \qquad (I)$$

where $\ln N_A$ is the natural logarithm of N_A, the mol fraction in the solution of A the substance crystallizing, ΔH_A is its molal heat of melting (hence, in the ideal case, its heat of solution also) and R is the constant of the ideal gas law. If we integrate this equation between T and T_A, the melting temperature (on the absolute scale) of pure A, on the basis that the change of ΔH_A with T is inappreciable, we get

$$\ln N_A = -\frac{\Delta H_A}{RT} + \frac{\Delta H_A}{RT_A} \qquad (II)$$

since N_A is unity (and hence $\ln N_A$ is zero) at the melting temperature T_A. When ΔH is expressed in calories, R = 1.9885; so we may write, converting to ordinary logarithms,

$$\log N_A = -\frac{\Delta H_A}{4.579}\frac{1}{T} + \frac{\Delta H_A}{4.579\,T_A} \qquad (IIIa)$$

This is of the form $\log N = a/T + b$, or $y = ax + b$, and therefore, under the conditions specified, the graph of log N against 1/T is a straight line[2], the slope of which is proportional to the heat of melting of the crystals in equilibrium with the solution. A special case of equation IIIa, applicable however only to dilute solution, is the familiar formula used in calculating molecular weight in solution from measurements of the change in freezing or boiling temperature of the solvent.

Before proceeding, I wish to emphasize the advantage of expressing concentration of a solution in appropriate units—in terms of chemical units instead of arbitrary units such as grams or liters. The most convenient chemical unit of quantity of substance is the mol, defined most simply as the number of grams in the simplest molecular weight of the substance. For the present purpose the best mode of expressing concentration is by means of the

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[1] The form of the heat-content curve of a solid at temperatures near its melting-point is a criterion of the purity of the sample in some cases, e.g. when by reason of the admixture a partial melting sets in.

[2] Obviously the graph of T log N against T is also linear; the slope of this line is proportional to the entropy increase accompanying melting of the solute. This form is for certain purposes more convenient.

mol fraction N (or the molar percentage C = 100N); thus if we have n_A mols of substance A and n_B of substance B, the respective mol fractions are

$$N_A = \frac{n_A}{n_A + n_B},\ N_B = \frac{n_B}{n_A + n_B}$$

The advantage of using this unit of concentration is especially marked in the case of organic substances. For example, the curves representing in these terms the solubility at various temperatures of a single solute in a series of solvents, form a sheaf converging to the melting temperature of the solute; whereas in terms of the usual arbitrary units, they may be scattered irregularly over the diagram. This regularity has the practical advantage that one can deduce the solubility, with sufficient accuracy for most practical purposes, at any temperature if it has been measured at a single temperature; and moreover, if the curves for a series of representative solvents are known, one can get a good approximation to the solubility in another solvent without having to make any new measurements.

In deriving equation IIIa we assumed that the heat of fusion of A does not vary with temperature, which is equivalent to the assumption that the specific heat of liquid and solid A (C_l and C_s respectively) are identical. Taking this difference into account, we write

$$\Delta H_A = \Delta H'_A + \alpha T + \beta T^2$$

(where α and β are empirical constants derived from the calorimetric data), and obtain, in place of equation IIIa,

$$\log N_A = -\frac{\Delta H'_A}{4.579}\left(\frac{1}{T} - \frac{1}{T_A}\right) + \frac{\alpha}{1.988}\log\frac{T}{T_A} + \frac{\beta}{4.579}(T - T_A) \quad \text{(III)}$$

The second and third terms introduce corrections which are comparatively small and in many instances negligible; correspondingly the graph of log N against 1/T is a slightly curved line instead of being rectilinear, as it would be if equation IIIa were strictly valid[1].

It has in fact been found that, in the specific type of system under discussion, the actual solubility curve follows equation III more closely, the more accurately the measurements have been made. Now the quantities which enter into this equation, for the solubility of A, refer only to the solute A and not at all to the solvent; consequently the solubility curve of A is *identical*, in so far as it extends, for all cases in which the other component or components form an ideal solution with liquid A. For component B there is a precisely similar equation and line, which starts from its melting temperature T_B at a slope which depends upon its characteristic heat of melting ΔH_B; and this

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[1] Equation III or IIIa was, apparently, first given by LeChatelier (Compt. rend., **100**, 50 (1885); it was discussed by Roozeboom ("Die Heterogenen Gleichgewichte" II - 1, pp. 270-283 (1904)) who also gives prior literature references. It was used by Schröder (Z. physik. Chem. **11**, 449 (1893)) and by Narbutt (Ibid, **53**, 697 (1905)) on organic systems; by Mazzotto (Nuovo Cimento, **13**, 80 (1907); **15**, 401, (1908)) on metal systems. It has been discussed by van Laar in 1903 in a series of papers in Verslag Akad. Amsterdam, summarized and extended in Z. physik. Chem., **63**, 216 (1908); **64**, 257 (1908). Its usefulness has recently been emphasized by the work of Washburn and Read (Proc. Nat. Acad. **1**, 191 (1915), Hildebrand et al. (in a series of papers in J. Am. Chem. Soc., from 1916 on, and in his recent monograph on Solubility), Kendall (J. Am. Chem. Soc. **43**, 691 (1921) et seq.,) and others.

line, likewise, is, under the specified conditions, independent of what A may be. With different pairs, the pairs of curves end at different temperatures, this end-point being the characteristic eutectic temperature below which the liquid phase is unstable. For a binary system this end-point is clearly at that value of T at which $N_A + N_B = 1$, or, on the plot of equation III, that at which the sum of the antilogarithms of log N_A and log N_B is unity; and this value of T is readily found by trial. Consequently one can calculate both eutectic composition and temperature from the solubility curves of A and B; or, conversely, use the observed eutectic temperature—which is readily measured with accuracy—as a check upon the course of the two solubility curves and the assumption of ideality.

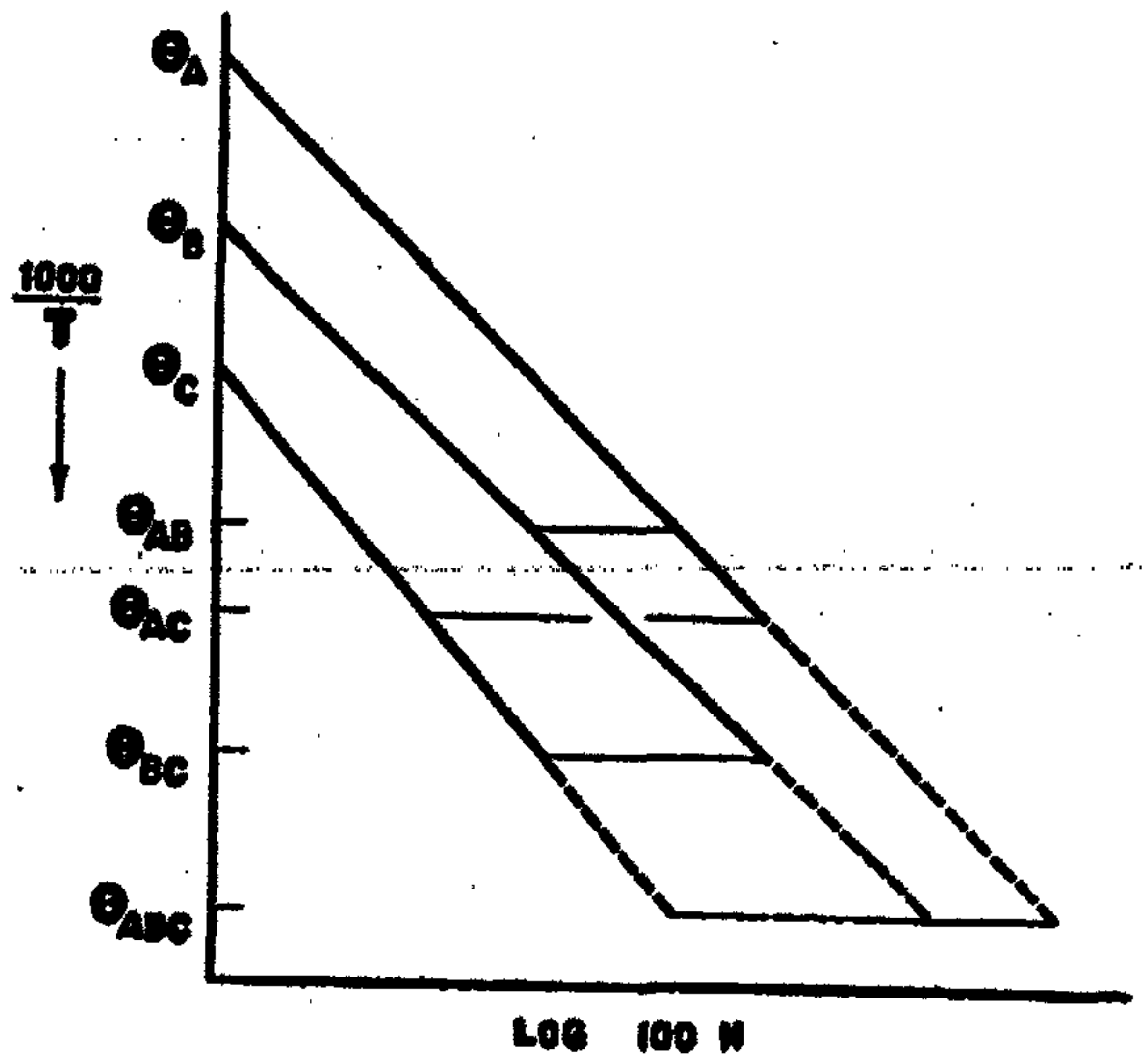

Fig. 1.

Plot of log 100N against 1000/T for an ideal ternary system, showing the three binary, and the ternary, eutectic temperatures.

If the *ortho*-compound (say) forms ideal solutions with both the *meta* and *para* separately, and the binary solutions of *meta* and *para* are likewise ideal, the behavior of the ternary solutions must also be ideal. In other words, the solubility curve of *ortho* in mixtures of *para* and *meta* together is the same as in either separately, and is therefore calculable as before. In the ternary system the eutectic corresponds to the condition $N_A + N_B + N_C = 1$, and is therefore readily derived from the three solubility curves. This is illustrated by Fig. 1 which represents a plot of log C (C = 100N) against 1000/T for an ideal ternary system; each of the three lines is the solubility curve of one component, starting at its melting temperature and ending at the ternary eutectic temperature, the several eutectic temperatures being derived as outlined above.

In this ideal type of case, therefore, the complete ternary solubility diagram—as required for analysis of unknown mixtures of the three components—may be constructed from a small number of observations. Indeed in principle one needs but six observations, three of which are the melting temperatures of the pure components; the other three are the heats of melting, or appropriate solubility measurements which in general are simpler to carry out. In practice one would usually determine the solubility of each component at more than one point, in part for the sake of accuracy, in part because one would wish to be assured that the system does in fact yield ideal solutions.

With the aid of the completed equilibrium diagram, one can readily analyze any mixture of the three pure *o*, *m*, *p* components. One observes the temperature of the cooling mixture at which the first crystals separate, and then that at which the second component begins to appear; if this is doubtful or impracticable, one adds a known proportion of one component and observes anew the temperature at which the first crystals separate. By proceeding in this way, one can determine the composition of such mixtures with an accuracy of 1 or 2%. If the material is always contaminated with a small proportion of water or a solvent (as it may well be if derived directly from a manufacturing operation), it suffices to make the original observations on material similarly contaminated, and to construct a modified diagram which can then be used directly, as outlined above.

In view of the result that the corresponding *ortho*, *meta* and *para* isomers form ideal solutions with one another, it was of interest to determine the solubility curve of each in a series of typical solvents, in order to ascertain if there are any substantial differences, as between the three isomers, in the form of solubility curve in a given solvent. Such determinations, which appear not to have been made in any systematic way hitherto[1], enable one to judge as to the advantage of a given solvent for the purification by recrystallization of one isomer initially contaminated with one, or both, of the others. Moreover, one might hope, in view of the regularities previously adverted to, that the behavior of one system could, within limits, be applied,—transferred so as to speak,—to a number of the related systems, at least to the extent of acquainting one with the general course of the solubility curve, and in this way saving work.

Starting from the point that we wished to be able to analyze certain mixtures of isomers, and proposing to use for this purpose the mutual solubility, we have been led to investigate a number of things which at first sight have little bearing upon the original question; and these, in turn, have led to others not initially contemplated. For this reason largely, the evidence in support of the general statements made above will be presented in a series of separate papers, under one general title, dealing with the several lines of investigation.

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[1] Except for the work of Sedgwick and his collaborators who have measured the solubility, through a range of temperatures, of several sets of *o*, *m*, *p* isomers in water and benzene, and in some cases in *n*-heptane, ethyl and butyl alcohol. (J. Chem. Soc. **119**, 979, 1001, 1013 (1921); **121**, 1844, 1853, 2256, 2263, 2586 (1922); **123**, 2813, 2819 (1923), **125**, 522 (1924).

NEW BOOKS

X-Rays and Crystal Structure. *By Sir W. H. Bragg and W. L. Bragg. Fourth edition, revised and enlarged. 22×14 cm, pp. xi+322. New York: Harcourt Brace and Co., 1924. Price: $7.00.* The chapters are entitled: introductory; diffraction of waves; the X-ray spectrometer; the production of X-rays; the absorption of X-rays; X-ray spectra; crystal structure; the analysis of crystal structure; analysis by the method of the powdered crystal; crystal analysis and crystal symmetry; crystal analysis and the atomic forces; the intensity of X-ray reflexion; organic crystals; the analysis of the Laue photographs; supplementary.

When the ionisation spectrometer is used, the angular setting of the crystal table is of secondary importance: it is the angular setting of the ionisation chamber which is recorded. "The method, in common with other 'powder' methods, measures glancing angles only: it gives no information as to the angles between reflecting planes. This is a somewhat serious *defect unless the crystal has the simplest of forms, because two planes are indistinguishable* if they have the same spacing though they may belong to entirely different zones," p. 26.

"A beam of X-rays loses energy as it traverses matter. Part of the loss is due to the *scattering* action of the electrons and other charged particles over which the radiation passes. This effect can be explained by the classical electromagnetic theory; and, in particular, the facts that the scattered radiation has the same wave length as the original and that it is partially polarised. Another fraction of the energy is transformed into energy of X-rays of different wave length, and of electrons in motion. The frequency of the new X-rays is always less than that of the original; and the energy of any one electron is always less than the quantum energy of the same radiation. These effects are to be classed with the parallel effects which occur in the case of light, and are grouped under the title of fluorescence and photoelectricity. It appears that classical electromagnetic theory cannot explain the phenomena attending these interchanges of energy," p. 40.

"Debye and Scherrer have examined also various samples of amorphous carbon, and have obtained the very interesting result that however the carbon is prepared it shows diffraction maxima, and that these occur at the same angles of reflection as for graphite. The bands are, however, far broader and more diffuse. The explanation which Debye and Scherrer give of this is very ingenious. It is ascribed to the fact that the homogeneous fragments of crystal in the 'amorphous carbon' are very minute. The number of regularly spaced planes in each crystal which reflect the X-rays is small, and in consequence the diffraction maxima lack sharpness. The effect may be compared to the diffraction of light by a grating with only a few lines," p. 132.

Powdered gold crystals and colloidal gold both give photographs showing marked interference maxima or haloes, occurring in exactly the same positions, though the haloes for the colloidal gold are far broader and more diffuse owing to the smallness of the individual gold crystals. "The fact that the haloes occur in exactly the same positions in these two photographs is very remarkable. Moreover, the dimensions of the crystal structure deduced from the positions of the haloes agree exactly with those deduced by Vegard in his determination of the structure of the reflection from large gold crystals. It would appear that the atoms take up exactly the same relative positions in these minute crystals as they do in large crystals. The forces which govern their positions of equilibrium must be extremely local since, in the case of the minute crystals of colloidal gold, we get no distortion of the structure in spite of the fact that no atom in the crystal has more than two or three other atoms between it and the exterior surface," p. 134.

"The general limitation to the properties of substances in the gaseous or liquid state is really severe. We remove it when by the aid of X-ray analysis we examine the structure of the crystal unit, because it displays all the properties of the solid. A crystal has elasticities, thermal expansions, thermal and electric conductivities, dielectric capacities, optical activities; and all these not only as scalars but as vectors also. Quartz, to take a simple example, has many properties as a crystal, some of them most remarkable, which are possessed to the full by the crystal unit of quartz. We now know that the unit consists of three molecules of SiO_2: and are well advanced towards a knowledge of the relative positions of the nine atoms in the unit. The power of rotating the plane of polarisation of light, to take one physical property as an example, is a property of the single unit, just as much as of the whole crystal, and is derived from the arrangement of the atoms within the unit. It is not a property of the molecule, still less of the separate atoms. We are in a position to consider this and all the physical properties of the crystal as dependent on the structure of the unit, and, ultimately, on the forces exerted by each atom; in other words, on the structure of the atom. The crystal unit ranks in its uses and very possibly in importance with the atom and the molecule," p. 150.

"The views of the nature of atomic structure which have been set out above may now be compared with the results of X-ray analysis. It appears at once that their probability is greatly strengthened by the new knowledge of the structure of polar compounds such, for example, as potassium chloride. In the structure each potassium atom is surrounded by six chlorine atoms situated symmetrically with regard to it, and each chlorine atom by six potassium atoms similarly arranged. The potassium atom is not bound to one chlorine atom so as to form a molecule, but exerts its attraction on several neighbours. This becomes comprehensible if the crystal be regarded as a pattern of potassium and chlorine ions, of opposite sign, held together by electrostatic forces, for these forces correspond to a valency bond which can be subdivided to any extent. The equality of the numbers of atoms of either kind, in solid potassium chloride, is not a result of the pairing of the atoms into potassium chloride molecules, but of the necessity of there being an equal number of oppositely charged ions so that the resulting structure should be electrically neutral. The same holds in the case of a more complex structure, such as that of calcite. The ions in this case consist of calcium with a double positive charge, and the group CO_3 with a double negative charge, these ions being again arranged so that they alternate in a structure very similar to that of potassium chloride," p. 155.

"The diamond is an instance in which the binding forces throughout the whole crystal structure are of a non-polar type. Every carbon atom in the structure is surrounded by four other atoms. There is here again no assemblage of molecules, but, whereas in the polar compounds there is complete association into charged ions, here there are no ions and the whole crystal must be regarded as a single molceule. The diamond structure is the best example of a structure in which all the bonds are of the kind we have agreed to call 'electron sharing', and its properties are characteristic of structures in which such bonds exist," p. 157.

"The temperatures of melting are no doubt connected with the nature of the bonds and probably for the same underlying reasons. The very high melting point of carbon, in all forms, may be ascribed to the strength of the electron-sharing bond that is to be found both in diamond and graphite, while the very low melting points of the organic substances are, no doubt, due to the weakness of the forces that bind molecule to molecule. Very little is known of these things as yet: the melting point of silicon, which resembles diamond in the nature of its bonds, is high, 1200 approximately; but no explanation can yet be given, in terms of the nature of the bonds, for the fact that this melting point is less than, for example, the melting points of tungsten or rhodium. It is probably safe to say, however, that sulphur has a low melting point because its atoms are bound into molecules, which, as in organic substances, are joined together by a weak form of bond," p. 191.

"There is a crystal unit which itself possesses all the properties of the crystal. It contains the substance of a small number of molecules. The chemical molecule may not be found in it: though the unit is divisible into similar atom groups, and a group, as in organic crystals, may be very close indeed to the chemical molecule. It must be the object of research to discover the relation between the structure of the unit and its properties. The researches described in this chapter may be considered as examples of the first experiments in this direction; necessarily fragmentary, and no more, surely, than a preliminary excursion into a very wide field of enquiry," p. 195.

"The structure of organic crystals offers a very inviting field of research by the methods of X-ray analysis. To the organic chemist the relative positions of the atoms in the molecule, as also of the molecules in the crystal, are of fundamental importance; and it is with these relations that the X-rays deal in a manner which is new and unique. The complexity of the molecule would seem at first sight to throw great difficulties in the way of arriving at any solution. There seems to be good reason, however, for supposing that the benzene ring or naphthalene double ring of carbon atoms has definite form and size preserved with little or perhaps no alteration from crystal to crystal. If this principle is accepted the problem, as regards the aromatic compounds, is simplified at once. For example, naphthalene is then to be regarded as a structure in which there is but one element, the naphthalene double ring, and no longer as an aggregate of ten carbon atoms and eight hydrogen atoms of unknown mutual arrangement. A more complex molecule such as either of the naphthols is not to be regarded as an addition of one oxygen atom to these eighteen, an idea on which nothing can be built, but as a naphthalene double ring of the same size and form as before, except that one particular hydrogen has been replaced by a hydroxyl group. It is then possible to think what changes in the disposition of the molecule might be caused by such a substitution, and to compare conceivable solutions with observations on the dimensions of the new crystal. Such a method of procedure is obviously in good agreement with the ideas of organic chemistry," p. 229.

"Owen and Preston have shown that the powder method can be successfully applied to the study of the crystallisation of metals and alloys using a plane surface, first made true and afterwards etched to remove irregularly placed surface crystals. They have employed the ionisation method of measuring results. Their observations were made with the object of finding the relative positions of the metals in alloys such as copper-aluminium, copper-silver and so on. They obtain the very interesting result that the atom of one metal can replace the atom of the other metal in the lattice. The substitution is easy in the case of copper and silver because the sizes of the atoms are approximately the same: but difficult otherwise as in the copper-aluminium alloy. To these facts can be ascribed both the restrictions on the possible proportions of the latter alloy, and the increase in hardness where the slip planes are, as it were, roughened by the insertion of atoms of larger size," p. 295.

Wilder D. Bancroft

Callinicus. *By J. B. S. Haldane. 16×11 cm; pp. 84. New York: E. P. Dutton and Company, 1925. Price: $1.00.* Callinicus was the Syrian who invented Greek fire and thereby saved Constantinople for over seven hundred years from the Turks. Chemical warfare is considered by Haldane as also an entirely new and effective method of warfare. "The most interesting thing about mustard gas is that though it caused 150,000 casualties in the British Army alone, less than 4,000 of these (or 1 in 40) died, while only about 700 (or 1 in every 200) became permanently unfit. Yet the Washington Conference has solemnly agreed that the signatory powers are not to use this substance against one another, though, of course, they will use such humane weapons as bayonets, shells, and incendiary bombs.

"It is worth while attempting to analyse the reasons for this rather curious decision. First, perhaps, we must put the complete and shameful ignorance of most of the politicians and many of the soldiers who took part in the Conference. Their ideas of gas warfare were apparently drawn from the descriptions of the great German cloud-gas attacks of 1915, which killed at least 1 in 4 of their casualties, and were written up on a large scale for recruiting and political purposes. But it is the business of politicians and soldiers, conceivably even of journalists, to know the truth about such matters before coming to decisions, or even impelling others to come to decisions about them.

"To this ignorance, however, there was joined one of the most hideous forms of sentimentalism which has ever supported evil upon earth—the attachment of the professional soldier to cruel and obsolete killing machines. I would remind you of the conduct of the Chevalier Bayard, whom his contemporary soldiers described as *sans peur et sans reproche.* To captured knights, and even bowmen, he was the soul of courtesy, but musketeers or other users of gunpowder who fell into his hands were invariably put to death. It is worth remembering that, until the invention of gunpowder, fighting had for many centuries been remarkably safe for everyone who could afford a good suit of armour, while the abominable arquebus and its descendants have saved the remnants of Christendom from the Turks, Mongols, and other paynims who had by Bayard's time successfully overwhelmed one half of its original extent.

"I remember an excellent example of Bayardism in the war. A Turkish airman had developed considerable flair for shooting down our observation balloons. A British officer sent up one of these latter with a large cargo of gun-cotton, and blew up the Turk in question. For this deed he was severely reprimanded by the local officer commanding R. A. F. for unsportsmanlike conduct. This gentleman, doubtless, felt little objection to bombing, for example, Turkish transport columns, consisting mainly of non-combatants and animals, incapable of retaliating. (One may remark that between wounds and thirst perhaps 30,000 Turkish transport animals perished during our final victory in Palestine.) But he objected to airmen being killed except by other airmen. I, fighting in the mud beneath them, and exposed to the bombs of both sides (I was severely wounded by one of our own), felt differently. An attempt by the professional soldiers to stereotype the art of war into the channels which correspond to the ideas of 1914 might lead to a future rather different from that which I shall venture to predict, a future in which the military organizations of the world were overthrown by the exponents of some other mode of thinking, employing all the resources of science, and fighting "dirty." The opponents of the present world-order may, therefore, welcome Bayardism in their governments," p. 26.

"I claim, then, that the use of mustard gas in war on the largest possible scale would render it less expensive of life and property, shorter, and more dependent on brains rather than numbers," p. 52.

"The reasons why explosives are more likely to be effective than posion on a town are as follows. Houses are far more vulnerable to explosives than earthworks, and do far more damage to their occupants in collapsing, besides being inflammable. And, on the other hand, they contain far more refuges which are nearly gas-proof. A shut room on a first or second floor would be nearly proof against gas released in the neighbourhood if it had not got a lighted fire to drag contaminated air from outside into it. Moreover, civilians could, and would, rapidly evacuate an area which has been heavily soaked with mustard gas, whereas soldiers have to stay on at the risk of their lives," p. 58.

"The objection to scientific weapons such as the gases of the late war, and such new devices as may be employed in the next, is essentially an objection to the unknown. Fighting with lances or guns, one can calculate, or thinks one can calculate, one's chances. But with gas or rays or microbes one has an altogether different state of affairs. Poisonous gas had a great moral effect, just because it was new, and incomprehensible. As long as we permit ourselves to be afraid of the novel and unknown, there will be a very great temptation to use novel and unknown weapons against us. Now, terror of the unknown is thoroughly right and rational so long as we believe that the prince of this world is a malignant being. But it is not justifiable if we believe that the world is the expression of a power friendly to our aspirations, or if we are atheists and hold that it is neutral and indifferent to human ideals," p. 81.

Wilder D. Bancroft

Bituminous Substances. *By P. E. Spielmann. 22×15 cm; pp. xvi+206. New York: D. Van Nostrand Company, 1925. Price: $4.50.* "Of all the various products derived from crude petroleum, asphalt or bitumen is that which was earliest known and utilised by man. Not only are records of its use found in the works of the earliest historians, but actual examples of its use are to be found in our museums. Its uses are today much more varied, and its importance to the life of the community much greater, and its applications and value are ever increasing......Asphalt or bitumen has proved itself an invaluable material for the construction of roads which will stand up to the heaviest traffic they are likely to have," p. vii.

The chapters are entitled: historical introduction; composition and origin; properties; effect of heat, ageing, and solvents; physical and chemical tests; concluding remarks.

"The human history of bitumen begins about 12,000 years ago, with the late Stone Age man who lived in the area of what is now the Mediterranean. By the time that he had become indigenous to that locality, he had developed from his most primitive beginnings to the point of becoming a semi-permanent resident in whatever land he found himself. He still had not yet learned the use of any metals, but employed implements of flint (in the making of which he had acquired considerable skill) and of bone. He made rough pottery, he sowed grain and raised cattle and pigs, and he had already acquired the companionship of the dog; his reaping hook was of flint when he could get it, otherwise it consisted of an earthenware scythe," p. 1.

"In the days even before Sargon and onwards, bitumen appears to have been in regular use in architecture and civil engineering. It must be realised that in certain directions the arts and sciences were continuously and highly developed. A fine stone bridge crossed the Euphrates; processional ways and boulevards were laid out. It became a common thing in Nineveh, Nimroud and Babylon for city and palace walls and private houses to be built of stones and bricks set in bitumen; and in Nineveh has been discovered a regular damp-course underneath a stone floor. A water conduit and a drain were found to have been constructed with the aid of bitumen. Several inscriptions have been discovered relating to the use of bitumen in connection with buildings in Babylon by Nebuchadnezzar, but the most remarkable of all, as an anticipation, was the use of this construction for roadway purposes—for a processional street leading from the King's palace in honour of Marduk, the most powerful local god of Babylon, and of Nabû, who was second only to Marduk and not always that," p. 5.

The Sargon of the preceding paragraph was found in a cradle water-proofed with bitumen among the bulrushes over a thousand years before Moses, p. 3, and the stones (or bricks) of the Tower of Babel were cemented together with bitumen instead of mortar, p. 9.

The author believes that petroleum was first converted into bitumen and this latter into asphaltites, p. 20. When discussing Trinidad asphalt which contains twenty-nine percent water and gas, the author says, p. 44:—"The water is in a most peculiar condition, in that there is no immediate indication of its presence. This is an example of the property of finely divided material to take up a liquid and yet appear to be dry, a surface action which, in such a case of water and clay, may be associated in part with incipient hydrolysis of the silicate. It is tempting to suggest that it is this mixture of two liquids and a fine solid that makes for the mechanical stability of the whole material, but in the light of what comes just below this is scarcely tenable. But it is the fact that a mixture of bitumen and dry clay is not so firm in consistency as a mixture of the bitumen and the clay in form of a slurry.

"If Trinidad asphalt, or even an artificial mixture of clay and water with bitumen, be dissolved out in carbon disulphide, no water separates. On the other hand, such a separation can be caused by alcohol. Notwithstanding these observations, there is undoubtedly some equilibrium between clay-and-water, which will mix with bitumen, rather than clay-and-bitumen, which will not mix with water, an observation throwing much confirmatory light on the theory for the formation of the Trinidad asphalt lake. And further, it has been observed that such an artificial mixture rapidly loses water till this has fallen to 29.5 per cent, the quantity (together with gas) that is present in the lake product itself.

"The above statement about the clay-water bitumen equilibrium must be modified in one particular—that emulsification, with water as the "external" phase, is made possible by the addition of a hydrocarbon flux."

One does not see at all why bitumen will adhere to sand and not to flint, p. 48, and it is interesting to note, p. 103, that while a correlation between the various properties of bitument is occasionally obvious, this is usually not the case. Of ten properties considered there was obvious correlation in forty-two percent of the cases and no correlation in fifty-one percent. This high percentage of independence is remarkable, particularly as it includes such expected relationships as penetration and loss in heating. Except in one case flash-point and fire-point do not show regularity with any other property, not even with one another." *Wilder D. Bancroft*

Synthèses et Catalyses industrielles. *By Paul Pascal. 25.5×16.5 cm; pp. vii+452. Paris: J. Hermann, 1925. Price: 45 francs.* This book is based on lectures given at the University of Lille in 1920-22. The volume is divided into three parts: the nitrogen cycle; the sulphuric acid industry; and the chlorine industry as involving catalysis. The section on the nitrogen cycle, which constitutes more than half the book deals with synthetic ammonia, with the oxidation of ammonia and of nitrogen, and with the concentrating of nitric acid.

The beneficial action of alumina, thoria, and magnesia with an iron catalyst in the synthesis of ammonia, p. 28, seems to be chiefly in acting as a support and keeping the iron from sintering. There is a good cut on p. 44 showing that hydrogen is a less effective reducing agent than carbon monoxide with oxides of iron at temperatures below 800°. There are interesting data on p. 128 for the effect of hydrogen sulphide in poisoning the catalytic oxidation of ammonia in presence of platinum.

Additive poisoning is discussed on p. 131. "The addition of acetylene to phosphoretted hydrogen does not stop the poisoning by the latter nor the gradual recovery of the catalytic agent when pure gas is passed through; the fatigue due to the acetylene is superposed on the intoxication caused by the phosphoretted hydrogen [rather a mixing of metaphors]. On the other hand hydrogen sulphide, though not especially poisonous itself has a remarkable effect on the action of the other two gases. Amounts of acetylene sufficient to fatigue the platinum have their effect neutralized by one-tenth the volume of hydrogen sulphide. Even when 0.5% of acetylene is mixed with 0.50% of hydrogen sulphide, the efficiency drops only from 96 to 93%. The simultaneous presence of these two impurities in industrial gases in this ratio eliminates the possibility of acetylene, in spite of its known toxicity, being the chief cause of the deterioration of industrial catalysts."

It is stated, p. 141, that the catalyst used at Merseburg for the oxidation of ammonia contains 6-8% MbO_3, about the same amount of Bi_2O_3, and more than 30% of Fe_2O_3. On p. 198 there is a discussion of the possibility of liquefying the nitrogen peroxide from the arc process and letting that react with water and oxygen to form nitric acid; but the necessary temperature is too low and the danger of explosions is too great. The author appears to consider, p. 209, that cyanamide is the cheapest form of fixed nitrogen if one could use it as such.

Coming to the formation of sulphuric acid, one would like to know, p. 264, why calcium salts should catalyze the oxidation of ammonium sulphite. It is interesting to note that in 1914 less than three percent of the sulphuric acid made in America was from sulphur, while the figure was forty-eight percent in 1918. Of course part of this change was due to the difficulty in importing pyrites. One wonders whether there are two liquid forms of sulphur trioxide, p. 298, and the reviewer did not know that pure, dry, sulphuric acid could be volatilized without dissociation, p. 303.

The author claims, p. 314, that water is the most serious poison in the contact sulphuric acid process, while its presence is essential in the chamber process, p. 343. Without having looked up the subject the reviewer feels that the ordinary theory of the chamber process is quite unsatisfactory, p. 345. The reviewer was interested to learn, p. 348. that sulphur dioxide can be made to reduce nitrous oxide to nitrogen.

On p. 378 is the statement that in 1915 there was only one platinum still in France for the concentrating of sulphuric acid. Ferrosilicon, fused quartz, and vitreosil are the materials now used. At the Copper Queen it is stated, p. 417, that the use of the Cottrell process permits the saving each day of five tons of argentiferous copper from the roasting furnaces. Since a mixture of ferric oxide and cupric oxide is better then either alone in the Hargreaves process for making sodium sulphate and hydrochloric acid from sulphur dioxide and hydrochloric acid, p. 439, it seems as though a similar mixture should be helpful when using iron oxide as a catalyst in the contact sulphuric acid process; but the two are not ordinarily considered together.

Wilder D. Bancroft

Labyrinth and Equilibrium. *By S. S. Maxwell. 20×16 cm; pp. 163. Philadelphia and London: J. B. Lippincott Company, 1923. Price: $3.00.* The aim of this volume is to present an objective study of the equilibrial reactions of vertebrate animals and the mechanism through which these reactions are produced. "The ears of fishes have proved to be in many ways the most favorable objects for these investigations. My own experiments on the functions of the different portions of the labyrinth, especially of the otoliths, were possible only because of the large size and the accessibility of the structures concerned," p. 7.

The chapters are entitled: introduction; compensatory motions and compensatory positions; forced positions and forced movements; the labyrinth as a whole; reactions of non-labyrinthine origin; experiments of the semicircular canals; experiments on the otoliths; the mechanism of the dynamic functions of the labyrinth; the mechanism of the static functions of the labyrinth; the tonus effects of the cristae and of the maculae; nystagmus.

"The facts described in the preceding chapter show that a mechanism exists through the action of which animals tend to maintain a definite position with reference to the lines of gravitational force. Any departure from that position calls forth changes in the tension of the muscles in such a way that the eyes and the locomotor organs are no longer held in a symmetrical position with reference to the body of the animal." p. 25 .... These changes of muscle tension take place as well in an animal in which the higher parts of the brain, the cerebral hemispheres, have been removed. They cannot therefore be attributed to volition, or to a conscious effort to avoid or to change a disagreeable sensation. They are determined with precision both as to amount and kind by the amount and kind of movement or change of position by which they have been called forth," p. 25.

"Flourens described the effects of section of the peduncles of the cerebellum in the rabbit. When the posterior peduncles were cut, violent forced movements occurred; the animal sprang backwards or made somersaults backwards. Section of the anterior peduncles caused the animal to hurl itself forwards. It is evident that these movements are analogous to those which are produced by one-sided injuries, only they are in another plane," p. 29.

"All investigators since Flourens have noted the remarkably violent rolling movements which take place in the rabbit when one labyrinth is destroyed. Magnus and deKleijn have been able, by the use of motion pictures, to analyze the rolling. They have shown that the rolling is really a running which is so interfered with by the extreme tonus differences on the two sides of the body that almost no forward progression can be made. Each revolution of the animal is the result of two leaps," p. 34.

"If we turn a planarian worm on its back (dorsal side) it immediately rights itself. The movement has the appearance of a true geotropic reaction; but if the worm is placed with its dorsal side in contact with a vertical surface, *e.g.*, the wall of an aquarium jar, the righting reaction takes place just as well. Even when the planarian, in swimming, comes to the top of the water, a righting reaction occurs in which the organism places itself with its ventral side up, and creeps on the under side of the surface film. It is evident that these reactions are not geotropic; they do not depend on the lines of force of the earth's attraction, but are brought about through the effects of contact stimuli. The worm is so organized that the touch of a solid body against the dorsal surface causes the coordinated muscular movements necessary to turn the animal over and bring its ventral side into contact with the solid," p. 48.

Wilder D. Bancroft

The Boys' Own Book of Science. *By F. L. Darrow. 20×13 cm; pp. ix+331. New York: The Macmillan Company, 1923. Price: $2.50.* This book "has been written for that host of boys everywhere who wish to experiment at home. It is not a book about science. It is a practical guide to real worth-while experimental work. Under its direction the amateur will come to feel that he is not only acquiring knowledge, but that he is becoming a real scientist. The book has been written out of an experience of twenty years in teaching and in directing the home activities of boys in this sort of work. As an inspiration to their efforts, there have been included sketches of a number of world-famous scientists who started as home laboratory workers."

The chapters are entitled: the home laboratory; laboratory manipulation; the alchemist; chemical magic; Priestly and Scheele; oxygen and hydrogen; Sir (?) Henry Cavendish; the atmosphere; Antoine Laurent Lavoisier; acids, bases, and salts; Sir Humphry Davy; soap; the examination of textile fibers; Michael Faraday; stains and bleaches; Jöns Jakob Berzelius; electric furnaces; some metals and their alloys; Justus von Liebig; more about the chemistry of combustion; Joseph Henry; fireworks; Sir Henry Bessemer; the chemistry of the electric current; Sir William Perkin; the chemistry of light; Thomas A. Edison; special tests; George Westinghouse; more real analysis; crystals; Guglielmo Marconi; some experiments in physics; the Hall of Fame."

The author has included a great many very interesting experiments and the reviewer has read the book with much pleasure. He does not know at all how many boys this book will reach; but the author probably knows and it is a very fine thing if the number is large. The inclusion of the short biological sketches is admirable. The book seems very free from errors. On p. 87 the author speaks of alkaline soils when he means acid soils; but that is the only real typographical error that the reviewer noticed.

Wilder D. Bancroft

The Foundations of Colloid Chemistry. *A Selection of Early Papers bearing on the Subject. Edited by Emil Hatschek. 23×15 cm; pp. 173. London: Ernest Benn Limited, 1925. Price: 18 shillings.* In previous years the Colloids Committee of the British Association has published five Reports on "Colloidal Chemistry and its General Industrial Applications" and this year it publishes an Annual Report on the Progress of Colloid Chemistry, which is included in the Annual Reports of the Chemical Society and deals with the progress made in the year 1924. The book under review represents, however, another phase of the activities of the Colloids Committee, in that Mr. Hatschek has collected together and edited, a number of classical papers, many of which have hitherto been inaccessible.

In these days of crowded syllabuses the student's time is so taken up with the work immediately before him, that it is difficult to find the leisure to delve among the early published papers on chemical subjects. The teacher is almost in the same position, since the number of journals, containing original work with which he must become acquainted, increases every year. Resulting from this, both the student and teacher are apt to neglect the study of the early literature, which so often contains papers which are of fundamental importance even at the present time. It is to obviate such neglect that the "Alembic Club reprints" in Great Britain, and Ostwald's "Klassiker der exacten Wissenschaften" in Germany have been published, and now we are indebted to Mr. Hatschek for this selection of fundamental papers on colloidal chemistry, whereby attention is directed to the investigations of early pioneers who have hardly received the notice they deserve.

In reading these papers one is continually arrested by the fact that the views expressed are so often strikingly in accord with modern ideas, and the editor further impresses this on the reader by means of notes giving the references to later literature.

The task of selection must have been very difficult, but the choice made can only be described as an admirable one, and chemists in general will owe a great debt of gratitude to the editor and to the Colloids Committee.

The contents are as follows: (1) "On the physiological Utility of the Fats and on a new Theory of Cell Formation based on their Co-operation and supported by several new Facts," by Dr. Ascherson. (2) "Studies on the Demulsion of Silver Chloride" by Francesco Selmi. (3) "A Study of the Pseudo-Solutions of Prussian Blue and of the Influence of Salts in destroying them," by Francesco Selmi. (4) "On the Products of Decomposition of Sulphuretted Hydrogen and Sulphurous Acid in aqueous Solutions," by Ascanio Solvero and Francesco Selmi. (5) "On the experimental Relations of Gold (and other Metals) to Light," by Michael Faraday. (6) "On the Properties of Silicic Acid and other analogous colloidal Substances," by Thomas Graham. (7) "The Question of the Silver Sub-oxide Compounds," by Wilhelm Muthmann. (8) "On the Nature of Colloids and their Water Content," by J. M. van Bemmelen. (9) "On allotropic Forms of Silver". by Carey Lea.

T. Slater Price

THE SURFACE CONCENTRATION OF CASEIN, CRYSTALLINE EGG-ALBUMIN AND CRYSTALLINE HAEMOGLOBIN

BY J. M. JOHLIN

In a previous paper[1] it was shown in what manner the surface tension of gelatine solutions changes with time, under varying conditions of temperature, hydrogen-ion concentration, etc. Certain deviations from the change of surface tension with time according to the equation

$$\sigma = a/t^n$$

were there noted. The logarithmic curves representing data obtained by the capillary rise method in the case of solutions of iso-electric gelatine are again reproduced in Fig. 1 of the present paper where it is to be noted that these apparent deviations as at first expressed denote but changes in the rate of change of the surface tension with time and that the change is continually progressing according to the given equation.

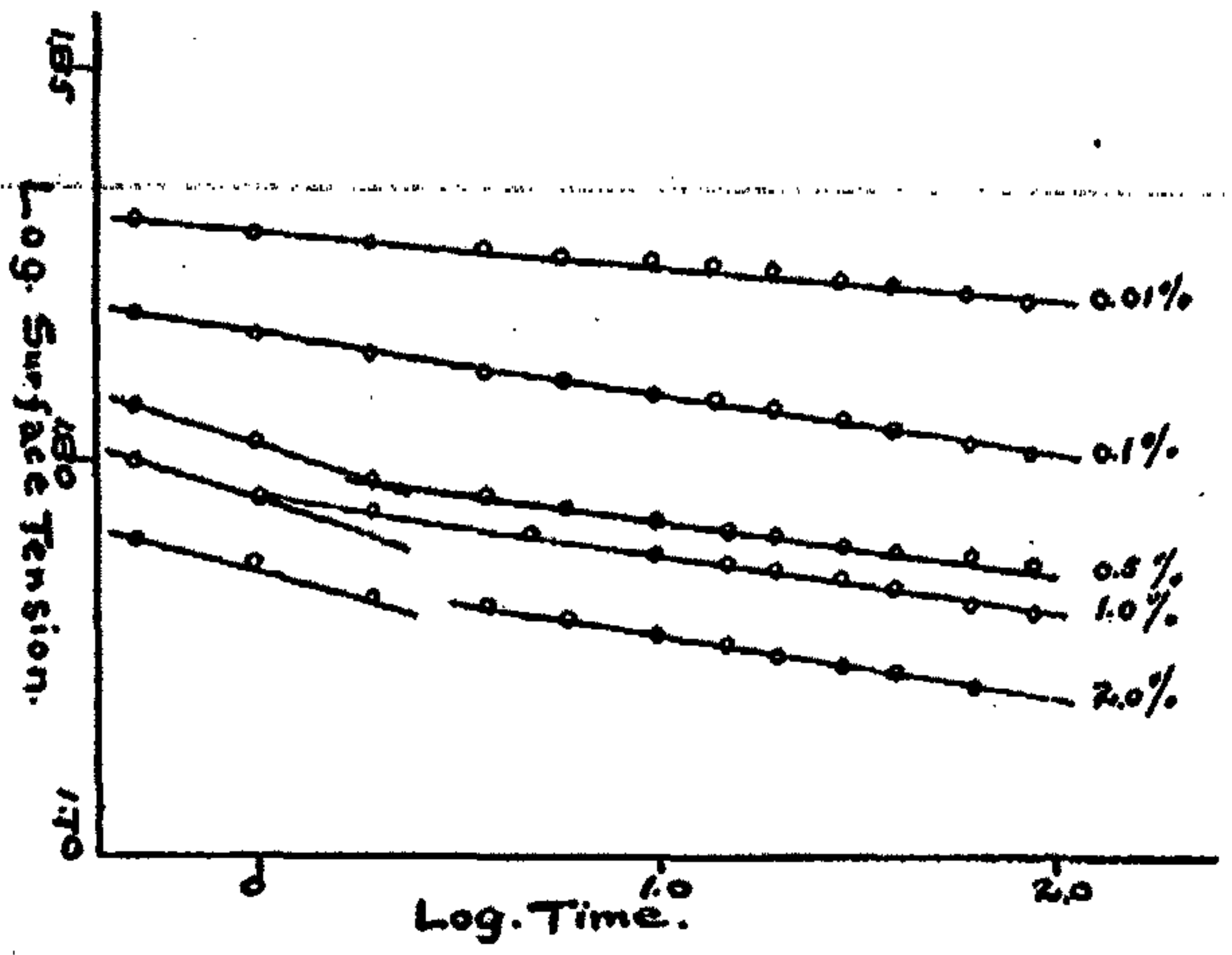

FIG. 1

Illustrating the change in the rate at which the surface tension changes with time in the case of solutions of iso-electric gelatine.

During the past few years a long series of papers has been published by duNoüy,[2] who used the ring method for measuring the change of surface tension with time in the case of serums. More recently he has extended his measurements to other colloids and has observed independently that the change of surface tension with time appears to be common to colloidal solutions in general. In all of his papers he has expressed the change of surface tension with time as taking place according to the equation

$$\sigma = \sigma_0 e^{-kt^{1/2}}$$

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[1] Johlin: J. Phys. Chem. 29, 271 (1925).

[2] J. Exp. Med. 35, 575 (1922), and a long series of subsequent papers.

If the exponential equation which he has given were correct then a plot of the logarithms of the surface tension against the values of the square root of the time should be a straight line. This is, however, not found to be the case when his data are thus graphically represented. If, on the other hand, the logarithms of the surface tension values as given in his experimental data are plotted against the logarithms of the corresponding time, the resulting graph is a straight line. These facts are illustrated by the curves of Figure 2. It is there shown that neither his theoretical curve nor the one plotted from his data fits his equation. It is also shown that the change of surface tension with time as given by his data is better expressed by the equation which the writer has given. The data from which the curves of Fig. 2 are made are some which duNoüy has repeatedly given[1] as representative of the change which takes place. They are reproduced below.

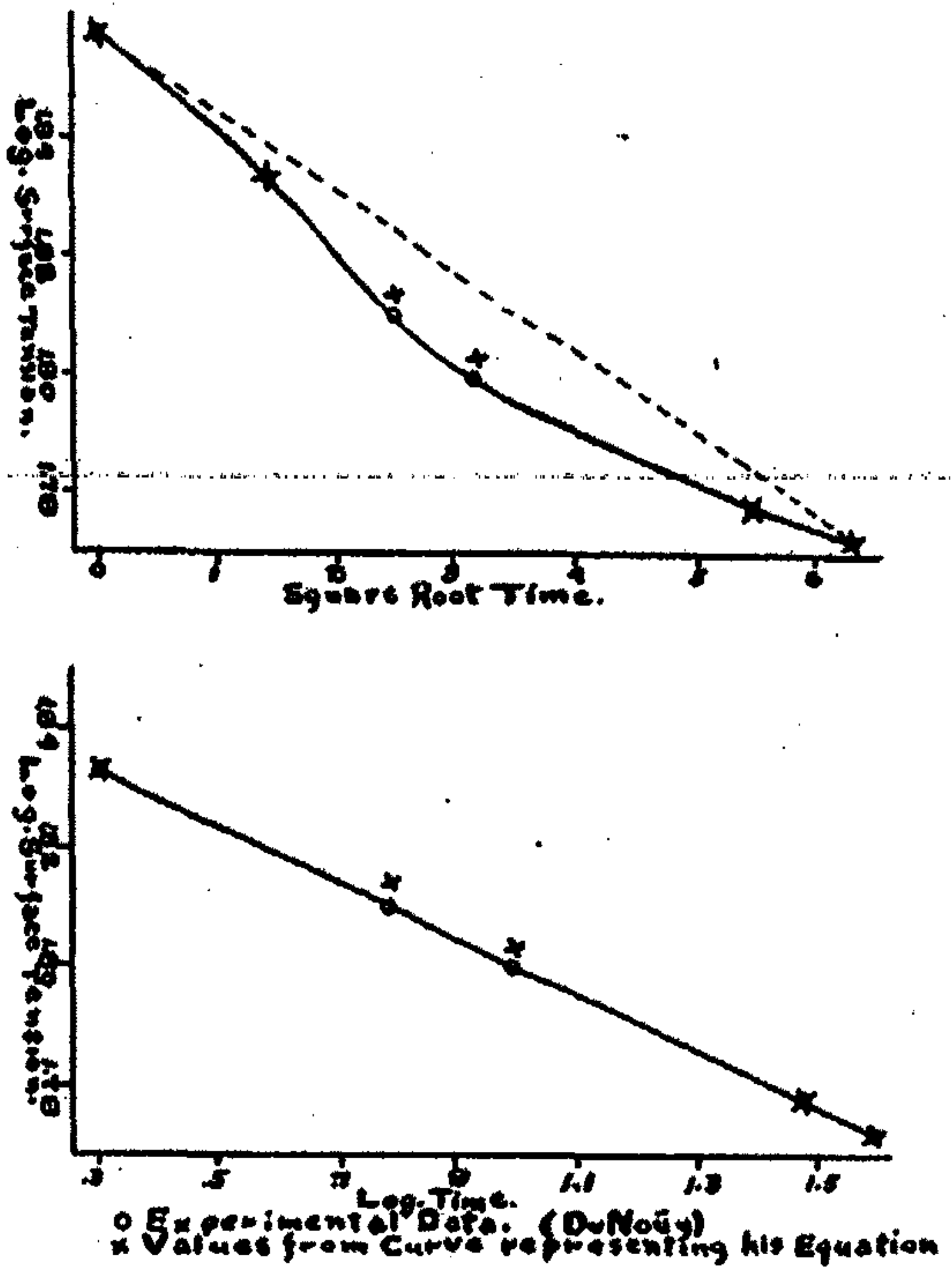

FIG. 2

Illustrating the fact that du Noüy's data support the writer's equation and that his own is incorrect.

Time (Minutes)	0	2	6	10	30	2 hours
Surface tension in Dynes per cm.	72.0	68.1	64.6	63.0	60.0	56.0

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[1] Du Nouy· Phil. Mag. (6) 48, 266 (1924).

The ring method has recently also been used by other investigators.[1] It is to be noted that too much reliability should not be accredited to this method. It has been supposed to be an ideal method because it is independent of the angle of contact. Ferguson,[2] however, in his classification of surface tension methods states that this method "is very convenient and exact if the conditions of the theory are properly observed." Freundlich[3] has pointed out that in the use of the ring method, the angle of contact is not usually known and that a zero angle cannot be assumed to exist. This he considers sufficient to account for the fact that the results of Timberg and of Weinberg have usually been too high.

This, however, should not prevent the method from being used for noting comparative changes. That it cannot be used with all solutions was shown in the present investigation. A platinum ring of the same dimensions as that used by Rideal and Wolf was attached to a carefully calibrated spiral spring which could be raised or lowered by means of a micrometer screw. It was found that the process of bringing the ring in contact with the solution caused a considerable disturbance of the surface. This was shown by placing minute amounts of a visible inert material upon the surface of the solution. When, in the case of a one percent solution of iso-electric gelatine, the ring was again lifted from the surface in order to measure the force required to break contact between the ring and the solution, it was found that a clean break did not take place. As increased force was applied by raising the spring, a stage was eventually reached where the ring was lifted from the surface a distance of about one centimeter, and contained between it and the bulk of the solution a cylinder of liquid. After resting in this position for a period varying from one to ten seconds this cylindrical film was lifted away from the main bulk of the solution in the form of a cup-shaped film which flattened out across the ring as the contact with the solution was broken. Under these conditions it would be difficult to state the relationship between the surface tension which existed before the ring was brought into contact with the solution and the force required to lift away the ring. A similar phenomenon was noted in the case of a 0.01 percent solution of potassium oleate, and would no doubt be found to occur in the case of any solution which readily forms a stable foam.

Lenard[4] has recently shown that accurate surface tension values should be obtained by measuring the force required to lift a straight wire from the surface of a liquid. No doubt some of the difficulties of the ring method might be eliminated by introducing this modification. The angle of contact would, however, still come into question and the method would lack the facility of making readings soon enough after the formation of the interface and rapidly enough to note all of the changes which apparently take place in the process of surface concentration. The bubble method naturally suggests itself as

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[1] Rideal and Wolf: Proc. Roy. Soc. **106**, 27 (1924).

[2] Trans. Faraday Soc. **17**, 372 (1921).

[3] "Kapillarchemie" (1922).

[4] Ann. Physik, **13**, 385 (1924).

the proper method because its use can be made entirely independent of the angle of contact. The dimensions available for measurement by this method would be so small, however, that the measurement of progressive changes would be quite inaccurate since the total changes themselves would be within the limits of accuracy of the method. As will be shown later on there are changes which take place which could not be observed by any other method than the capillary rise method. It has been shown that the change of surface tension with time as indicated by this method is the same as that comparatively indicated by two other independent methods. Its use if further justified by the observation of Quincke[1] who noted that, in making similar measurements by the capillary rise method, the angle of contact did not change appreciably as the surface tension changed with time.

Information concerning the surface tension of casein solutions is even more meagre than that concerning gelatine. Bottazzi[2], using a Traube stalagmometer, measured the surface tension of water in which casein was suspended. He found that casein of different origin lowers the surface tension and concluded that this must be due to the presence of soluble impurities. The addition of caustic soda was found to cause a further decrease. Berczeller[3] found by similar measurements that casein does not markedly lower the surface tension of water unless it has been boiled with it, and that the surface tension rose again when the solutions were allowed to stand. This he ascribed to a change in the size of the particles. The addition of acid or alkali was found to lower the surface tension in proportion to the amount of these reagents added. Later he found by the same method[4] that the surface tension of a casein solution changed as he varied the time of drop formation between 0.76 and 4.9 seconds. His solutions were prepared by dissolving one part of casein in 100 parts of 0.5 normal potassium hydroxide. He found similar variations in the case of gelatine solutions and in those of other proteins and soaps and concluded that the method affords a means of distinguishing between colloidal and crystalloidal solutions. Palitzsch[5] in describing measurements on the compressibility of casein solutions, mentions the fact that the surface tension of these solutions changes with the hydrogen-ion concentration. No data are given.

In the present investigation, the surface tension of casein solutions was measured at 25°C, by the capillary rise method, using the narrower tube which was employed in making similar measurements with solutions of gelatine. To prevent particles of casein from depositing upon the walls of the capillary tube previous to beginning measurements, the solution was not admitted into this tube until it had reached the temperature of the thermostat. The tube was then thoroughly wetted by forcing a considerable amount of the solution through the open end and absorbing it on clean filter paper.

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[1] Pogg. Ann. **160**, 560 (1877).

[2] Atti. Accad. Lincei, **21**, 221 (1912).

[3] Biochem. Z. **53**, 215, 232 (1913).

[4] Berczeller: Int. Z. Biol. **1**, 124 (1914).

[5] J. Am. Chem. Soc. **41**, 346 (1919).

When the solution was then allowed to seek its level in the capillary under the force of gravity, measurements were begun immediately. The first reading, as in previous experiments, was taken ten seconds after the formation of the interface. In some cases it was found possible to repeat a series of readings without recleaning the apparatus. Whenever it was evident, however, that particles of denatured casein were clinging to the walls of the tube, it was recleaned before repeating any of the measurements. Even with these precautions it was found far more difficult to repeat results consistently than it was in the case of solutions of gelatine.

Casein from two different sources was used for preparing the solutions. One sample was prepared by Kahlbaum and labelled "nach Hammersten." It was further purified by grinding it in a mortar with alcohol and then with ether as recommended by Robertson.[1] The other sample was prepared according to the method of Van Slyke and Baker.[2] In both cases the solutions were found to have a pH of 4.7. One of the objects of using casein from both of these sources was to obtain a check on the solubility of casein. Casein prepared "nach Hammersten" is generally supposed to have been especially subjected to the denaturing action of acidification in its preparation, while the other has not. The latter like the former was, however, subjected to the supposed denaturing action of alcohol and ether.

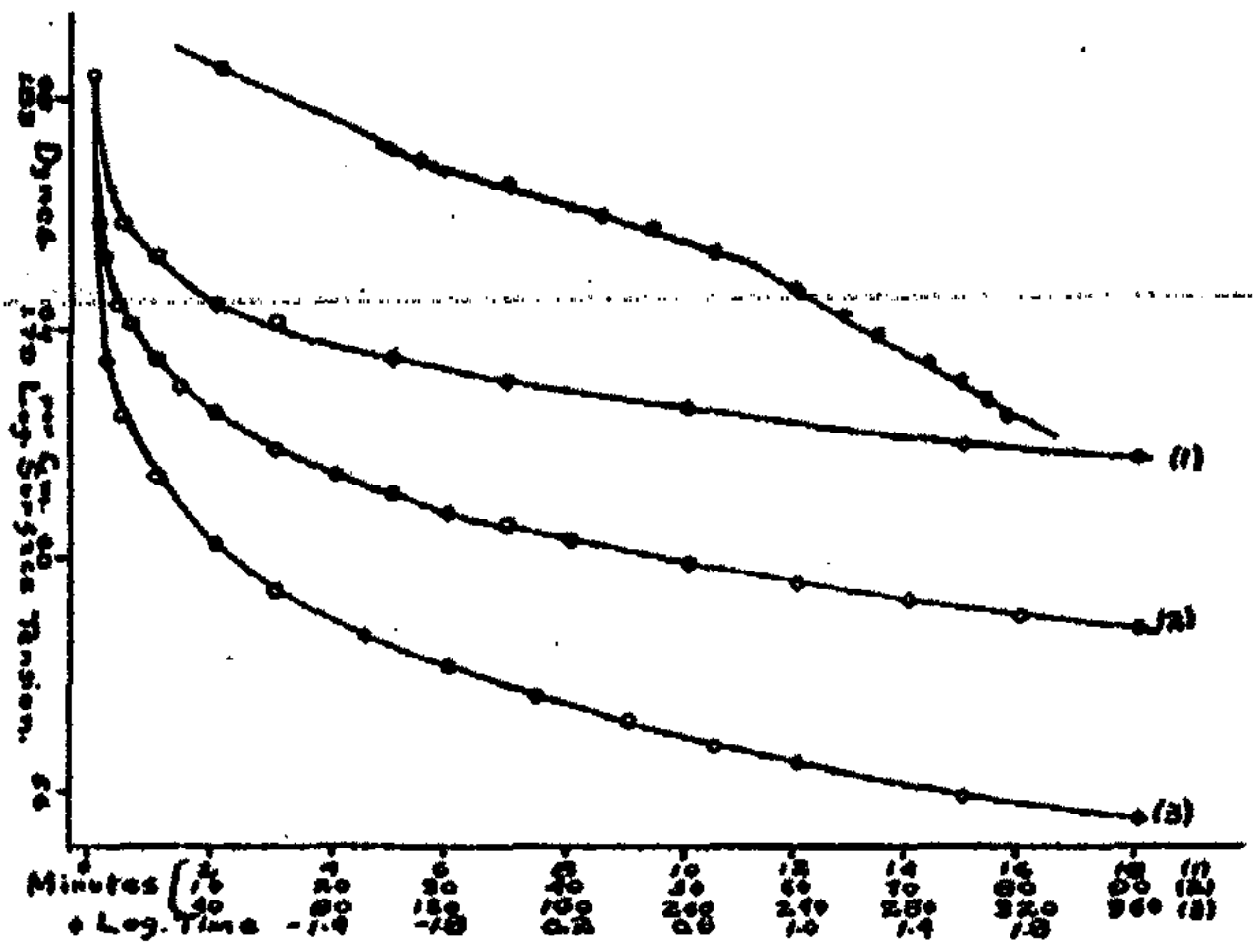

FIG. 3

Illustrating the change of surface tension with time in the case of a solution of casein.

The solubility of different samples was found to vary between 0.021 and 0.024 gram per liter. There was no essential difference in the solubility of the caseins of different origin. The solutions were prepared by shaking one gram of casein per liter of distilled water in a hard-glass bottle in a shaking machine for three days. Small amounts of toluene were added to prevent

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[1] "Physical Chemistry of the Proteins" (1921).

[2] J. Biochem. 35, 127 (1918).

putrefaction. In some cases the shaking bottle was completely filled so as to prevent denaturation of the casein at the solution-air interface. This precaution did not appear to influence the solubility of the casein but was taken in view of the fact that Cohn[1] had found the solubility of casein to be 0.1 gram per liter. In preparing his casein he avoided the possibility of denaturation by precipitating the casein from a solution of its salt at the iso-electric point. In doing so he found that the iso-electric point was reached before the calculated amount of acid had been added. It would be difficult to state without further experimentation whether he was not precipitating a salt of casein containing a small amount of the base. His data regarding the solubility of casein vary considerably. If his figures for the solubility of casein are correct then so-called denatured casein must have a characteristic solubility of its own. The solubility was determined by evaporating 250 ccm. of the solution in preference to making a Kjeldahl determination with so dilute a solution.

In the case of a solution whose surface tension does not change appreciably with time shortly after the formation of an interface, it is to be observed that the column of liquid in the capillary tube when disturbed will rapidly seek a definite level and not change its position appreciably five seconds later. In the case of solutions whose surface tension changes with time a continued change will follow as was illustrated in the case of gelatine solutions. It was shown by Lord Rayleigh[2] that even in the case of soap solutions, whose surface tension decreases with time with tremendous rapidity, there is an appreciable period after the formation of the interface during which the surface tension does not change but remains practically that of water. The present method does not permit of properly defining this initial period of inactivity in cases where it comes to an end within four or five seconds after the formation of the interface. In the case of gelatine solutions the decrease in surface tension

TABLE I

Time	Dynes per cm.	Time	Dynes per cm.	Time	Dynes per cm.
10 sec.	68.44	20 min.	61.42	1.5 hrs.	58.63
30 "	65.84	25 "	61.08	2.0 "	58.09
1 min.	65.26	30 "	60.75	2.5 "	57.58
2 "	64.42	35 "	60.54	3.0 "	57.11
3 "	64.10	40 "	60.26	3.5 "	56.62
5 "	63.46	50 "	59.82	4.0 "	56.36
7 "	63.01	60 "	59.46	5.0 "	55.75
10 "	62.52	70 "	59.14	6.0 "	55.36
15 "	61.88	80 "	58.87	7.0 "	55.05

Data obtained with a 0.021 percent solution of iso-electric casein at 25°C, by the capillary rise method.

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[1] J. Physiol. 1922, 697; 1923, 521.

[2] Proc. Roy. Soc. 47, 281 (1890).

followed the formation of the interface so soon that a period of inactivity could not be definitely observed. In the case of casein solutions it was, however, frequently observed that the meniscus came to a definite halt and then dropped again according to the given equation as the surface tension decreased. By repeating the phenomenon the exact point where this initial period came to an end could be determined by means of a stop watch. It was frequently observed that the surface tension did not decrease appreciably until six seconds after the formation of the interface. Later on longer periods of inactivity will be referred to and their possible effect upon the formation of stable foams.

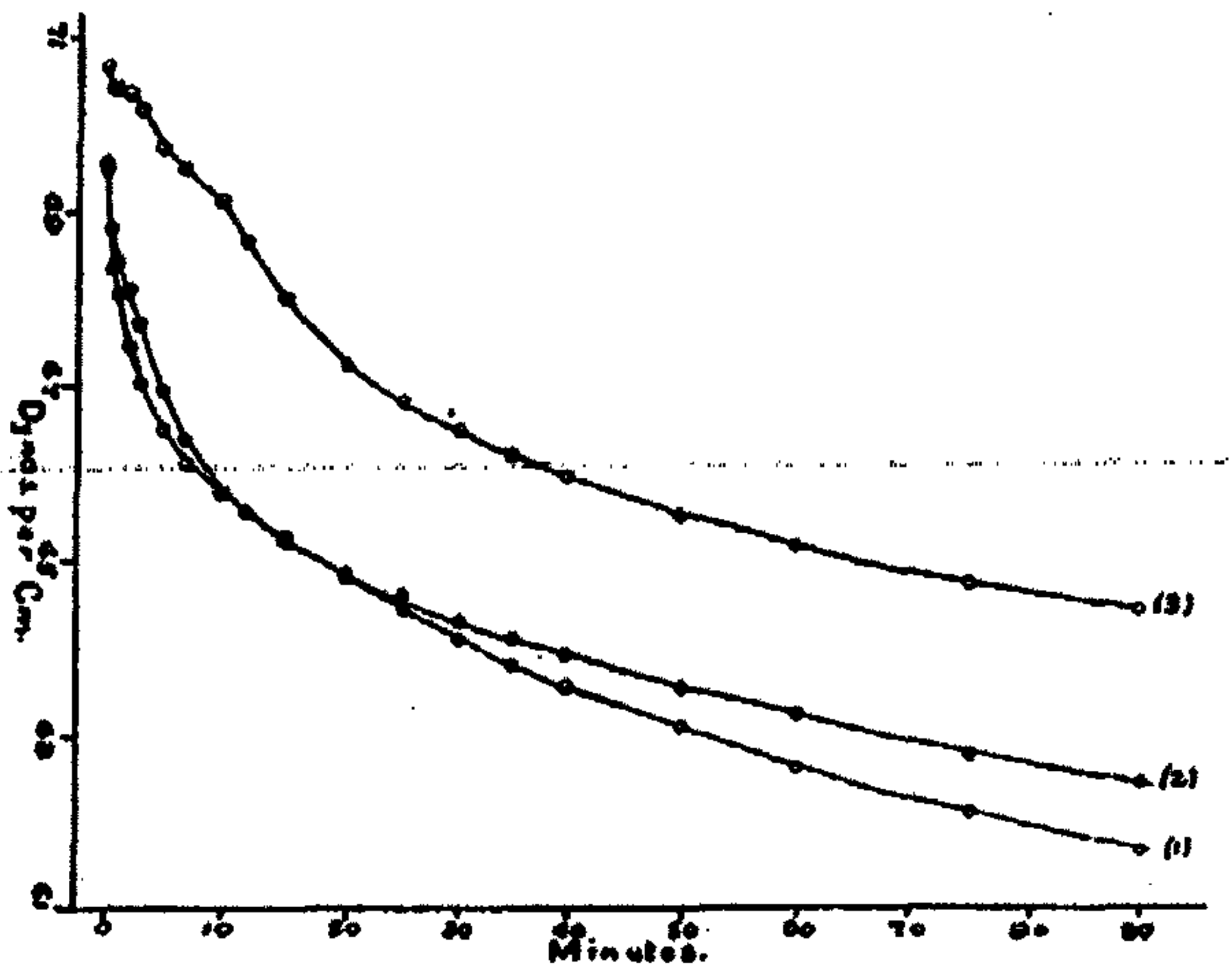

FIG. 4

Illustrating the effect of adding hydrochloric acid and sodium hydroxide to solutions of casein

(1) .021 percent solution + 56×10^{-5} moles HCl per gr. casein
(2) .021 percent solution + 17×10^{-4} moles NaOH per gr. casein
(3) .021 percent solution + 28×10^{-4} moles NaOH per gr. casein

It may be seen by the curves of Fig. 3 that the change of surface tension with time, in the case of casein solutions, takes place according to the given equation. Curves 1, 2, and 3 represent the change for periods of 18 minutes, one and one half hours, and six hours. It is evident that an approach to an equilibrium value is not soon reached. The logarithm curve shows that there may be changes in the rate at which the surface tension is changing with time but that the change continues to take place according to the given equation. The effect of adding alkali and acid to a solution of casein is shown by the data of Table II and by the curves of Fig. 4. The addition of acid did not appear to affect the tendency of the solution to foam. As increasing amounts of alkali were added the tendency to foam disappeared altogether. At the same time there was an increasing irregularity in the change of surface tension with time. A comparison of curves 2 and 3 of Fig. 4 shows how relatively small is the decrease in the case of the solution to which the larger amount of alkali had been added during the earliest period of the change when the decrease

TABLE II

Time	1. Dynes per cm.	2. Dynes per cm.	3. Dynes per cm.
10 sec.	69.57	70.71	69.54
30 "	68.81	70.44	68.35
1 min.	68.43	70.44	68.05
2 "	68.09	70.38	67.45
3 "	67.77	70.17	67.04
5 "	66.93	69.76	66.50
7 "	66.35	69.50	66.12
10 "	65.76	69.14	65.76
12 "	65.53	68.66	——
15 "	65.24	68.00	65.18
20 "	64.81	67.22	64.77
25 "	64.56	66.80	64.40
30 "	64.26	66.36	63.06
35 "	64.06	66.16	64.74
40 "	63.85	65.93	63.50
45 "	63.67	65.67	——
50 "	63.49	65.49	63.04
60 "	63.19	65.14	62.58
75 "	62.75	64.70	62.05
90 "	62.41	64.38	61.60

Data obtained with 0.021 percent solutions of iso-electric casein to which were added: Column 1, 17×10^{-4} moles of NaOH per gram of casein, Column 2, 28×10^{-4} moles NaOH per gram of casein, Column 3, 56×10^{-3} moles hydrochloric acid per gram of casein.

with time is normally most rapid. An even more pronounced effect will be noted in the case of solutions of egg-albumin and sodium oleate to which alkali has been added.

Reference has been made to the observation of Quincke who noted that the surface tension of strong salt solutions rapidly decreased with time. In the present investigation it was also noted that this effect was to be observed only when the tube was not properly cleaned. The surface tension of a concentrated solution of very pure potassium chloride did not change with time. The addition of small amounts of casein to the solution produced no pronounced effect. If, however, the apparatus was rinsed with a casein solution and then with distilled water there was a rapid decrease of surface tension with time when the potassium chloride solution was again charged into the apparatus. This decrease amounted to about forty percent of the original value.

Experiments with Crystalline Egg-albumin

The readiness with which egg-albumin is removed from its aqueous solutions by concentration at the surface was demonstrated by Ramsden[1], who

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[1] Proc. Roy. Soc. 72, 156 (1904).

showed that the whole of the egg-albumin in an aqueous solution could under favorable conditions be rendered permanently insoluble by repeatedly shaking the solution in an exhausted vessel.

There are but few available data concerning the surface tension of solutions of this material. It is only in recent years that purified form of this substance has been used for investigation. Quincke[1] made surface tension measurements with freshly filtered aqueous solutions of egg-white, and found that the surface tension of these solutions was lower than that of water. Iscovesco[2] in making such determinations more recently with the use of a stalagmometer used solutions of albumin prepared by dialysing egg-white. He found the surface tension of these solutions to be higher than that of water, while globulin prepared from egg-albumin had a lower surface tension. While the present investigation was in progress duNoüy[3] published data obtained by the ring method by which he showed that certain minima were obtained for the equilibrium values of the surface tension of very dilute solutions of crystalline egg-albumin of varying concentration. He assumed that all of the solute was adsorbed either at the solution-air interface or on the surface of the glass and drew certain conclusions concerning the formation of monomolecular layers and the molecular dimensions of the molecule of egg-albumin.

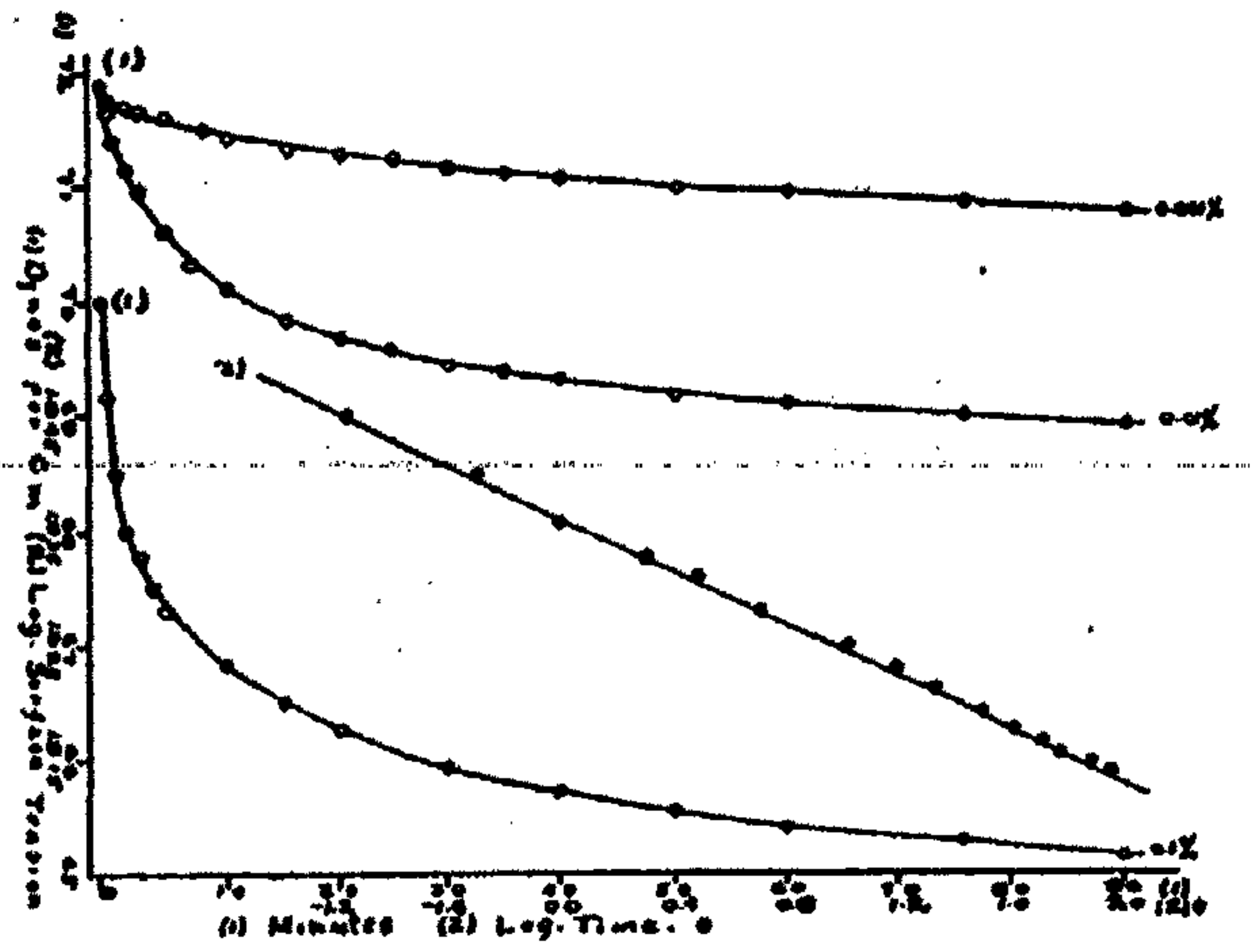

FIG. 5

Illustrating the change of surface tension with time in the case of solutions of crystalline egg-albumin.

The crystalline egg-albumin used in the present investigation was prepared by the method of Hopkins and Pinkus[4]. For the last recrystallization especially pure, ash-free ammonium sulphate was used. This was removed from the purified albumin by prolonged dialysis against running distilled water. 0.1 percent solutions of the albumin were found to have a pH of 4.7.

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[1] Wied. Ann. 35, 580 (1888).

[2] Compt. rend. Soc. Biol. 69, 622 (1910).

[3] Compt. rend. 178, 1904 (1924).

[4] J. Physiol. 23, 130 (1898).

Measurements were made at 25 °C, by the capillary rise method. The same precautions as with casein were used to prevent denatured material from interfering with the measurements. Because of the readiness with which this substance becomes denatured stronger solutions than 0.1 percent could not be used. The results obtained with solutions of 0.1, 0.01 and 0.001 percent solutions are given in Table III and Fig. 5. The initial readings as in previous measurements were taken ten seconds after the formation of the interface. That the change with time takes place according to the given equation is shown by the logarithmic curve which represents data which were obtained with a 0.1 percent solution.

TABLE III

Percent Concentration.

Time	0.1 Dynes per cm.	0.01 Dynes per cm.	0.001 Dynes per cm.
10 sec.	70.00	71.85	71.87
30 "	69.18	71.65	71.77
1 min.	68.50	71.41	71.72
2 "	68.02	71.16	71.70
3 "	67.77	70.97	71.66
5 "	67.31	70.60	71.58
7 "	—	70.33	71.49
10 "	66.83	70.12	71.42
15 "	66.52	69.86	71.36
20 "	66.28	69.68	71.31
25 "	—	69.58	71.27
30 "	65.94	69.45	71.17
35 "	—	69.39	71.14
40 "	65.73	69.32	71.10
50 "	65.55	69.18	71.01
60 "	65.41	69.12	70.96
75 "	65.89	69.01	70.88
90 "	65.18	68.92	70.81

Data obtained with solutions of crystalline egg-albumin at 25°C, by the capillary rise method.

A pronounced effect was produced by the addition of sodium hydroxide to solutions of albumin of 0.1 percent concentration. Different solutions were given the following normalities with respect to this reagent: n/350, n/700, n/1400, n/2800, n/5600 and n/11200. In all but the last case an almost similar effect was produced. This effect is illustrated in the case of the second of these solutions by the upper curve of Fig. 6 and by the data of Table IV. The periodicity here observed is comparable to that observed in preliminary tests which were made with solutions of silicic acid and other colloids in which the solute exists in the form of molecular complexes although the change here was much greater. The approach to a normal behavior is shown by the least alkaline of these solutions as indicated by the data of Table IVa and the lower curve of Fig. 6.

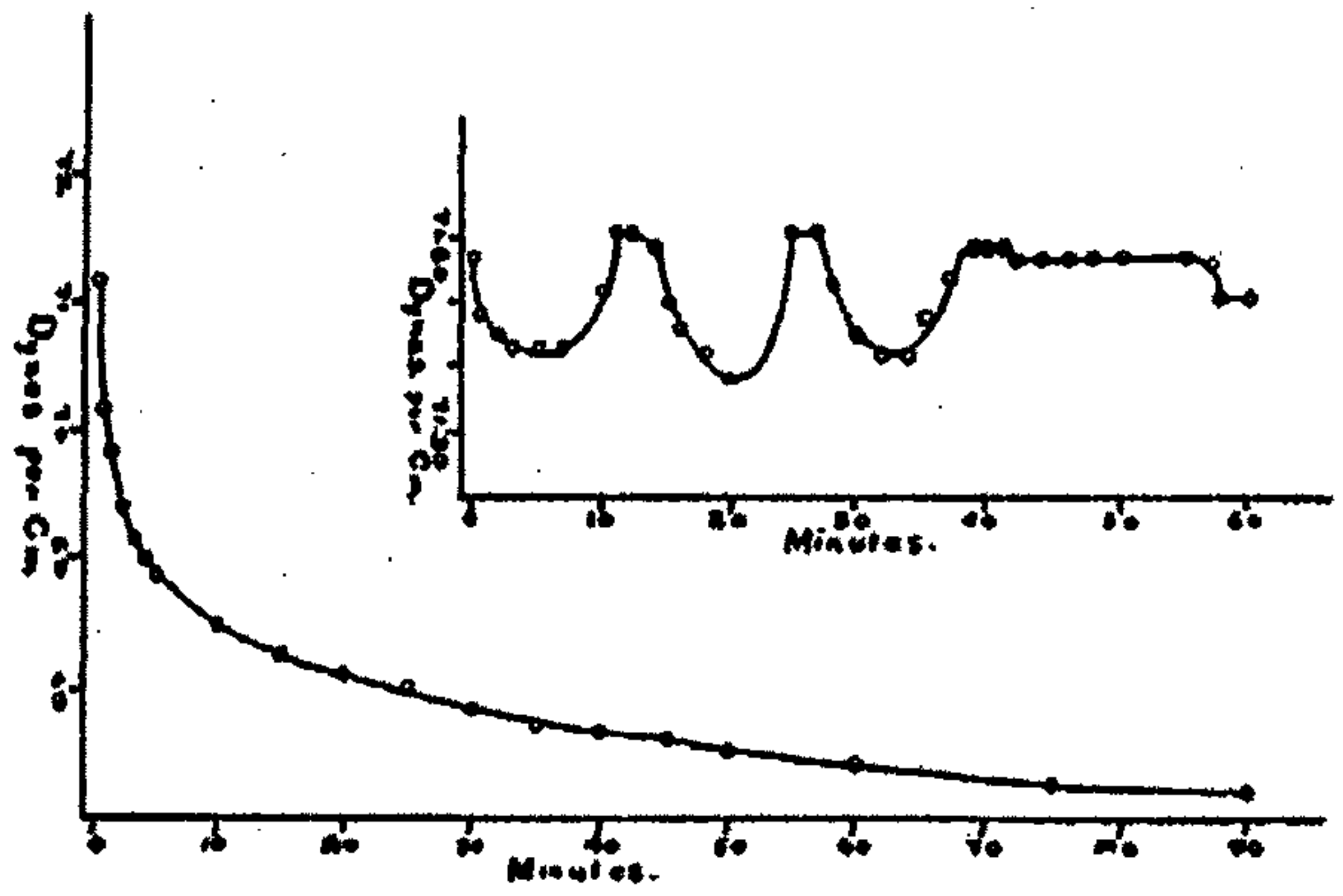

FIG. 6

Illustrating the effect of adding varying amounts of sodium hydroxide to 0.1 percent solutions of crystalline egg-albumin.
(1) 1/11200 normal with respect to NaOH
(2) 1/700 normal with respect to NaOH

TABLE IV

Normality with respect to sodium hydroxide

Time	1/350 Dynes per cm.	1/700 Dynes per cm.	1/1400 Dynes per cm.	1/2800 Dynes per cm.	1/5600 Dynes per cm.	1/11200 Dynes per cm.
10 sec.	71.69	71.57	71.42	71.35	71.08	71.18
30 "	71.87	71.46	71.53	71.50	71.15	70.18
1 min.	71.93	71.48	71.62	71.42	71.13	69.84
2 "	71.55	71.45	71.52	71.39	71.08	69.41
3 "	71.29	71.43	71.64	71.31	71.08	69.15
4 "	71.16	71.43	71.69	71.25	71.08	69.00
5 "	71.15	71.43	71.74	71.28	71.06	68.88
6 "	71.15	—	71.70	71.26	71.04	—
7 "	71.15	—	71.43	71.66	71.27	—
8 "	71.15	—	71.69	71.25	—	—
9 "	71.15	—	71.69	71.22	—	—
10 "	71.14	—	71.52	71.76	—	—
11 "	71.12	—	71.61	71.72	—	—
12 "	71.12	71.61	71.78	71.16	—	—
13 "	71.12	—	71.76	71.16	—	—
14 "	71.14	71.59	71.79	71.08	—	—
15 "	71.11	71.50	71.80	71.08	70.95	68.24

Data obtained with solutions of egg-albumin (0.1 percent concentration) to which varying amounts of sodium hydroxide had been added. The approach to a normal behavior as the amount of alkali is decreased is shown by the data of columns 5 and 6, which are given in full in Table IVa.

TABLE IVa

	Normality.			Normality.	
	1/5600	1/11200		1/5600	1/11200
Time	Dynes per cm.	Dynes per cm.	Time	Dynes per cm.	Dynes per cm.
10 sec.	71.08	71.18	20 min.	70.94	68.09
30 "	71.15	70.18	25 "	70.94	67.99
1 min.	71.13	69.84	30 "	70.91	67.83
2 "	71.08	69.41	35 "	70.87	67.71
3 "	71.08	69.15	40 "	70.87	67.66
4 "	71.08	69.00	45 "	—	67.59
5 "	71.06	68.88	50 "	70.72	67.49
6 "	71.04	—	60 "	70.60	67.38
7 "	71.02	—	75 "	70.47	67.26
10 "	70.99	68.50	90 "	70.38	67.19
15 "	70.95	68.24	3 hrs.	70.92	—

Data obtained by the capillary rise method with 0.1 percent solutions of egg-albumin which were very slightly alkaline.

TABLE V

	Hydrogen-ion Concentration		
	pH 3.0	pH 3.6	pH 4.3
Time	Dynes per cm.	Dynes per cm.	Dynes per cm.
10 sec.	70.46	69.37	69.14
30 "	69.99	68.78	68.04
1 min.	69.78	68.50	67.58
2 "	69.60	68.28	67.04
3 "	69.36	68.16	66.69
5 "	69.28	67.97	66.32
10 "	69.13	67.66	65.91
15 "	69.20	67.30	65.62
20 "	69.16	67.26	64.88
25 "	69.20	66.98	64.71
30 "	69.20	66.82	64.56
35 "	69.20	66.78	64.46
40 "	68.88	66.74	64.39
45 "	68.72	66.68	—
50 "	68.57	66.62	64.25
60 "	68.37	66.53	64.16
75 "	68.19	66.41	64.03
90 "	68.07	66.31	63.90

Data obtained at 25°C, by the capillary rise method, with 0.1 percent solutions of egg-albumin to which small amounts of sulphuric acid had been added.

The effect of adding varying amounts of sulphuric acid to 0.1 percent solutions of albumin is shown by the data of Table V and by the curves of Fig. 7, whilst that of adding varying amounts of potassium chloride is shown

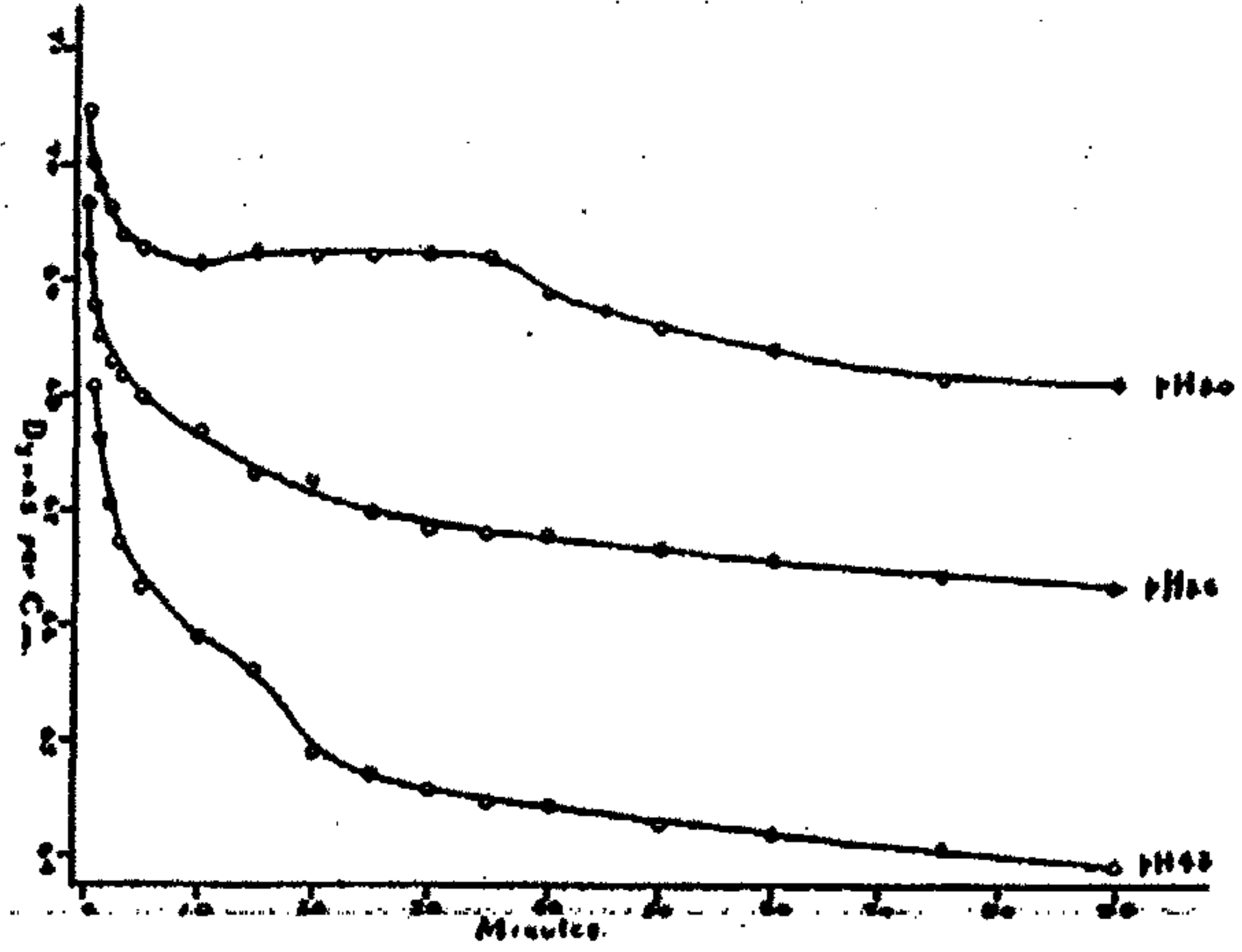

Fig. 7

Illustrating the effect of adding varying amounts of sulphuric acid to 0.1 percent solutions of crystalline egg-albumin.

Table VI

Normality with respect to potassium chloride.

Time	2.0 Dynes per cm.	1.0 Dynes per cm.	0.5 Dynes per cm.
10 sec.	74.29	75.22	72.31
30 "	74.02	74.64	71.40
1 min.	73.49	74.49	71.17
2 "	73.30	74.12	70.86
3 "	73.13	74.01	70.62
5 "	72.90	73.82	70.20
7 "	72.67	73.61	69.96
10 "	72.50	73.44	69.74
15 "	72.31	73.17	69.47
20 "	72.19	72.94	69.29
25 "	72.10	72.80	69.11
30 "	72.04	72.67	68.98
35 "	71.94	72.57	68.87
40 "	71.90	72.50	68.76
45 "	—	72.41	68.68
50 "	71.86	72.36	68.60
60 "	71.81	72.03	68.45
75 "	71.67	71.90	68.16
90 "	71.57	71.75	68.07

Data obtained at 25 C, by the capillary rise method with 0.1 percent solutions of egg-albumin to which varying amounts of potassium chloride were added.

by the data of Table VI and by the curves of Fig. 8. These results indicate that the effect of sodium hydroxide is not merely that of an electrolyte. It was noted that the addition of sodium hydroxide diminished the tendency of these solutions to foam. The addition of the other reagents did not produce a similar effect. Results such as these and others to be noted later in the case of soap solutions might indicate that an immediate rapid decrease in the surface tension of a solution is necessary for the formation of a stable foam and that a large decrease following a longer period of inactivity is not sufficient.

Experiments with Crystalline Haemoglobin

Information concerning surface tension measurements with solutions of haemoglobin is still more meagre than in the case of the other substances which have been investigated. Iscovesco[1] mentions the bare fact that haemoglobin lowers the surface tension of water by an amount which is proportional to the concentration. Berczeller[2] found that the surface tension of one percent solutions of haemoglobin was lowered as the time of drop formation decreased. DuNoüy[3] has recently also shown that the surface tension of haemoglobin solutions is lowered with time.

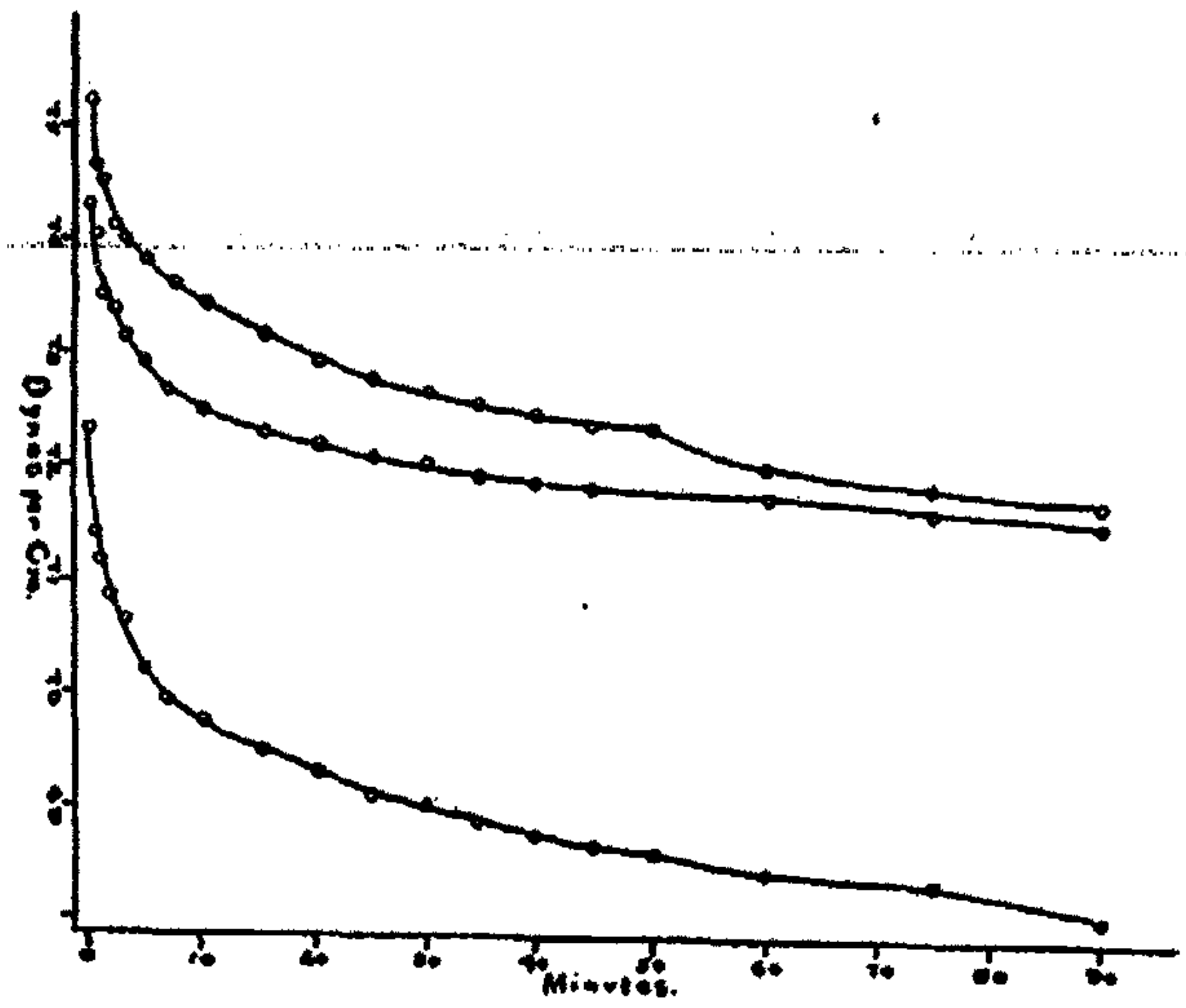

Fig. 8

Illustrating the effect of adding varying amounts of potassium chloride to 0.1 percent solutions of crystalline egg-albumin.
(1) 0.5 normal with respect to KCl
(2) 1.0 normal with respect to KCl
(3) 2.0 normal with respect to KCl

A few experiments were carried out in the present investigation to compare the behavior of this substance with that of the other proteins which have

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[1] Compt. rend. 150, 11 (1911).
[2] Int. Z. Biol. 1, 124 (1914).
[3] Phil. Mag. (6) 48, 266 (1924).

TABLE VII

Time	Percent Concentration. 0.5 Dynes per cm.	0.1 Dynes per cm.	0.05 Dynes per cm.	0.01 Dynes per cm.	0.001 Dynes per cm.
10 sec.	68.17	69.52	70.64	69.54	72.17
30 "	66.56	68.62	70.37	69.11	72.09
1 min.	65.07	68.15	70.14	69.06	72.03
2 "	65.39	67.57	69.83	69.01	71.95
3 "	65.00	—	69.60	68.96	71.87
5 "	64.55	66.88	69.22	68.85	71.80
7 "	64.19	66.69	68.92	68.77	—
10 "	63.87	66.35	68.59	68.72	71.67
15 "	63.48	66.03	68.14	68.62	71.51
20 "	63.18	65.45	67.80	68.50	71.27
25 "	62.92	65.07	67.47	68.39	71.20
30 "	62.74	64.71	67.18	68.32	71.09
35 "	62.50	64.46	60.96	68.24	71.00
40 "	62.35	64.24	66.76	68.14	70.92
45 "	62.21	64.01	66.55	68.05	70.79
50 "	62.03	63.88	66.36	67.97	70.73
60 "	61.77	63.85	66.03	67.78	70.62
75 "	61.48	63.46	65.62	67.54	70.53
90 "	61.18	63.14	65.24	67.31	70.40

Data obtained at 25°C, by the capillary rise method with solutions of oxy-haemoglobin of varying concentration.

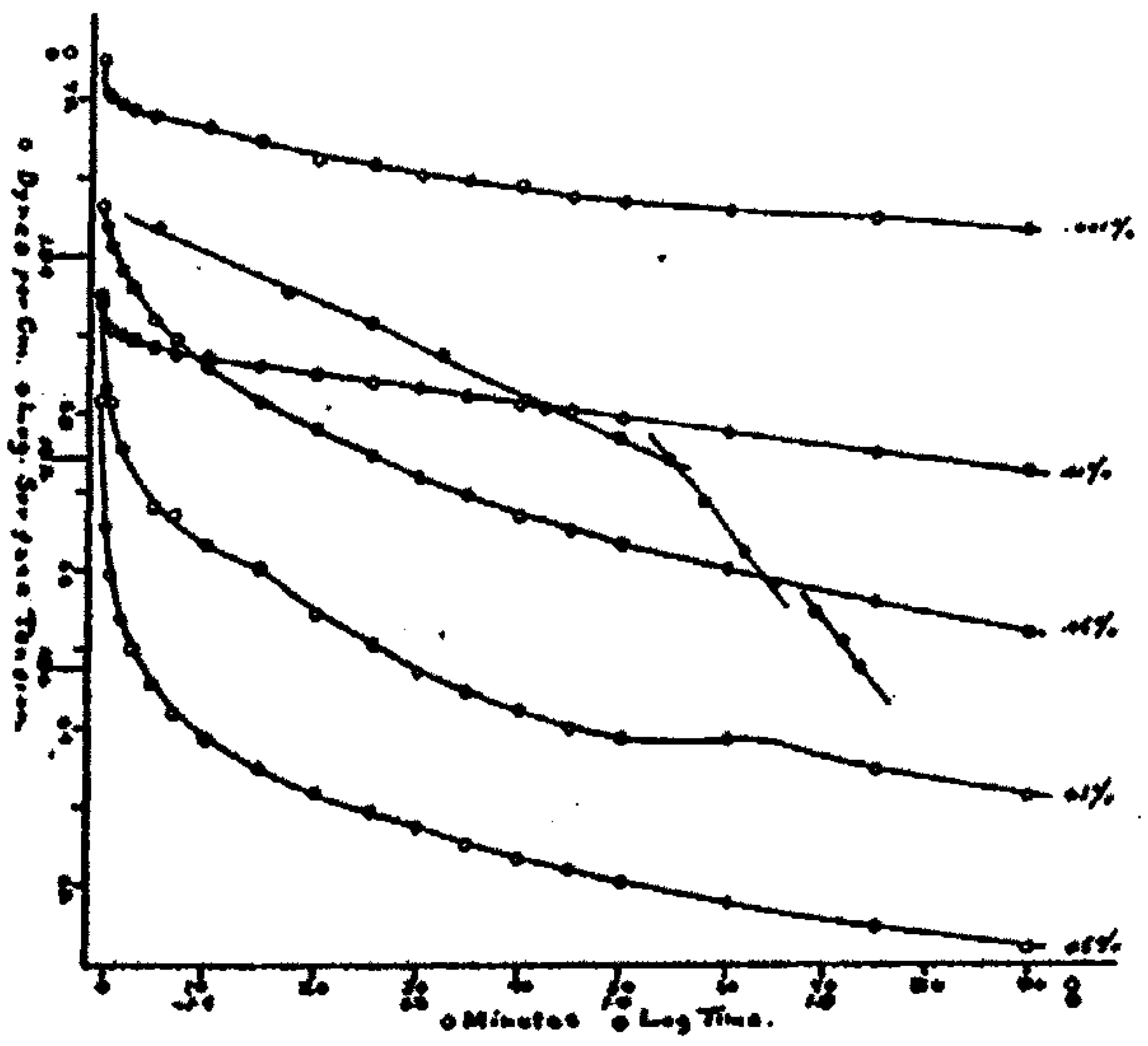

FIG. 9

Illustrating the change of surface tension with time in the case of solutions of oxyhaemoglobin of varying concentration.

TABLE VIII

(1) Reduced Haemoglobin. (2) Haemoglobin Carbonmonoxide

Time	(1) Dynes per cm.	(2) Dynes per cm.	Time	(1). Dynes per cm.	(2) Dynes per cm.
10 sec.	69.17	70.50	25 min.	63.55	65.06
30 "	68.18	69.49	30 "	63.20	64.79
1 min.	67.64	68.79	35 "	62.95	64.49
2 "	67.20	68.04	40 "	62.71	64.33
3 "	66.75	67.56	45 "	62.55	64.15
5 "	66.12	66.96	50 "	62.40	63.96
7 "	65.59	66.64	60 "	62.13	63.63
10 "	65.05	66.26	75 "	61.69	63.24
15 "	64.41	65.74	90 "	61.51	62.92
20 "	63.98	65.36			

Data obtained at 25°C, by the capillary rise method with 0.5 percent solutions.

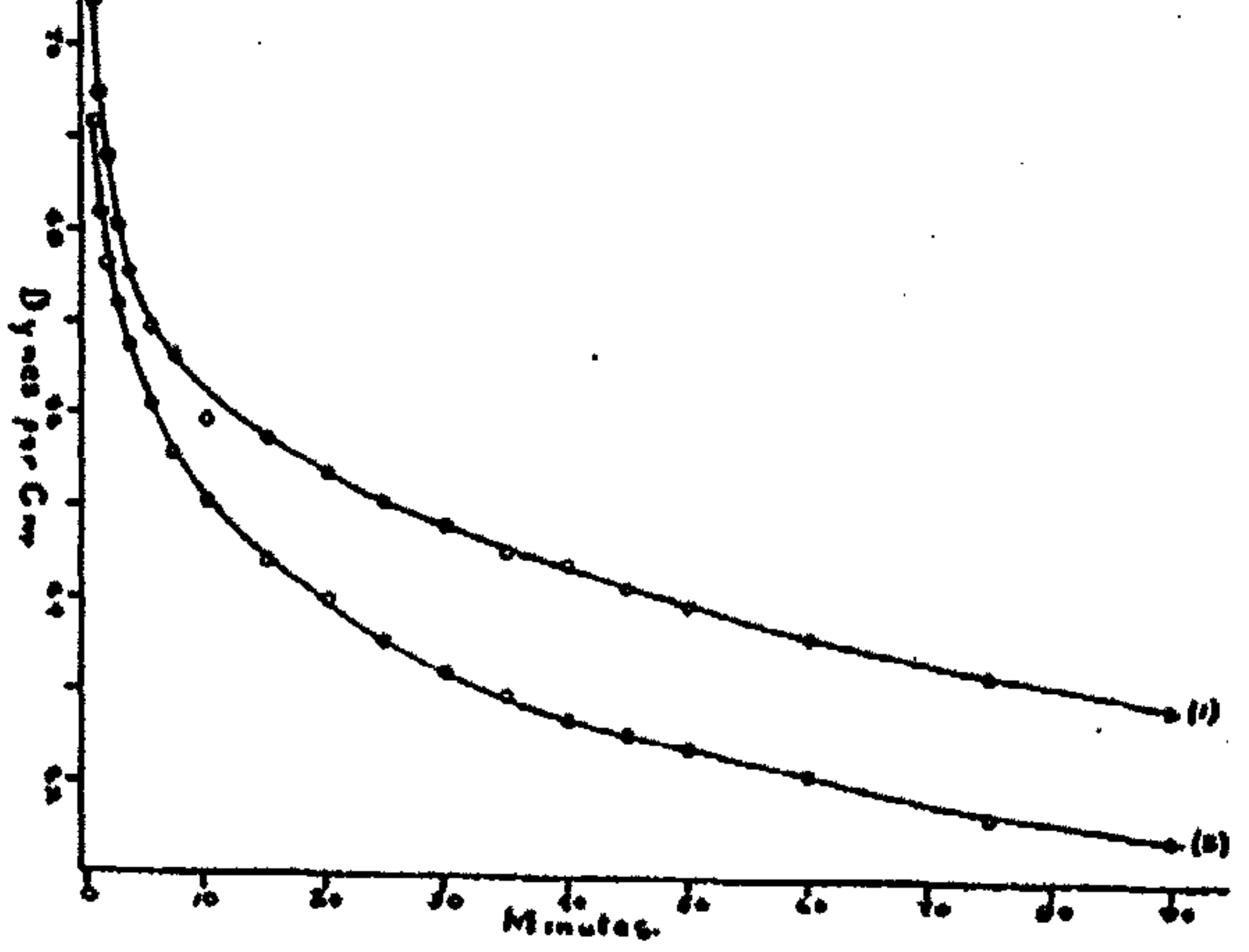

FIG. 10

Illustrating the change of surface tension with time in the case of solutions of reduced haemoglobin and haemoglobin-carbon monoxide.
(1) Haemoglobin-carbon monoxide
(2) Reduced haemoglobin

been studied and to note the effect of reducing oxyhaemoglobin and of converting it into the carbon monoxide compound. The material was prepared in a crystalline form according to the method of Dudley and Evans[1]. The crystals were dissolved in distilled water and the solutions used before there was an appreciable change to methaemoglobin. The hydrogen-ion concentration of a 0.05 percent solution was found to be that corresponding to a pH value of 6.55. The color of the various solutions was that usually ascribed to them. Measurements were made at 25°C, by the capillary rise method.

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[1] Biol. J. 15, 486 (1921).

The results obtained with solutions of oxyhaemoglobin of various concentrations are shown by the data of Table VII and by the curves of Fig. 9. The logarithmic curve is that representing a 0.1 percent solution. It shows that the change takes place according to the given equation but that there may be a change in the rate. The data of Table VIII and the curves of Fig. 10 show the change which takes place in the case of 0.5 percent solutions of reduced haemoglobin and of haemoglobin-carbon monoxide. No precautions were adopted to protect the reduced haemoglobin from the oxygen of the air while the measurements were made.

The writer wishes to thank Professor F. G. Donnan, F. R. S., for much helpful criticism.

The Sir William Ramsay Laboratories of Physical and Inorganic Chemistry.
University College, London.
April 15, 1925.

SOLUBILITY RELATIONS OF ISOMERIC ORGANIC COMPOUNDS.
II. THE DETERMINATION OF FREEZING TEMPERATURES OF BINARY MIXTURES.

BY DONALD H. ANDREWS, GIRARD T. KOHMAN, AND JOHN JOHNSTON*

In the course of the investigation of the solubility equilibrium in binary (and ternary) mixtures of the three isomeric substances,—*ortho*, *meta* and *para* XY-benzene, respectively—it was found that the method and apparatus commonly used for this type of work yield results of insufficient accuracy for our purposes. It was therefore necessary to go into the design of the whole apparatus, in order to ascertain where refinements could be introduced, and to consider the theory underlying the mode of experiment as a means of evaluating the results correctly. To a discussion of these points, which have not always received due consideration, the present paper is devoted.

The general type of method which may be used is largely determined by the fact that it is not practicable—at least, before the equilibrium diagram is known—accurately to analyze mixtures of *ortho*, *meta* or *para* isomers. Consequently we cannot use a method in which the solution is analyzed after the temperature of equilibrium has been observed,[1] but must have recourse to a determination of the temperature at which the stable solid phase just appears (or disappears) in a mixture made up to a given composition. Moreover, the former method would require relatively large amounts of the *pure* substances, amounts which, as we have found, can not in many cases be readily obtained by reason of the shrinkage of material attending repeated recrystallisation. It is necessary therefore to use the familiar method of taking time-temperature curves, and to refine the mode of experimentation so that the desired accuracy may be attained.

In the first place, by reason of the small heat conductivity of the substances under investigation, the temperature-measuring device must have a small heat capacity, a small lag, and must itself conduct away from the solution as little heat as is possible. These conditions are best fulfilled by the thermoelement,[2] especially if it is made of very fine wires, which is moreover an altogether convenient and satisfactory instrument to use, and incomparably better adapted to this purpose than is the mercury thermometer which has been used by some authors. In the second place, and for the same reason again, much clearer indications can be obtained with a small quantity of

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* Constructed from the dissertations presented, in June 1923, by Donald H. Andrews and Girard T. Kohman to the Graduate School of Yale University in candidacy for the Degree of Doctor of Philosophy.

[1] As, for instance, by L. H. Adams: J. Am. Chem. Soc. 37, 481 (1915), who measured the freezing point lowerings of dilute salt solutions with an accuracy approaching 0.0001°.

[2] The construction and use of thermoelements have been most fully discussed by W. P. White: J. Am. Chem. Soc. 36, 1856, 2292, (1914); Phys. Rev. 6, 234 (1915).

material—namely, of the order of 1 cc.—than with large quantities;[1] for, in the latter case, there will be appreciable differences of temperature throughout the mass, and the heat set free by the transition of the outer layers (which cool most quickly) is transferred only slowly to the thermometer. Moreover, one must see to it that the degree of undercooling, when crystallization is induced, is not excessive; otherwise the heat set free does not suffice to bring the mass up to the equilibrium temperature and at the same time to compensate for the losses by conduction and radiation. The form of the time-temperature curve is, of course, itself the best criterion of the usefulness of any refinement; though it is possible to deduce, from Newton's Law of cooling, the main conditions which a satisfactory set-up must fulfil.

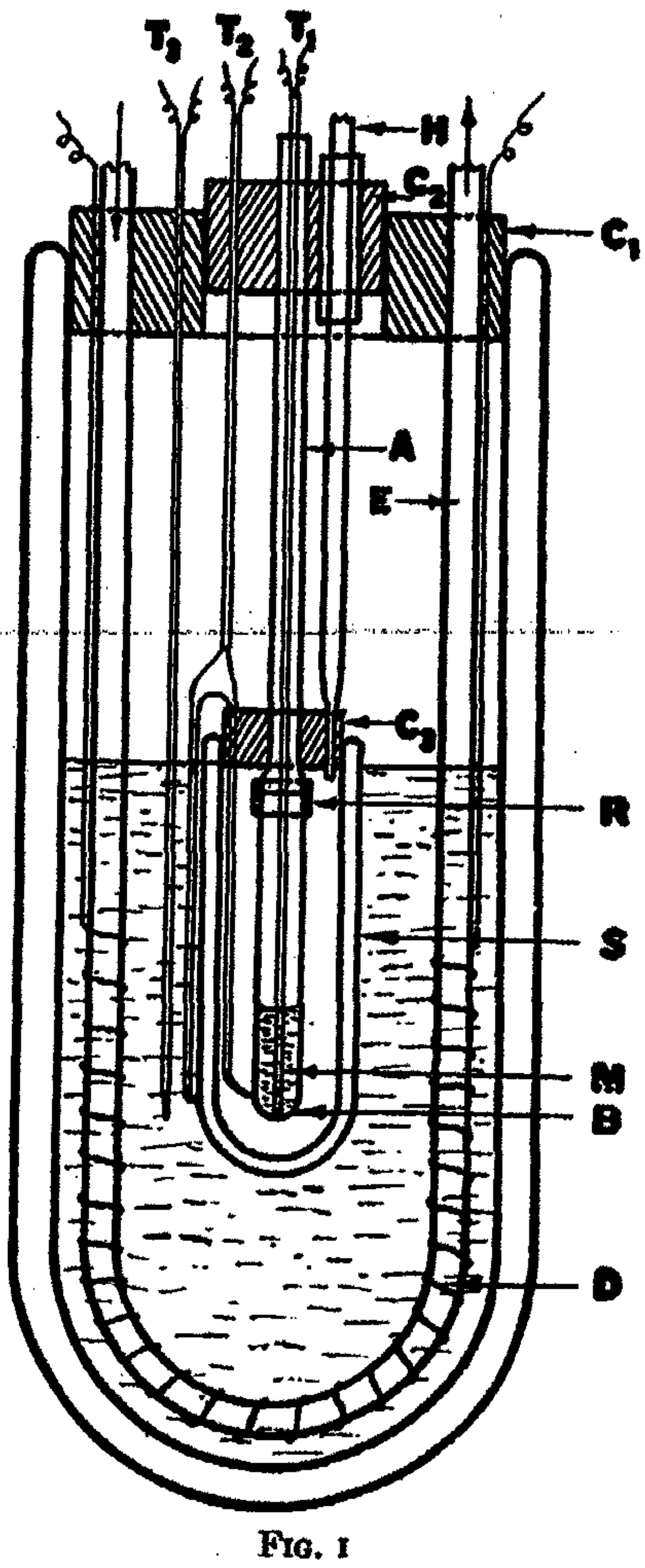

FIG. 1

Sketch showing the form of apparatus used.

The glass tube B containing the sample M is attached by a rubber band to the central tube A, through which the thermoelement T_1 passes. The thermoelement T_2 gives the effective temperature head between surroundings S and tube B. H is an air heater to reheat M; and D a nichrome coil to heat the fluid in the outer Dewar vessel.

In brief, it is necessary to have an apparatus such that the rate at which the material loses (gains) heat can be closely controlled—e. g., such that this rate is very nearly constant while the material changes 10° (or more) in temperature; and this implies that the effective temperature head which controls the rate in question can be measured and controlled. These conditions are fulfilled by the form of apparatus illustrated in Fig. 1, which will now be described in detail.

The Form of Apparatus used.

The external vessel is a Dewar tube (one quart size) silvered except for a longitudinal slit, for visual observation of the melt; it is closed by a cork stopper C_1 into which was fitted: (1) a smaller stopper C_2; (2) a U-shaped tube carrying a nichrome resistance element which serves to heat the bath fluid (usually paraffin or, at temperatures above 100°, air); (3) a thermo-

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[1] The same conclusion was reached by W. P. White, with respect to silicates (Am. J. Sci., 28, 453, 477 (1909)) who indeed, in the papers cited, gives a discussion in many respects similar to that which follows.

element T_3. The stopper C_2 supports centrally a glass tube A, on which has been fitted a third stopper C_3 which in turn fits into the shield S[1]; this was in some experiments a small empty unsilvered Dewar tube (as illustrated in Fig. 1), in others merely a thin-walled glass tube which proved to be practically just as effective. The substance under investigation M is contained in a thin-walled glass tube B (6 mm. diameter, 30 mm. long) attached to A by means of a rubber band; its temperature is measured by the thermoelement T_1, made of copper (#46 B and S gauge, 0.04 mm.) and constantan (#40, 0.08 mm.), the copper wire being wound helically about (but not in contact with) the other for a distance of about 5 cms., so as to minimize the heat flow along this wire. The junction of T_1 was, wherever practicable, immersed directly in the melt to a depth of 2 - 3 cm.; otherwise it was protected by a very thin-walled capillary tube filled with paraffin oil. This safeguard however may cause differences of as much as 2° between the temperature as recorded and the real temperature of the melt when the latter is no more than 25° above room temperature. The melt is stirred sufficiently by means of a small electric vibrator (not shown in Fig. 1) attached to the shield tube of T_1; but stirring is unnecessary when crystallization is once started throughout the melt, and indeed becomes impossible when about a fourth of it has crystallized.

One junction of a second thermoelement T_2 is arranged to touch tube B external to the melt, the other junction to touch the outside of the shield S; this enables one to read directly the effective temperature head. The temperature of the material is raised, when desired, by a stream of heated air directed down through the tube H. This tube is sealed to a wider glass tube closed by a cork through which passes an inlet tube and a porcelain tube carrying a resistance coil in the axis of the glass tube; the air pressure and the voltage can both be regulated. This arrangement was found to be very convenient, as it proved very desirable to be able to re-heat the sample without otherwise disturbing it. Indeed we replaced the paraffin and its heater in the large Dewar vessel, by air and a second hot air blast when a temperature higher than 100° was required there, and found it very satisfactory.

An experiment is carried out in the following manner. From 0.5 - 0.8 gram of the material (M) to be investigated is placed in tube B, which is then, with the thermoelement T_1 and T_2, set in position within the shield S. Paraffin in amount appropriate to establish of itself a cooling rate of about 0.5° a minute within the temperature range investigated, is put in the external vessel; its temperature is raised 1° or 2° above the melting temperature of M, and M is melted directly by a stream of heated air. The melt is then agitated by means of the electric vibrator, the system is allowed to cool, and the electromotive force of T_1 is observed on the even minute, that of T_2 (or of T_2 connected in opposition to T_1) on the half-minute. When the temperature of M has fallen about half a degree below its melting temperature (as ob-

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[1] Some form of shield at a controllable temperature is essential; otherwise the rate of cooling, over any reasonable range of temperature, would be too rapid. Quite recently, we have been trying another form of shield, consisting essentially of a brass tube about which a heating coil is wound; and the results are very promising.

served, if necessary, in a preliminary approximate experiment), the melt is inoculated by introducing through tube A a minute crystal of the solid phase and touching it to the surface of the melt. In this process, it is very important that no appreciable amount of heat should thereby be conducted away, as otherwise the equations of heat loss will not be valid. A good procedure is to use two glass threads, a short one which remains in the melt but extends above its surface; on the tip of the other is placed the seed-crystal, and it is then touched to the surface near the other thread, which aids in the growth and spread of the nuclei through the liquid.

This form of apparatus, in which the rate of temperature change can readily be regulated at will, can be used in place of the method, now used in metallurgical work where accuracy is desired, of lowering the specimen through a furnace in which a uniform temperature gradient has been established. For instance it proved easily possible, with an alloy of 69% tin 31% bismuth, to maintain the rate of cooling practically constant over a range of more than 100°, and to determine from a single time-temperature curve both the primary and the secondary freezing temperature. For work at high temperature the paraffin or air of the external bath would be replaced by a low-melting alloy or salt-mixture.

Heating curves too may be readily made by slowly raising the bath temperature. In the case of these organic substances, however, heating curves are less satisfactory than cooling curves, which may be due in part to the fact that in the solid the temperature distribution, as indicated by a number of thermoelements frozen into it, is uneven. It was found that a spiral of aluminum foil imbedded in the solid and attached to the thermoelement improves the results of heating curves.

The Interpretation of Time—Temperature Curves

I. For a Single Substance.

The form of the time-temperature curve for the period of freezing of a single pure substance is given in Fig. 2, the dotted portion at B representing the limiting case of no undercooling before freezing sets in.

The temperature of a mass of a pure liquid, surrounded by a shield cooling at a uniform rate (along RS), falls along the line AB to C, at which crystallization is initiated. The heat supplied by crystallization raises the temperature to that of the true equilibrium between solid and liquid; and the curve is horizontal, along DE. When crystallization is substantially complete, at E, the effective temperature head is relatively large, and so the solid mass at first cools rapidly; but finally the curve, at F, again becomes parallel to RS[1].

The shape of the time-temperature curve during freezing is one of the best criteria of purity. With a perfectly pure sample, the temperature remains quite constant during freezing (DE, Fig. 2); and in fact readings differing

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[1] The curve for the solid would however be slightly nearer RS than that of the liquid, since the specific heat of the solid is somewhat the smaller.

by no more than 1 microvolt (0.02°) over an interval of five minutes or more can readily be obtained, if the substance is really pure. If the substance contains admixed impurity, the initial temperature of freezing will likely be depressed, the temperature falls off as freezing progresses and the concentration of the impurity in the solution increases. White[1] has given a thorough discussion of this matter, and of its usefulness as a means of estimating the amount of impurity.

For the measurements of solubility, specific heat, etc., which we wished to undertake, really pure material was requisite and one of the requirements set for the apparatus was that it should yield cooling curves which could be trusted as a criterion of purity. It was rather disturbing to find that, without exception, the substances bought as pure organic chemicals contained impurity ranging from 2% up to 10%. In the case of the disubstituted benzenes, the presence of 1 mol per cent impurity causes about 0.5 - 0.8° lowering of freezing temperature; so that in this case when the material is three-fourths frozen, the freezing temperature would have fallen off by at least 2°. By fractional crystallization we succeeded in purifying samples of our materials so that when 75% frozen the temperature differed from the initial freezing temperature by less than 0.1°, indicating therefore less than 0.2% impurity.

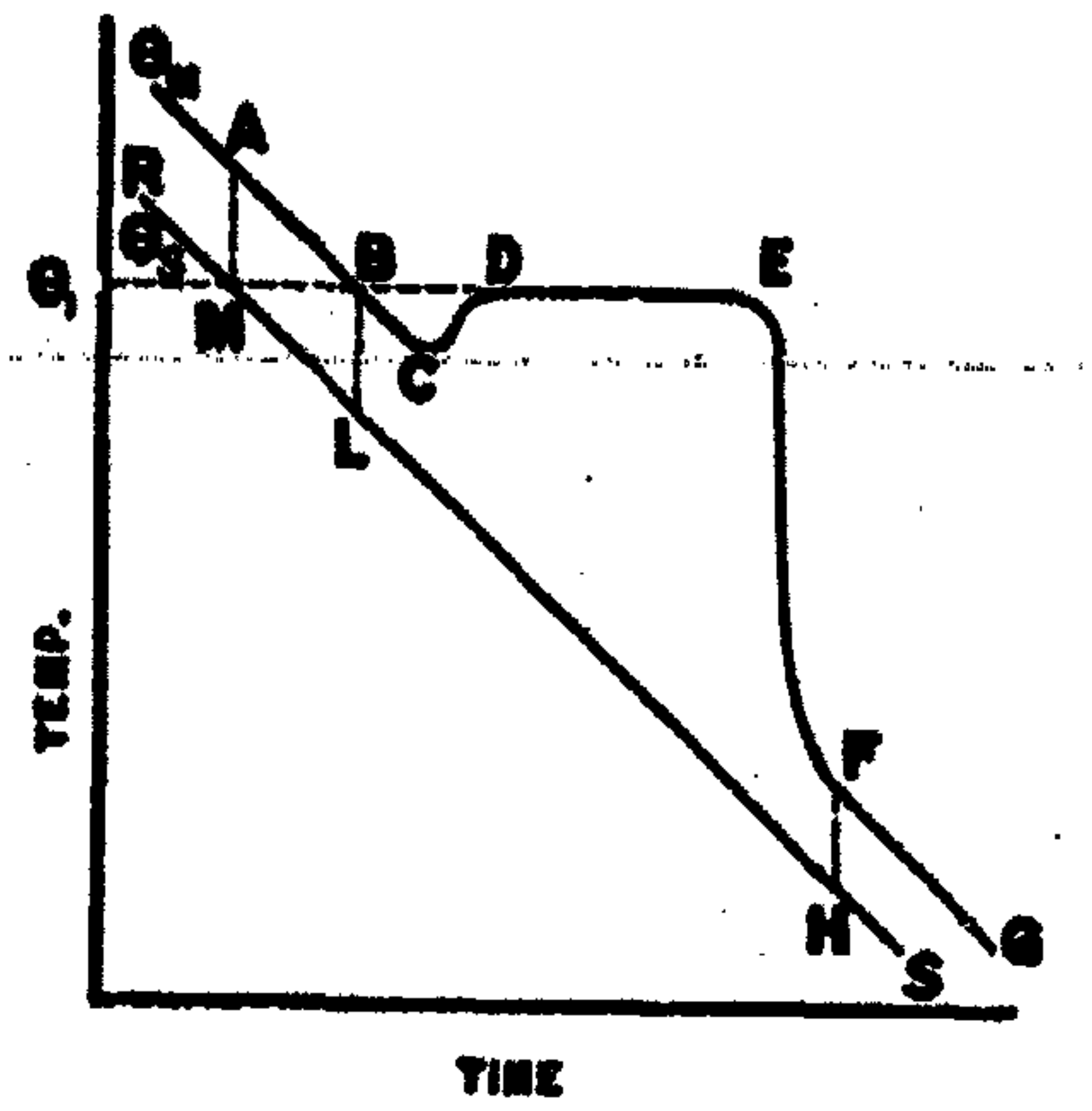

FIG. 2

Typical time-temperature curve for a pure substance.

During the last quarter of the freezing interval the temperature may fall off more rapidly, but this is to be attributed in part to non-ideal conditions. For instance it is likely that the last fraction crystallizing cannot supply heat to the thermoelement and its surroundings fast enough to enable the true equilibrium temperature to be

Time Minutes	Temperature-microvolts I	II	Time Minutes	Temperature-microvolts I	II
0	4003	3928	10	3738	3738
1	3801	3813	11	3735	3738
2	3609	3707	12	3666	3737
3	3740	3739	13	3209	3736
4	3740	3740	14	3014	3733
5	3740	3739	15	2884	3725
6	3740	3739	16		3708
7	3740	3738	17		3651
8	3740	3738	18		3453
9	3739	3738			

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[1] W. P. White: J. Phys. Chem., 24, 392 (1920); *q. v.*

maintained. It has therefore seemed best not to make use of this last portion of the curve in judging purity.

As an illustration, the original data on two cooling curves on a purified sample of *m*-dinitrobenzene are appended; in the more rapid the surroundings were at 2340 microvolts, in the second at 2980 microvolts (5 microvolts = 0.1°) In order to be sure that the time rate of heat loss by the material M in our apparatus is proportional to the effective temperature head, in accordance with Newton's law, we made some observations of the rate of cooling of liquid naphthalene under various heads. The results show that Newton's law is very closely followed, as is evident from the last column of Table I, even for a head much larger than any used in our work. We are therefore justified in using this law in the interpretation of time-temperature curves observed with this form of apparatus.

TABLE I

The rate of cooling of naphthalene, for various temperature heads.
(1° = about 50 microvolts)

Time half-minutes	Temp. head microvolts $\Theta_m - \Theta_s$	Temp. of material microvolts Θ_m	$-\Delta\Theta_m$	$\frac{\Delta\Theta_m}{\Theta_s - \Theta_m}$
1		6178		
2	1627		570	0.351
3		5608		
4	1192		420	.352
5		5188		
6	883		298	.338
7		4890		
8	662		233	.352
9		4657		
10	497		178	.358
11		4479		
12	372		130	.350
13		4349		
14	280		97	.347
15		4252		
16	210		77	.367
17		4175		
				Mean 0.352

Newton's law may be written

$$\frac{d\,\Theta_m}{dt} = K'\,(\Theta_s - \Theta_m)$$

where Θ_s and Θ_m are the temperature of shield and melt respectively, t is time, and K′ a constant for the particular set-up and material. Now if H is the heat content of the melt, and C its heat capacity, $dH = Cd\Theta$ by definition, and $\frac{dH}{dt} = C\frac{d\Theta}{dt} = CK'(\Theta_s - \Theta_m)$. In the case of the organic substances under discussion we are justified in considering C to be effectively constant over the temperature interval in question[1], and also in taking the heat capacity of the solid to be sensibly equal to that of the liquid, which implies in turn that the heat of melting is, for this purpose, independent of the temperature. On this basis we may write K instead of CK′, and the heat lost from A to B (Fig. 1) is

$$-\Delta H = H_B - H_A = K\int(\Theta_s - \Theta_m)\,dt.$$

Now if the temperature of the shield Θ_s and that of the material Θ_m are recorded at regular intervals of time, and plotted as in Fig. 2, the integral is the area ABLM; and therefore the heat loss of the material—hence its heat capacity—in cooling from A to B, is proportional to the area ABLM. By similar reasoning, the heat loss from B to F is proportional to the area BCDEFHL; of this area the part BFHL corresponds again to the heat capacity (provided that the virtual head is maintained sensibly constant throughout) and BCDEF to its latent heat of freezing. This was confirmed by a series of curves taken on naphthalene, which showed that this area (as measured by counting squares on the plot of the several curves) is very closely proportional to the weight of naphthalene taken.

Thus from time-temperature observations it is possible to deduce both the heat capacity and heat of fusion of a substance by measuring the appropriate areas and multiplying by a factor evaluated from a similar curve, made under identical conditions with the same set-up, for some reference substance. This method of "radiation" calorimetry has been proposed[2], though little has been done with it; it appears however that results of satisfactory accuracy could be secured, especially at temperatures up to 200° or 250°, by proper design of apparatus, and that such a method might prove to be very convenient.

In this connection it may be remarked that temperature may not be uniform throughout the cooling body, especially if it is not a good conductor of heat. On this point White[3] has published some interesting observations. He found in a cylinder of naphthalene, about 7 mm. diameter, cooling about 1° a minute, no difference of as much as 0.1° so long as the naphthalene was liquid, but immediately after freezing the difference from outside to center exceeded 1°. Burger[4] also has made similar observations.

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[1] This has been shown by actual measurements of heat capacity of a series of these organic substances, both as liquid and as solid; these measurements will be described in a later paper.

[2] Ruff and Plato: Ber. 36, 2357 (1903); Hüttner and Tammann: Z. anorg. Chem. 43, 215, (1905); W. Plato: Z. physik. Chem., 55, 721, (1906); 58, 350, (1908); 63, 453, (1908); W. P. White: Am. J. Sci. 28, 485, 1909; R. Schwarz and H. Sturm: Ber. 47, 1730, (1914). G. D. Roos: (Z. anorg. Chem., 94, 329 (1916)) has used it to obtain values of heat of melting of some metals.

[3] W. P. White: J. Phys. Chem., 24, 392, (1920).

[4] H. C. Burger: Proc. Acad. Amsterdam, 23, 45 (1920). "Observations of the temperature during solidification"; Ibid. p. 616. "The process of solidification as a problem of conduction of heat."

II. For a Binary Mixture.

A binary mixture cools similarly along AP (Fig. 3) until the component X begins (in absence of undercooling) to separate at P, when there is a change in direction (along the curve PD) but no horizontal portion of the curve. The heat set free now causes the rate of cooling of the melt to change in a perfectly definite way, because to any temperature below P there corresponds a definite composition of the residual liquid, hence a definite amount of the component has crystallized and a definite total amount of heat has been disengaged. The composition of the residual liquid approaches that of the eutectic as the eutectic temperature is approached; at that temperature the liquid still remaining behaves as a pure substance. In this case therefore the momentary composition of the solution is a factor in the cooling curve and in its interpretation.

The typical experimental curve for a binary mixture differs only in that some undercooling is unavoidable and, indeed, not undesirable provided that the curve be interpreted properly. When crystallization is induced, at C, equilibrium between X and solution is soon attained and maintained thereafter, and the heat set free raises the temperature rapidly to a maximum D, beyond which it then falls off as before, a state of equilibrium being maintained. It is clear that the composition of the liquid phase at D differs from that of the original solution by the proportion of X which has then crystallized; and in careful work this fact must be properly taken into account. The usual methods of making this correction are not based upon sound principles and are unsatisfactory, as will be shown on a later page. In order properly to learn how to interpret this form of curve, it was necessary to consider the theory of the process, as based upon Newton's law of cooling which is—as we have seen—valid under our conditions of experiment.

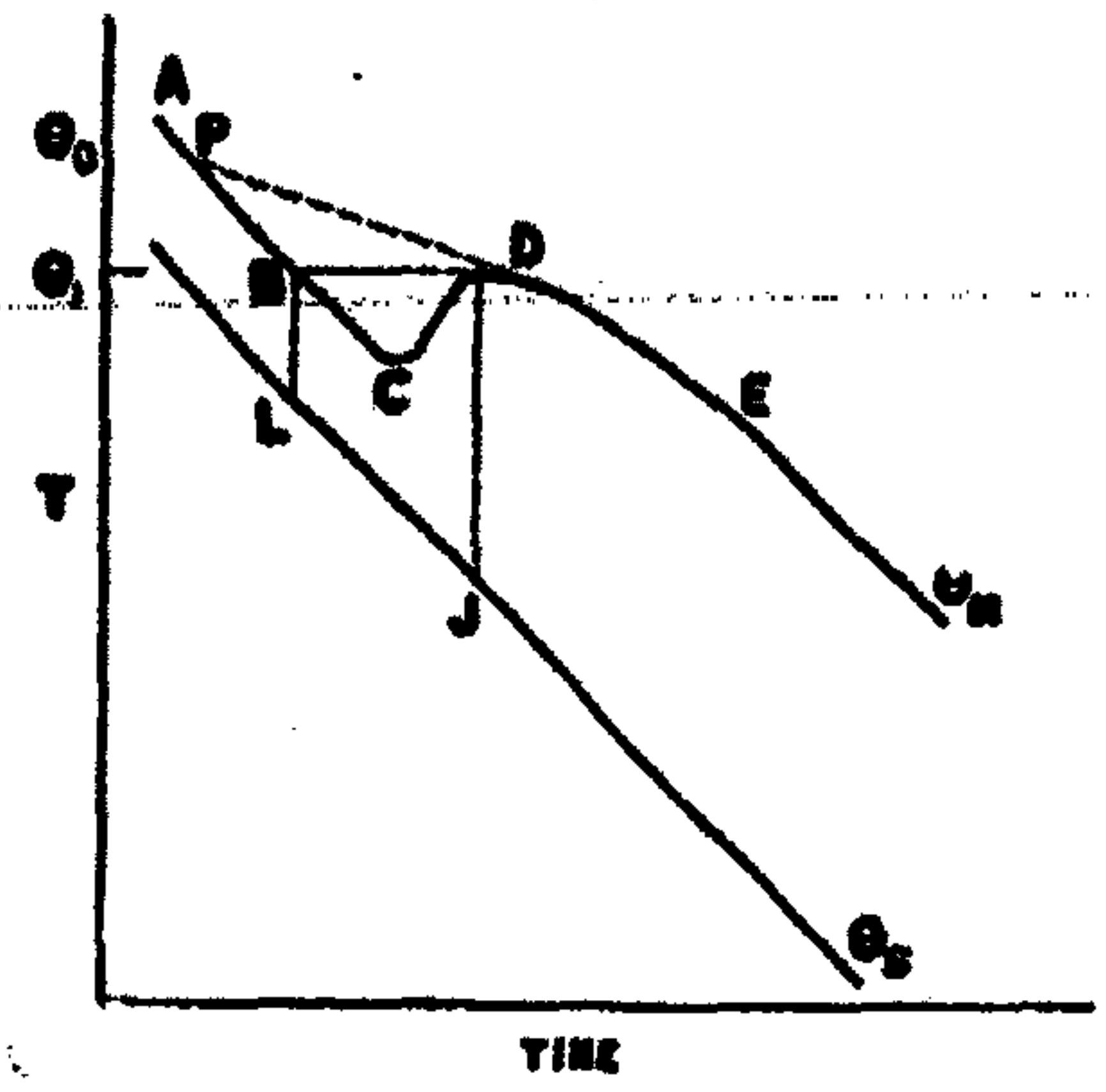

FIG. 3
Typical time-temperature curve for a binary mixture.

In proceeding along the curve from B to D the system passes from solution at Θ_1 to a mixture of solution with n mols solid X, again at Θ_1; and the heat lost by the cooling mixture is nL, where L is the molal heat of fusion of X. But the heat lost is also, as we have seen, proportional to the area BCDJL. Now if, for the given mixture of X and Y, Θ_0 be the real equilibrium temperature—i. e. the temperature at which the first trace of X would tend to crystallize—the system passes from a state of equilibrium at P (Θ_0) through an unstable region to substantial equilibrium again at D (Θ_1). For this small range of composition the equilibrium concentration (solubility) of X is practically a linear function of the temperature; that is, the lowering of equilibrium temperature is proportional to n, the (small) number of mols of X which then have separated. Hence this lowering, namely ($\Theta_0 - \Theta_1$), is proportional to nL and therefore to the area BCDJL (estimated for instance, by counting squares). From this it is clear, in the first place, that by varying slightly the point C at which the mixture is inoculated, both this area and the maximum D (Θ_1) will change correspondingly; and, in the second place, that the several values of Θ_1 plotted against those of the area will lie on a straight line; and, in the third place, that this line extrapolated to zero area corresponds to $n = 0$—that is, the particular point so obtained is the equilibrium temperature Θ_0 corresponding to the known initial composition of the solution.

This method has been used in the determination of the solubility diagram of a number of systems composed of *o*, *m*, *p* isomers—namely, e. g. the chloronitrobenzenes, nitroanilines, dinitrobenzenes and nitrobenzoic acids. Indeed

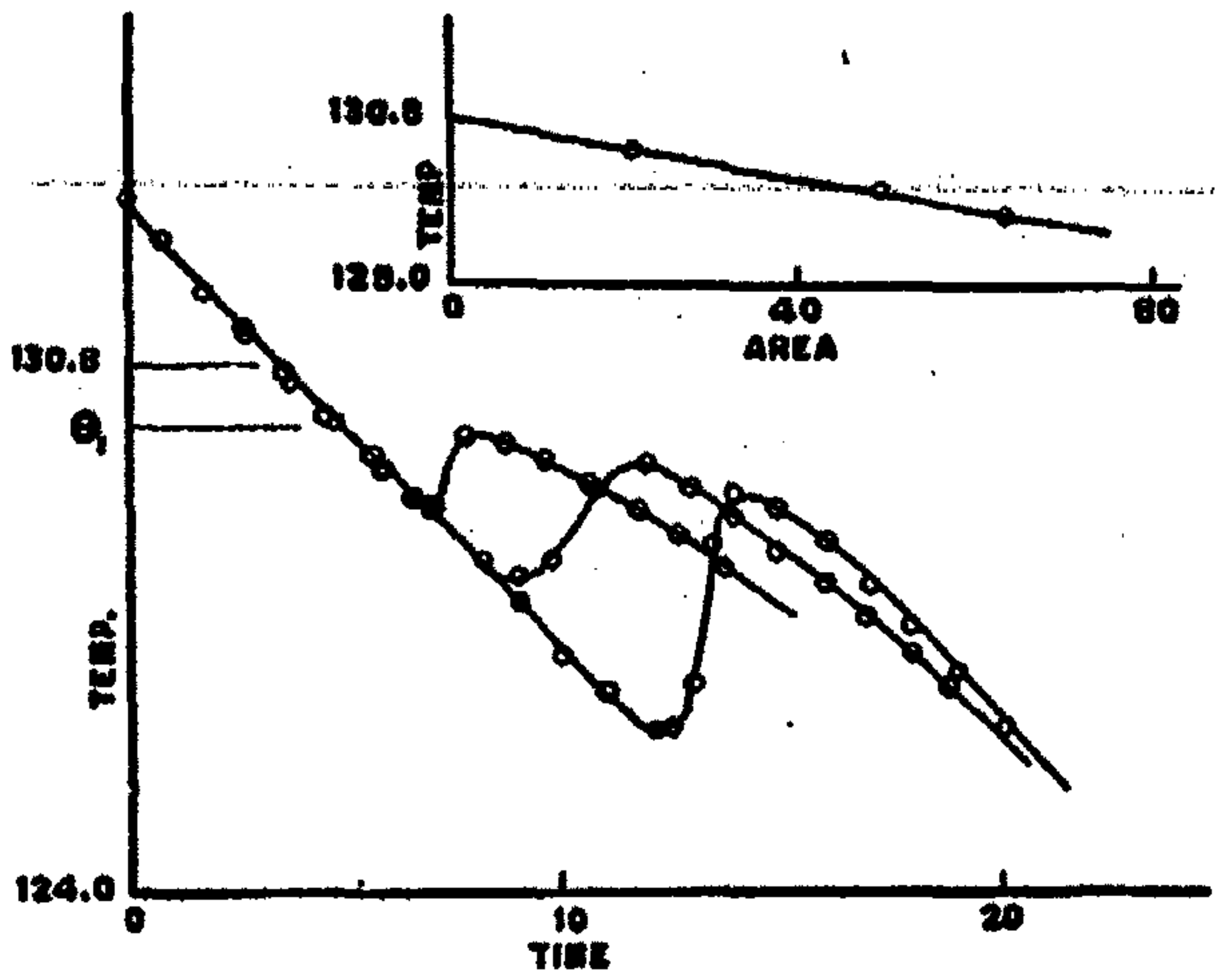

FIG. 4

Shows three actual curves for the same sample, with different degrees of undercooling, superposed; showing that the maximum changes, and that back extrapolation is uncertain. It also shows the graph of area against maximum, leading to a correct extrapolation.

in these cases we have an independent proof of the accuracy of this method of interpretation; for these systems—as will be shown in a later paper—behave as ideal solutions and the solubility curve as calculated on this basis (from the melting temperature, heat of melting and specific heat of the substance crystallizing) coincides with that derived as above from cooling curves. For any given mixture, two or three time-temperature curves usually suffice; three such curves are given, superposed, in Fig. 4, which also shows the corresponding plot of area against maximum temperature. With the apparatus described the error of determination is not more than 0.1° or 0.1% in composition even near the eutectic point. For comparison the error introduced by assuming, as many authors have done, that the maximum temperature Θ_i corresponds to the initial composition may well be 4°, equivalent to 5 - 8 mol per cent in composition.[1]

Another method of interpretation has frequently been used, for instance, by Bell and Herty[2], working with systems similar to ours. It consists in considering the initial portion *DE* of the graph (Fig. 3) to be linear, producing it backwards to meet *AB*, and assuming that this intersection represents the temperature corresponding to the initial crystallization of X from the given solution. Now with different degrees of undercooling, of a single solution, this procedure leads to different values, as is evident from Fig. 4; and is therefore unsatisfactory where accurate results on solubility are desired. Moreover, with solutions initially near the eutectic point, the curvature of the portion *DE* is so great as to render back entrapolation very uncertain, if not impossible. The approximate character of this method of extrapolation has also been remarked in two recent papers[3].

Temperature—Heat Loss Curves

In time-temperature curves the scale of time is arbitrary. The fundamental factor is heat-loss. A temperature - heat loss plot, which has some significant properties, may be constructed as follows. The temperature Θ_m°, taken at some arbitrary time as zero, is plotted on the zero axis of heat loss, as in Fig. 5. The temperature head $(\Theta_m - \Theta_s) = h_1$ is then measured one-half minute later; h_1 is assumed to be the average temperature head for that minute, and consequently the heat loss in that minute is proportional to h_1. The temperature Θ'_m at 1 minute is therefore plotted h_1 units to the right of the zero axis; similarly h_2 is measured in the middle of the second minute and Θ''_m at the end, and Θ''_m is plotted at $h_1 + h_2$; and so on. Now the heat lost by the system in passing from a stable state at one temperature to a stable state at another is always the same; consequently if a second curve of this type, for the same solution, is plotted on the same diagram, with the same temperature as zero point, the two curves will coincide throughout the range of stable states, but not over the unstable range—that is, the central portion of the curve will be different with different degrees of undercooling. This is evident from the series of three such curves reproduced in Fig. 5, which is based upon the same experimental data as is Fig. 4. Now the left hand branch of the curve,—that is, for the liquid—is linear if the specific heat is constant, as over this range it is for practical purposes; and since, as we have seen, the initial lowering of equilibrium temperature is proportional to heat loss, the upper portion of the right hand branch is now also linear. This straight line corresponds exactly to the straight line of the area—maximum temperature plot; and if extrapolated backwards it cuts the left hand branch

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[1] Nevertheless this maximum temperature is, under constant experimental conditions, quite reproducible, and could be used as a calibrated control method for the analysis of mixtures.

[2] J. M. Bell and C. H. Herty, Jr.: J. Ind. Eng. Chem. **11**, 1124 (1919).

[3] A. L. MacLeod, M. C. Pfund and M. L. Kirkpatrick, J. Am. Chem. Soc. **4**, 2260 (1922); C. A. Taylor and W. H. Rinkenbach: **45**, 104 (1923).

at the true equilibrium temperature Θ_0 corresponding to the initial composition of the solution. It was in fact found that both methods of extrapolation yield identical results.

If a time-temperature curve is taken under conditions such that $\Theta_m - \Theta_s$ is very *large*, and hence liable to change by only a few per cent in the course of the curve, then the heat loss will, if Newton's law holds, be nearly proportional to the elapsed time; under these conditions the time-temperature curve is effectively a temperature-heat loss curve, and the method of back extrapolation (as commonly used heretofore) would lead to accurate results. On the other hand, a temperature head large enough to be taken as constant, would in most cases cause the rate of cooling to be too rapid for accurate observation of the actual temperature. Consequently the temperature head is usually in practice small, and hence liable to considerable relative change unless special precautions are taken to maintain it constant. Moreover if the temperature head is small, the portion DE of the Θ_m curve—corresponding to the gradual crystallization—must be more or less parallel to the Θ_s curve[1], hence also to the Θ_m curve before freezing set in; consequently this point of view leads again to the conclusion that back extrapolation can yield only approximate results.

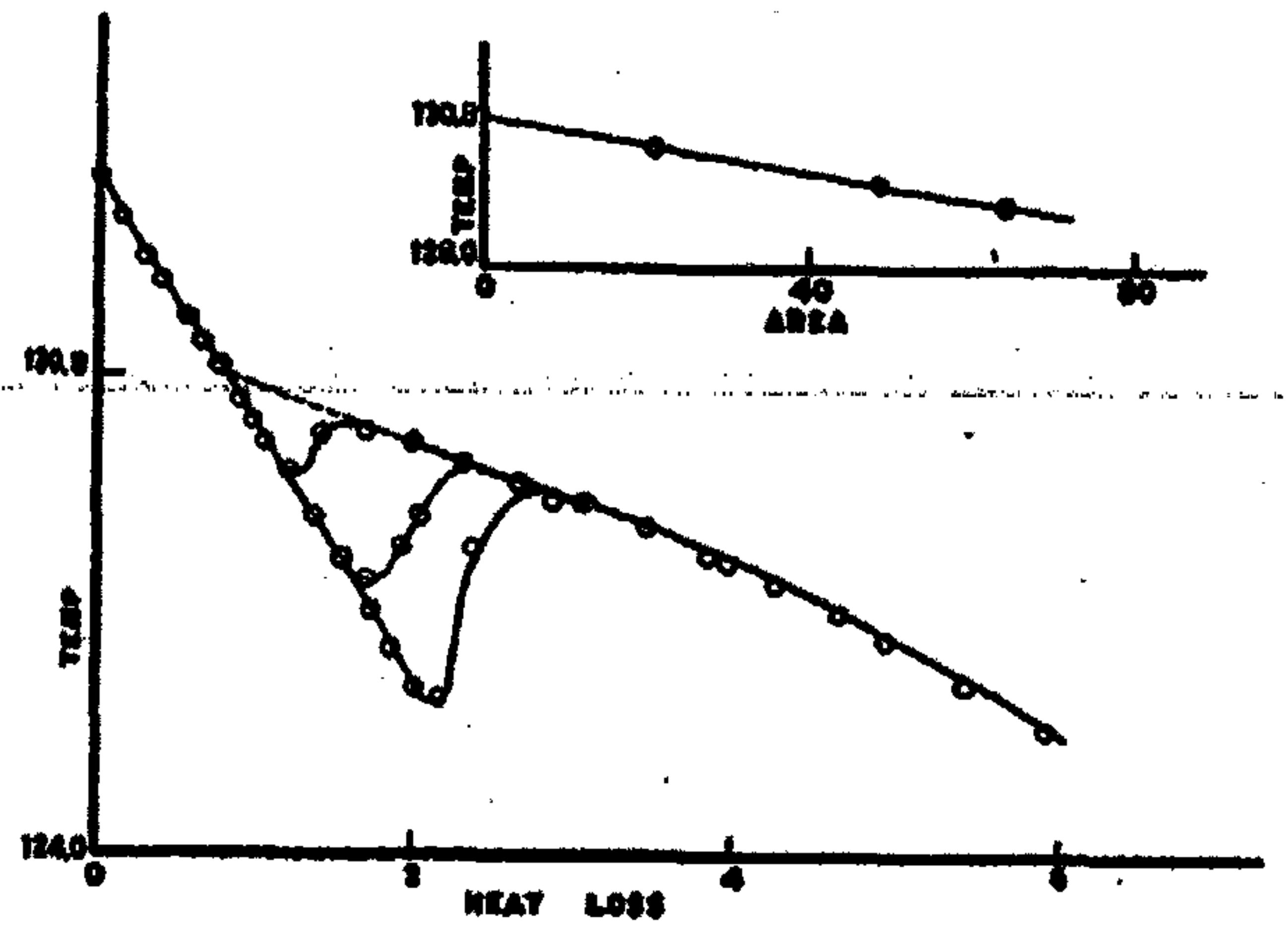

FIG. 5

Shows the same three curves as in fig. 4 plotted in terms of heat loss against temperature; the right hand branch is now a single curve which when produced backwards, leads again to the same extrapolated value.

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[1] That the Θ_m and Θ_s lines must be parallel, if the former is straight, may be proved as follows: The differential equation for heat loss in a cooling binary (or ternary) system from which X is crystallizing, may be written:

$$-\frac{dH}{dt} = C\frac{d\Theta_m}{dt} + L_x\frac{dn}{dt}$$

where C is the heat capacity (assumed constant) of the system, n the number of mols X separated as crystals, and L_x the molal heat of fusion of X. If the Θ_m line is straight, $d\Theta_m/dt$ is constant; for the short range considered, dn/dt is also constant. Consequently dH/dt is constant and hence, from Newton's law, $(\Theta_s - \Theta_m)$ is constant, i. e. the two lines are paralel.

In order therefore to secure an accurate value of Θ_0, the temperature at which X tends first to crystallize, for any given solution, it suffices to take two or three cooling curves on that solution, inoculating it at slightly different temperatures (point C, Fig. 3); to note in each case the maximum temperature Θ_1; to measure (e. g. by counting squares) in each case the area BCDJL; to plot this area against Θ_1 and extrapolate to zero area which corresponds to the true value Θ_0. This method of interpretation is simple, satisfactory and free from the uncertainties which attach to the other methods which have been used for this purpose. Detailed results, obtained in this way, for a series of systems of the *ortho*, *meta* and *para* isomers of disubstituted benzenes will be presented in other papers; and it will be shown that these solubility curves are in very close accord with those predicted, by means of the law of the ideal solution, from thermal data.

Summary

1. A form of apparatus is described which enables one to make accurate time-temperature curves for systems such as the disubstituted benzenes, singly or in binary or ternary mixture. In this set-up, the effective temperature head is controlled and measured; a small quantity only (about 1 cc.) of the material is needed; and its temperature is read by means of a thermoelement of very fine wire, hence of small heat-capacity and small lag.

2. On the basis of Newton's law, which was found to be valid for the apparatus as used, the theory of cooling curves under a controlled temperature head is discussed. This leads to a mode of interpreting the cooling curve of a binary mixture which yields correct results; whereas the methods hitherto generally used for this purpose are inexact and unsatisfactory.

PHOTOSYNTHESIS IN TROPICAL SUNLIGHT

BY N. R. DHAR AND R. P. SANYAL

During recent years Baly[1] and his coworkers have published a series of important papers on photo-chemical transformations analogous to those occurring in plant life. Their researches indicate the possibility of the process first suggested by Baeyer on assimilation of carbon in plants. They have first tried to prove the synthesis of formaldehyde from carbon dioxide and water, and its further polymerisation into reducing sugars on exposing to ultraviolet light. In the subsequent paper they have proceeded to synthesise nitrogenous compounds of carbon by starting from carbon dioxide in water or formaldehyde and a nitrate or nitrite and arrive at results which lead to the possibility of further formation of complex substances. In the third paper they start from formaldehyde and ammonium hydroxide for the formation of higher nitrogenous substances such as proteins and alkaloids. Their results in the first two papers are in line with similar observations of Moore and Webster[2] on the one hand and those of Baudisch[3] on the other; consequently their results agree but not always. Baly and his workers have, however, given little details of their experimental procedure in the first part of their work. In fact, Spoehr's criticism[4] doubting the accuracy of some of the published results, elicited the details[5] of their *modus operandi*. In all their work on the photo-synthesis and photo-catalysis both Moore and Baly have used the mercury vapour lamp as their source of ultraviolet light and have used quartz vessels as the receptacle of their reactants. Moore, who worked extensively on the formation of formaldehyde and reducing sugars by photosynthesis, found that no formaldehyde was formed when water alone, saturated by a stream of carbon dioxide was exposed to bright sunlight in quartz tubes. In the presence of 1% $FeCl_3$, carbon dioxide and water combined in sunlight to give distinct test of formaldehyde with Schryver's reagent, while a similar solution kept in the dark gave negative results and hence Moore concluded that an inorganic transformer is necessary, and that formaldehyde is actually built up by the inorganic colloid absorbing the energy of the sunlight and becoming activated.

Baly, Heilbron and Barker, have succeeded in condensing water and carbon dioxide into formaldehyde by ultraviolet light without the use of any catalyst. Instead of taking a saturated solution of carbon dioxide in water, they have passed carbon dioxide into water in the presence of light from mercury vapour lamp. They are of the opinion that Moore's failure to obtain formaldehyde from solutions of carbon dioxide exposed to sunlight or to ultraviolet light without the presence of an inorganic catalyst is due to the poly-

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[1] J. Chem. Soc., 119, 1025 (1921); 121, 1078 (1922); 123, 185 (1923).

[2] Proc. Roy. Soc. 87B, 165, 556 (1914); 90B, 168 (1918).

[3] Ber. 46, 113 (1913).

[4] J. Am. Chem. Soc. 45, 184 (1923).

[5] Nature, Sept. 1 (1923).

merisation of formaldehyde into carbohydrate as fast as it is formed. While in an agitated solution, some of the formaldehyde formed is carried to the back of the vessel and thus protected from the further action of light. This explanation is open to objection.

Baly and his coworkers further state that the effective light for the formation of formaldehyde has very short wave length, i. e., 200 $\mu\mu$ and for the formation of sugars, 290$\mu\mu$. They have been definite in their assertion that there are present in sunlight no rays of the very short wave lengths necessary for the direct photosynthesis of formaldehyde and in their photocatalysts[1] they state that no reaction takes place if ammonia saturated with carbon dioxide is exposed to ultraviolet light in glass tubes behind a screen of plate glass.

In spite of these assertions, it is idle to dismiss sunlight off hand, as incapable of photosynthesising reactions which are generally occurring in plant life where sunlight is the only source of illumination. The decomposition of ozone by light gives us a case in support of our contention. Weigert[2] employed ultraviolet light and found that the effective deozonising region for the photochemical decomposition of ozone was in the neighbourhood of 254$\mu\mu$. It was known that in the presence of chlorine light of longer wave length, e. g., that of the blue and violet portions of the spectrum would cause the decomposition. Griffith and Shutt[3] showed that by the light of the carbon arc projection lamp consuming 30-35 amp. at room temperature ozonised oxygen is deozonised by the action of visible light of wave lengths between 760 to 670$\mu\mu$ and 615 to 510$\mu\mu$. Thus the older theory that ultraviolet light alone was responsible for deozonisation falls flat. To our mind similar doubts exist about the correctness of the statement of Baly and his coworkers, about the failure of sunlight in formaldehyde synthesis. A number of experiments were therefore carried out by us during the last two years throughout in glass vessels and tropical sunlight. In some cases the reacting mixtures were sealed in thin glass tubes and exposed to sunlight. In other cases the solutions under examination were placed in the sun in glass beakers or evaporating dishes, or else in wide-mouth boiling tubes, carbon dioxide was passed in a number of solutions for a whole day in the sun. The rapidity with which the solutions in open vessels evaporated made it difficult to expose the same solution to the sun for a very great length of time.

The well-known chemical tests (given in Tognoli's "Reagents and Reactions") were applied in all cases. Benedict's solution was used for detecting sugar and not Fehling's solution as formaldehyde itself reduces Fehling's but not Benedict's. Control blank tests were carried on side by side to ensure correctness of results. Wherever possible the solutions were distilled before testing for formaldehyde. The melting point determination and the microscope were also utilised to examine the various nitrogeneous products. In Table I are given the results of the experiments carried on in the sunlight.

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[1] J. Chem. Soc. **123**, 185 (1923).

[2] Z. physik. Chem. **80**, 78 (1912).

[3] J. Chem. Soc. **123**, 2752 (1923).

TABLE I

A. *Experiments in Sunlight:—*

(a) formation of formaldehyde.

Experiment	Time of Exposure	Results
CO_2 passed in water	1 hour	traces of formaldehyde obtained.
Do	6 hours	formaldehyde obtained, no sugar.
Do + methyl orange (catalyst)	Do	Do
Do + methylene blue	Do	Do
Do + chromium salt	Do	Do
Do + uranyl nitrate	Do	Do
Do + copper sulphate	Do	Do
Do + $FeCl_3$	Do	Do, ferric salt reduced.
Do + colloidal $Fe(OH)_3$		Do
Water saturated with CO_2 in a sealed tube	90 hours	traces of formaldehyde obtained.
Do + colloidal ($Fe(OH)_3$ in a sealed tube	90 hours	Do, no sugar
A sealed tube containing CO_2 saturated in water placed into another tube containing chlorophyll solution.	75 hours	formaldehyde, no sugar.
Paraldehyde solution + CO_2 in a sealed tube.	36 hours	Formaldehyde, no sugar.
CO_2 passed in chlorophyll extract in a beaker.	6 hours	Formaldehyde in the distillate.
$NaHCO_3$ solution in a beaker	18 hours	Do, in the distillate.
Glucose solution	30 hours	No formaldehyde in the distillate, no sugar.
Cane sugar solution	Do	Do
$K_2C_2O_4$ solution	Do	Do
$H_2C_2O_4$ solution	Do	Do
$H_2C_2O_4$ + ferrous ammonium sulphate solution.	Do	Formaldehyde formed.
Do + uranium salt	Do	Do
Sodium tartrate solution	Do	Do
Sodium citrate solution	Do	Do
Methyl alcohol in water	6 hours	Do
Glycerol in water	30 hours	Do
Acetone in water in a sealed tube	90 hours	Formaldehyde and sugar obtained.
Chlorophyll in water	8 hours	Formaldehyde formed.
Chlorophyll in alcohol + $FeCl_3$	8 hours	Do

TABLE I (continued)

Experiment	Time of Exposure	Results
Oxygen passed in methyl alcohol and water	1 hour	Do
(b) formation of sugar.		
HCOH in water in a basin	5 hours	No sugar, no formic acid.
Do	25 hours	Do, only paraformaldehyde
HCOH in water and CO_2	5 hours	No sugar.
HCOH + $FeCl_3$ in water	12 hours	Sugar obtained.
HCOH + Ni, Co, Cr or Cu salts.	12 hours each	No sugar in any case.
HCOH + aluminum salt, $KMnO_4$, H_2O_2 or cerium salt.	12 hours	No sugar.
HCOH in water in sealed tube	90 hours	No sugar.
HCOH + oxalic acid	Do	Do
HCOH + $Fe(OH)_3$ colloid	12 hours	Do
(c) Formation of Nitrogenous Compounds.		
KNO_2 + HCOH solution in a beaker.	50 hours	A yellowish colour developed. No form-hydroxamic acid.
Do, in a sealed tube	100 hours	Oxygen gas, traces of KNO_3 formic acid, reducing sugar obtained.
$KNO_3 + CO_2$ + water	110 hours	Nitrite formed. No sugar, no formaldehyde, no form-hydroxamic acid.
$NH_4OH + H_2O + CO_2$ in a beaker.	5 hours	Traces of nitrate and nitrite. No amine, no urea.
$NH_4OH + CO_2$ + HCOH in a beaker	20 hours	Methylamine. M. P. of hydrochloride 195°. No pyridine.
NH_4OH + HCOH + $CuCO_3$ in a beaker.	80 hours	An amine, an alkaloid obtained. No nitrite, nitrate or sugar.
(d) Other Reactions.		
NH_3 gas + O_2 in sealed tube	150 hours	Nitrogen formed.
NH_4OH solution + O_2	6 hours	Nitrite formed.
Do	6 hours in diffused light.	Do
HIO_3 solid in a sealed tube	10 hours	Iodine formed.
HIO_3 solution	10 hours	No iodine formed.
KNO_3 solution	2 hours	KNO_2 formed.
$KClO_3$ solution	30 hours	Traces of KCl formed.

TABLE I (continued)

Experiment	Time of Exposure	Results
CS_2 in a sealed tube	4 hours	Slightly decomposes and becomes orange-red; longer exposure makes it black due to the separation of carbon.
Chloral hydrate.	10 hours	Partly decomposes into a soluble chloride.
Oxygen passed through aqueous alcohol.	1 hour	Formation of acetaldehyde.
B. *Experiments in Ultraviolet Light from a Quartz Mercury Lamp.*		
CO_2 passed in water in a beaker.	1 hour	Traces of formaldehyde.
Water saturated with CO_2 in beaker.	1 hour	Traces of formaldehyde (greater than the previous one)
Dilute HCOH in a basin	Do	No sugar.
Do, in a sealed tube.	Do	Do
HCOH containing $Fe(OH)_3$ colloid.	2 or 3 hours	No formation of sugar.
HCOH in water	Do	Do
Do + $FeCl_3$	Do	Do
Do + $NaHCO_3$	Do	Do
Glycerol + H_2O	Do	Appreciable quantity of sugar and formaldehyde formed.
Air freed from nitrites by passing through $FeSO_4$ solution was bubbled through conductivity water.	Do	Traces of nitrite obtained.

While these experiments were being carried on the solar spectrum was examined with a Rowland's grating on a specially sensitised film. It was found that there existed no line in the spectrum of wave length less than $290\mu\mu$. Thus from the results of our experiments where we have definite proof of the synthesis of formaldehyde from carbon dioxide and water with or without the use of any organic or inorganic catalyst, we can safely say that Baly's statement that there exists in sunlight no rays of very short wave length capable of carrying out this particular synthesis is not quite correct. We are of the opinion that the intensity and prolonged exposure have much to do with this photosynthesis of formaldehyde in sunlight.

Weigert[1] in a theoretical paper has shown that supposing according to Thienberg[2] the following scheme represents the photosynthesis of formaldehyde,

$$2\,H_2O = H_2 + H_2O_2 - 92000 \text{ cal.}$$
$$CO_2 + H_2 + H_2O_2 = HCOH + H_2O + O_2 - 18000 \text{ cal.}$$

then in this reaction the light energy 2 Nhν is necessary. Calculation shows that in this case light rays of wave-length 517$\mu\mu$ are effective and that the radiation is transformed completely into chemical energy, in the presence of chlorophyll. This chlorophyll in this case is supposed to transfer the light energy in effecting the decomposition of water into H_2 and H_2O_2. Were this correct, evidence would have been found of the decomposition of H_2O in sunlight alone in presence of chlorophyll. This result has not yet been observed but seems to be likely. We have frequently observed that many of the experiments giving negative results show that a positive result can only be obtained under very favourable circumstances when the intensity of light is very great and the exposure has been sufficiently long. Formaldehyde which could be detected in a solution of carbon dioxide in water when exposed to the sun for a little more than an hour on an intensely lighted day, could not be obtained when a similar solution was exposed to six hours on a dusty or cloudy day. The experiments giving positive results in March or April are difficult to reproduce in November or December.

Though we have got definite evidence of the formation of formaldehyde from carbon dioxide and water, in the synthesis of sugar we have not yet been so successful. But here too we are compelled to doubt Baly's statement that sugar is synthesised by radiation of wave length 290$\mu\mu$. For in this case wherever formaldehyde is formed according to Baly, sugar ought to be also formed. Heilbron[3] has rather modified the theory first put forward by them in 1921, that in the process of carbon assimilation there are two definite stages i. e. an activated formaldehyde is first formed and then it polymerises into reducing sugar. They believe that this two-step theory is not quite tenable. But what they put forward now is that as soon as formaldehyde is formed, it is transformed into sugar and this redecomposes into formaldehyde of which we get the tests. This modification of their views is quite in accordance with Moore's statement that all compounds of biological origin decompose into formaldehyde when exposed to light. Without doubting Moore's results, we are inclined to view the previous theory of two stages as put forward by Baly as more probable. That formaldehyde is not at once polymerised into sugar we can safely say. Only twice did we get any trace of sugar when formaldehyde was exposed to the sun in presence of $FeCl_3$ and methyl orange in dilute solution.

Oxidation in Sunlight. Sunlight is very effective in helping oxidation. Thus we have found that ethyl and methyl alcohols are oxidised to the respective

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[1] Z. physik. Chem. 106, 313 (1923).

[2] Z. physik. Chem. 106, 3c6 (1923).

[3] Nature, April 14 (1923).

aldehydes. When air or oxygen is passed into the solution, ammonia gives easily tests for nitrites even in diffused light. NH_3 and O_2 when exposed in sealed tube for a long time are completely decomposed into N_2. Glycerin gives a coloration with Schiff's reagent if oxygen is passed into it for a day in bright light.

These results in oxidation are interesting in view of the previous results obtained by Mittra and Dhar[1] in the induced oxidation of methyl alcohol, ethyl alcohol, glycerin, etc., in presence of sodium sulphate or ferrous hydroxide by passing air or oxygen through the mixture.

In the above reactions light behaves as an inductor or a positive catalyst.[2]

The reducing nature of sunlight is no less apparent, HIO_3 solid gives I_2; $KClO_3$ gives traces of KCl; KNO_3 solution easily breaks into KNO_2; $FeCl_3$ solution is reduced by passing carbon dioxide, dilute formaldehyde reduces $FeCl_3$ solution.

The influence of catalyst such as colloidal ferric hydroxide or uranium hydroxide or methyl orange is not very clear. Though formaldehyde formation is in general helped by organic and inorganic catalysts, the best of which is chlorophyll, their action on the formation of sugar is not so marked. It seems the intensity of light is of more importance in such cases than the presence of the catalyst. Even when we have used ultraviolet light, the influence of the catalyst in sugar synthesis has not been marked. Hence it is difficult to assert with Moore, whether the catalytic change is a surface action in which the light energy is converted into chemical energy at the surface of the colloidal aggregate or whether each catalyst absorbs selectively those rays which polymerise formaldehyde into sugars. Ferric chloride which Moore has found to catalyse the reaction between water and carbon dioxide to form formaldehyde, was found by us to help in the production of reducing sugar when formaldehyde and ferric chloride were exposed in solution together.

Ultraviolet light is undoubtedly more effective in certain photosyntheses. But tropical sunlight, particularly from April to July when its intensity is at its highest, contains a number of rays which under ordinary circumstances, can effect synthesis of complex compounds from very simple compounds. Especially in the case of alkaloids, the experiments show conclusively that there is a tendency in the photochemical transformation to pass from simple and lower order of combinations to the higher and complex organic compounds. Methylamine, which is formed in about 12 hours in tropical sunlight when ammonia and formaldehyde solution are exposed, passes into a number of complex nitrogenous substances akin to alkaloids, one of which Baly claims to have identified as coniine but not confirmed by our experiments.

A further conclusion may be drawn that in the synthesis of natural nitrogenous compounds, the origin of nitrogen may either be ammonia or a nitrate. Potassium nitrate gives potassium nitrite and so does ammonium hydroxide

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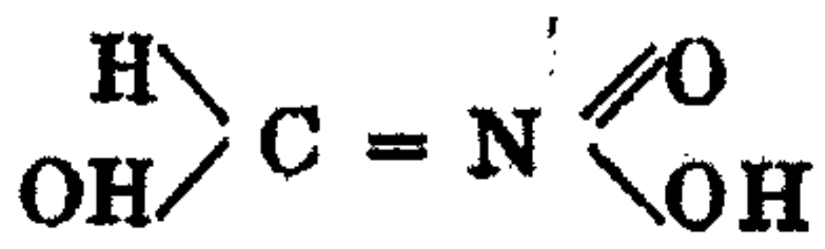
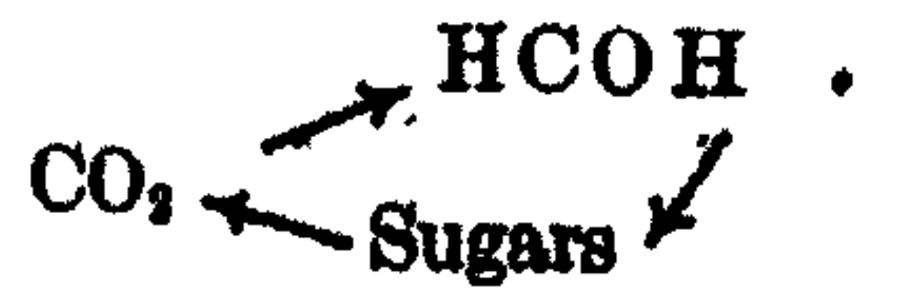
[1] Z. anorg. Chem. 122, 146 (1922).

[2] Compare Dhar: Proc. Akad. Wet. Amsterdam, 18, 1097 (1916).

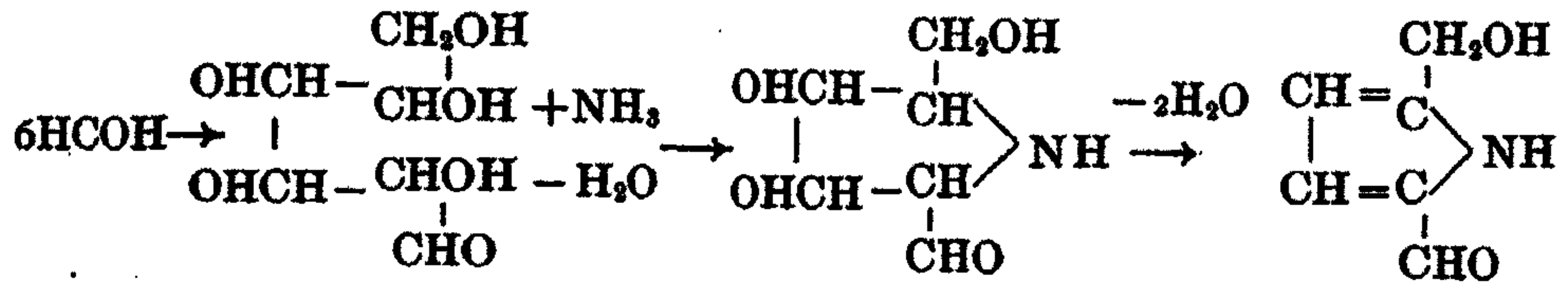
give ammonium nitrite on exposure. Ammonium salts, amines, and even carbanide break up into ammonia and then into a nitrite. This transformation of ammonium hydroxide into amines and also nitrites complicate the final products which necessarily depend on the amount of exposure. The failure in our experiments to detect form-hydroxamic acid  ${}^{H}_{OH}{>}C = N{<}^{O}_{OH}$ in nitrite and formaldehyde reaction can perhaps be explained by the fact of Baudisch's observation, that formhydroxamic acid on further exposure to light is reduced to ammonia. Thus we can start from potassium nitrite to get ammonia, either of which substance can be utilised as a source of nitrogen for plant life.

Our experiments with ultraviolet light show that nitrogen and oxygen can directly combine in its presence to form higher oxides or nitrogen. We are of the opinion that the same change can also take place in tropical sunlight. The experiments are likely to throw a flood of light on the nitrogen assimilation by plants.

Another series of photochemical transformation was first indicated by Moore, that all substances of biological origin give formaldehyde on exposure to light. Or as Baly suggests that an equilibrium is set up between



Stewart[1] has indicated a line which is perhaps more analogous to what actually occurs in photosynthesis in the plant life. Starting from sugar and ammonia,



we can get a pyrrole derivative by the simple process of dehydration. By a similar process we can theoretically arrive at alkaloids where the light would be helping by dehydrating and rehydrating the intermediate compounds. Form-hydroxamic acid, which according to Baly is the first step to complex nitrogenous photosynthesis, is perhaps the origin of ammonia which acting on the carbohydrates leads to the formation of further highly complex substances. Ammonia and formaldehyde can form aci-nitromethane (according to Baudisch) and this is a very reactive substance which at once undergoes

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[1] "Recent Advances in Organic Chemistry," 258 (1918).

further transformation specially in the presence of many catalysts which are present in plants, the nature of which is difficult to elucidate. It is yet too premature to declare with any degree of certainty what lines the actual photosynthesis in nature follow to produce the simplest of vital products. But from our experimental results we conclude that the difference between sunlight and artificial ultraviolet light is one of degree and not of kind.

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THE RATE OF REPRODUCTION OF LEMNA MAJOR AS A FUNCTION OF INTENSITY AND DURATION OF LIGHT[*]

BY NORMAN ASHWELL CLARK

In the course of a study[1] of certain plant growth stimulants of organic nature which occur in soil, manure, etc., the need arose, during the winter months, for conditions which should be more favorable for the growth of plants, especially with regard to light, than those obtained from sunshine. Attention was therefore given to the cultivation of Lemna major under electric light.

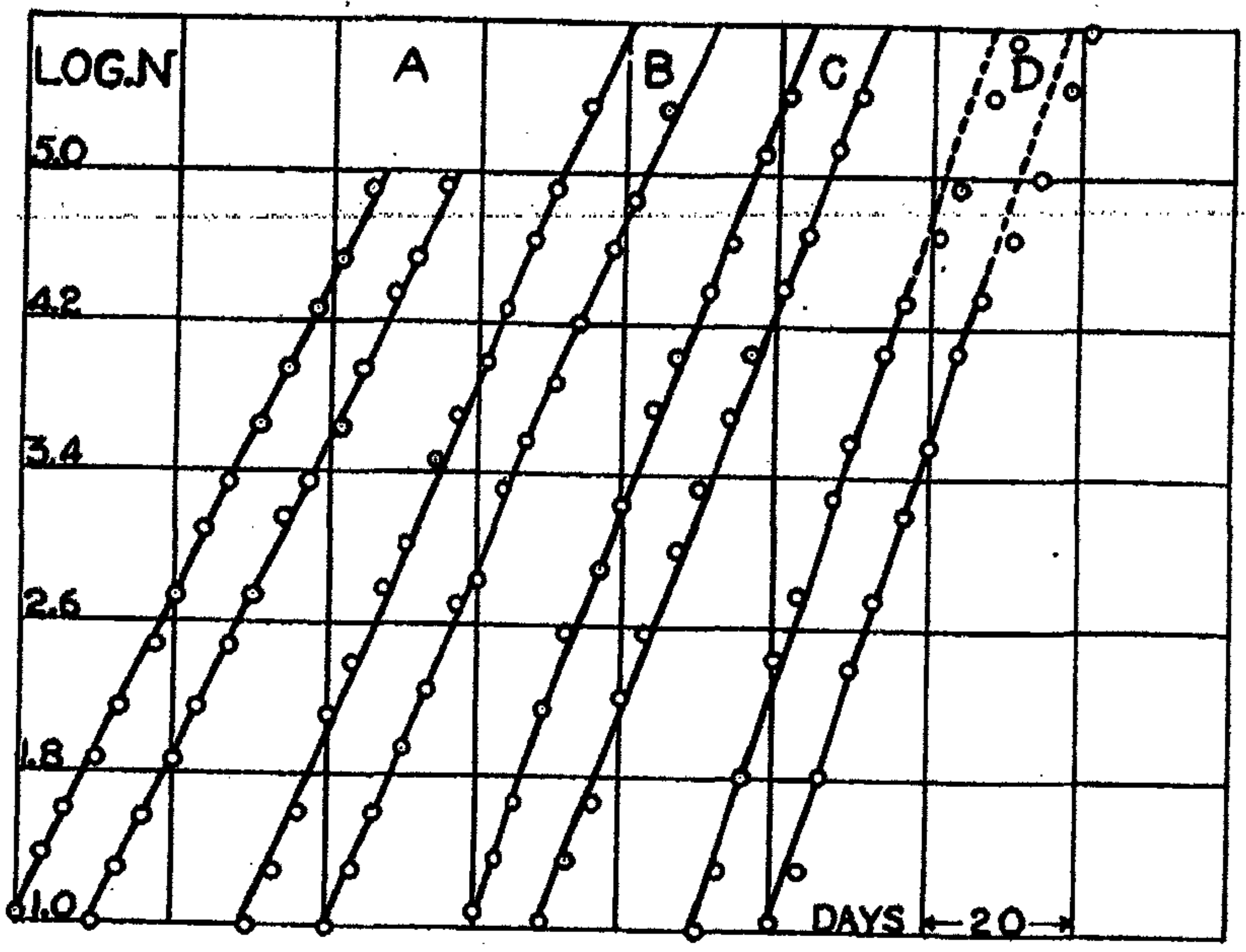

FIG. 1

Reproduction of Lemna with varying length of day. 900 footcandles. Cultures in duplicate. Each square represents 20 days. A - 12 hours light. K = 0.085. B - 15 hours light. K = 0.093. C - 18 hours light. K = 0.107. D - 24 hours light. K = 0.125.

The Lemna used in the following experiments had been grown continuously for more than a year in a medium composed of inorganic salts without organic matter, and the size, general health and appearance of the plants were excellent. The continued growth in the salt solution, as previously pointed out[2] indicates that Bottomley's 'auximones' cannot be considered essentials for plant development:[3] nevertheless, an increase in the growth of many plants

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[*] Contribution from the Department of Chemistry, Iowa State College.

[1] Clark: Ind. Eng. Chem. 16, 249 (1924).

[2] Clark and Roller: Soil Science, 17, 193 (1924).

[3] Bottomley: Proc. Roy. Soc. 88B, 237 (1914); Ann. Bot. 34, 345 (1920).

occurs in water cultures when organic matter from soil is added[1] and investigations as to the function and nature of the stimulating agent are in progress in this laboratory.

Interest in the use of electric light for the growing of plants is increasing. The early work was done with the arc light. Siemens[2], in 1880, reported good growth with many fruits when the light was covered with a glass globe and used as an addition to daylight. Growth proceeded to maturity under continuous illumination. Déherain[3] however, failed to get seedlings to grow to maturity by the use of electric light only, although full grown plants were maintained for two months with no other illumination. Bailey[4], at Cornell, supplemented daylight with the arc light and concluded that it was not true that plants needed alternating day and darkness, and that plants did not become worn out because of the stimulating influence of continuous light. He also attempted to find the effect of color screens, but his results here were inconclusive. Bonnier[5], in 1895, in a study of the influence of continuous electric light on the structure and form of plants, found he could not grow every plant in this way but that many were able to adapt themselves to the new environment: of the latter, the water plants showed the smallest modification due to the electric light.

More recently Gardner and Allard[6] reported that the length of day was a factor of the first importance in the growth and development of plants, some species needing a long day of light and some a short period in order to attain the flowering and fruiting stages. The rate of growth was found to be directly proportional to the length of daily exposure to light, but light intensity, within the range of full normal sunlight to a third or fourth of the normal or even less, was not a factor of importance. The length of the winter day, increased eight hours by a low intensity of light, was sufficient to give vigorous growth with a number of plants when the controls remained practically dormant. In a further study Gardner, Bacon and Allard[7] found the light period influenced the acidity of the cell sap and the form of carbohydrates present in the plant. McClelland[8] reported that the same 'photoperiodism'—the influence of the length of day—existed in plants in the tropics. Harvey[9] did not find this effect when using artificial light altogether and allowing no sunlight to reach the plants. He grew wheat, oats, barley and a number of other plants by the use of Mazda lamps from 200 to 1000 watts and found that with the continuous light he could obtain flowers and seeds for a large variety.

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[1] Livingston: Bur. Soils Bull. 36, (1907); Mockeridge: Biochem. J. 14, 432 (1920).

[2] Proc. Roy. Soc. 30, 210, 293 (1880).

[3] Ann. Agron. 7, 551)1881).

[4] Cornell Agr. Exp. Sta. Bull. 30; 42; 55 (1891-3).

[5] Rev. gén. Botanique, 7, 241 (1895).

[6] J. Agr. Res. 18, 553 (1920); 23, 871 (1923).

[7] J. Agr. Res. 27, 119 (1924).

[8] J. Agr. Res. 28, 445 (1924).

[9] Bot. Gaz. 74, 447 (1922).

In a report of the experiments carried out at the Boyce Thompson Institute for Plant Research[1] it is noted that the tomato grew faster and made better plants as the daily illumination increased from 5 to 17 hours, but that 19 hours was injurious and constant illumination killed the plants.

Little work has been reported on the application of electric light to plants grown in culture solutions, so that the effect on assimilation, growth and reproduction when the composition of the medium is varied is almost unknown. Lemna major, which belongs to the duckweed family and is an aquatic plant, is admirably adapted for study of this effect in nutrient solutions.

The culture solution consisted per liter of 16 mg. of calcium added as monocalcium phosphate; 313 mg. of potassium as KNO_3; 24 mg. of magnesium as $MgSO_4$, with iron as $FePO_4$, made up as described in the Plan for Cooperative Research of the National Research Council, to give 0.6 mg. of iron per liter. The water used was three times distilled; the ordinary laboratory distilled water was treated with alkaline permanganate and redistilled, and this was distilled a third time in an all pyrex glass apparatus, the steam passing through two traps before being condensed.

The Lemna were grown in 250 cc. pyrex beakers which were covered with Petrie dishes to prevent the entrance of dust. Each beaker contained 250 cc. of the solution and this was changed twice a week. When the plants became crowded, from 10 to 20 were left and the remainder discarded. The beakers were placed in a water bath kept at 25 degrees C., although this varied as much as 2 degrees; the water was just low enough to allow air access under the Petrie dishes. The air over the bath was replaced constantly by means of a pump and the temperature varied from 30 to 35 C. with the intensity of the light.

Lemna major reproduces by budding; the mother and daughter fronds separate and both bud again. When conditions are suitable for growth and are kept uniform, the rate of increase at any time is proportional to the number of plants present: that is, where N is the number of plants at any time t,

$$dN/dt = kN$$

and $$\int dN/N = \int kdt$$

whence $$\log_e N/N_o = k(t - t_o)$$

or $$\log_{10} N/N_o = K(t - t_o)$$

When the log. of the number of plants is plotted against time the result is a straight line with slope K, from which the average time for a plant to reproduce itself—the generation time or G. T.—can be obtained.

$$G.\,T. = \frac{\log_{10} 2}{K} = \frac{0.3010}{K}$$

Preliminary attempts to grow the Lemna under electric light, both in soil and artificial cultures, by Mr. H. W. Wright and the author, resulted in

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[1] Science, (2) 60, No. 1560.

reproduction with as low an intensity of light as that given by a 75 watt Mazda lamp at 12 inches from the plants. An increase in the rate of growth was noted with increasing light intensity.

Two sets of reproduction curves were obtained by using 600 and 1500 watts from Mazda C lamps of 300 watts at 15 inches from the filament to the plants. These gave average illuminations of 400 and 900 footcandles at the surface of the solution. The beakers were moved to different places each day to minimize the variation in the light. The intensity was measured with a Macbeth Illuminometer by Professor Kunerth of the Physics Department, to whom my thanks are due. Mr. A. C. Bailey, using the lithopone method for measuring ultra-violet light[1] found no darkening of the lithopone, indicating the almost total absence of ultraviolet light. Cultures in duplicate were exposed to the light for 12, 15, 18 and 24 hours for each intensity. Table I gives the constant K and the Generation Time for each set, and Figure 1 shows the curves for the 900 footcandles.

TABLE I

Reproduction of Lemna major with varying light.

Hours exposed to light - per day	400 Footcandles		900 Footcandles	
	K	G.T.(days)	K	G.T.(days)
12	0.073	4.1	0.085	3.5
15	0.081	3.7	0.093	3.2
18	0.087	3.4	0.107	2.8
24	0.101	3.0	0.125	2.4

In both sets, the increased length of day at first quickened the rate of reproduction—the longer the illumination, the greater the speed—but the 24 hour exposure soon affected the health of the plants; their color became lighter and from a deep green waxy appearance they changed to a yellow green, in many cases almost transparent; the size also decreased and the plants seemed unable to separate, until after about three weeks there was a distinct drop in the rate of reproduction. The slower growth, as well as a slight change in color, was seen to a smaller extent with the 18 hour exposure, but was not observed in the plants given 15 hours light; these continued to reproduce at the same rate, and color and general health was excellent.

When the constant K is plotted against the time of exposure, the rate of reproduction is seen to be directly proportional to the length of time the light was supplied. This is the case for both the 900 and 400 footcandles. It will be noted also that the slope of the curve for the higher intensity is steeper than for the lower, showing that the extra light is utilized by the plant. It should be pointed out, however, that there were slight differences in the conditions of the two experiments e. g. a small variation in the temperature of the water bath and the air above the beakers. Figure 2 shows the constant K plotted against the time of exposure for both 900 and 400 footcandles.

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[1] J. H. Clark: Am. J. Physiol, 69, 200 (1924).

Renewal of Medium.

The increase in the number of plants with the 24 hours illumination was greater than the increase found in summer with all the daylight possible and direct sunlight during the afternoon[1].

Under the electric light there were indications that the solution altered sufficiently, during the 3.5 days which elapsed between changes, to retard the rate of reproduction when the beakers were nearly full of plants. To test this a series was run in which the time of renewal of the solution was varied. Results showed that changing every 12 hours gave an appreciable increase in the rate of reproduction, and that there was a gradual slowing down of the speed as the length of time increased during which the plants were kept in the solution without changing. In the three cases where the solutions were changed every 4, 5, and 6 days respectively, the Lemna became very light colored and looked unhealthy.

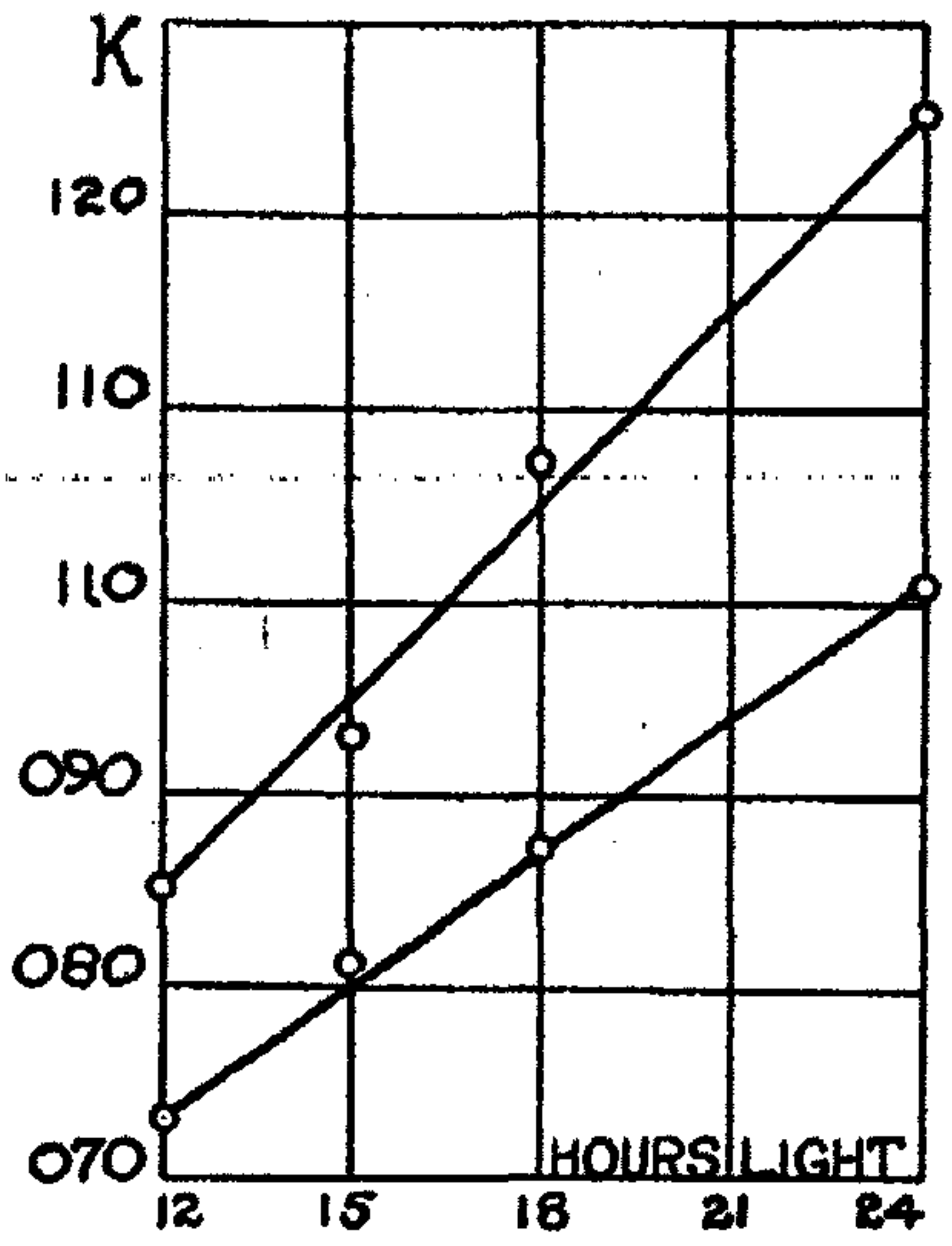

FIG. 2

Rate of reproduction and daily illumination.

The upper curve shows K for 900 footcandles and the lower curve K under 400 footcandles with light supplied from 12 to 24 hours a day.

Variations of Medium.

As the availability of the iron in $FePO_4$ has been questioned, ferric chloride and ferric nitrate were supplied separately in the same basal medium in place of the phosphate. The chloride, which had an optimum concentration near 0.6 mg. of iron per liter when under the 900 footcandles for 15 hours, was found better than either nitrate or phosphate. The color of the plants grown in solutions containing the chloride was slightly darker green and there was a small increase in size. Higher concentrations than 0.6 mg. per liter slowed the reproduction. The plants grew well with the iron supplied as nitrate but were not better than with phosphate

Advantage was taken of the fact that renewal of the medium every 12 hours produced better growth, in order to obtain healthy plants with 24 hours continuous light. Cultures were made with iron as phosphate, nitrate and chloride, and the solution changed every 12 hours. In each case the amount of iron supplied was 0.6 mg. per liter. The Lemna were grown with the average illumination of 900 footcandles and given the 24 hours light. The plants were counted daily.

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[1] Clark and Roller: Soil Science, **17**, 193 (1924).

All three cultures reproduced much faster than in any other case—the constant K for the medium containing chloride being the highest obtained. Table II shows K and the generation time, and the graphs are given in Figure 3.

TABLE II

Rate of Reproduction of Lemna with 900 Footcandles for 24 Hours.

	K	G. T. (days)
Iron as phosphate	0.161	1.9
Iron as chloride	0.178	1.7
Iron as nitrate	0.167	1.8

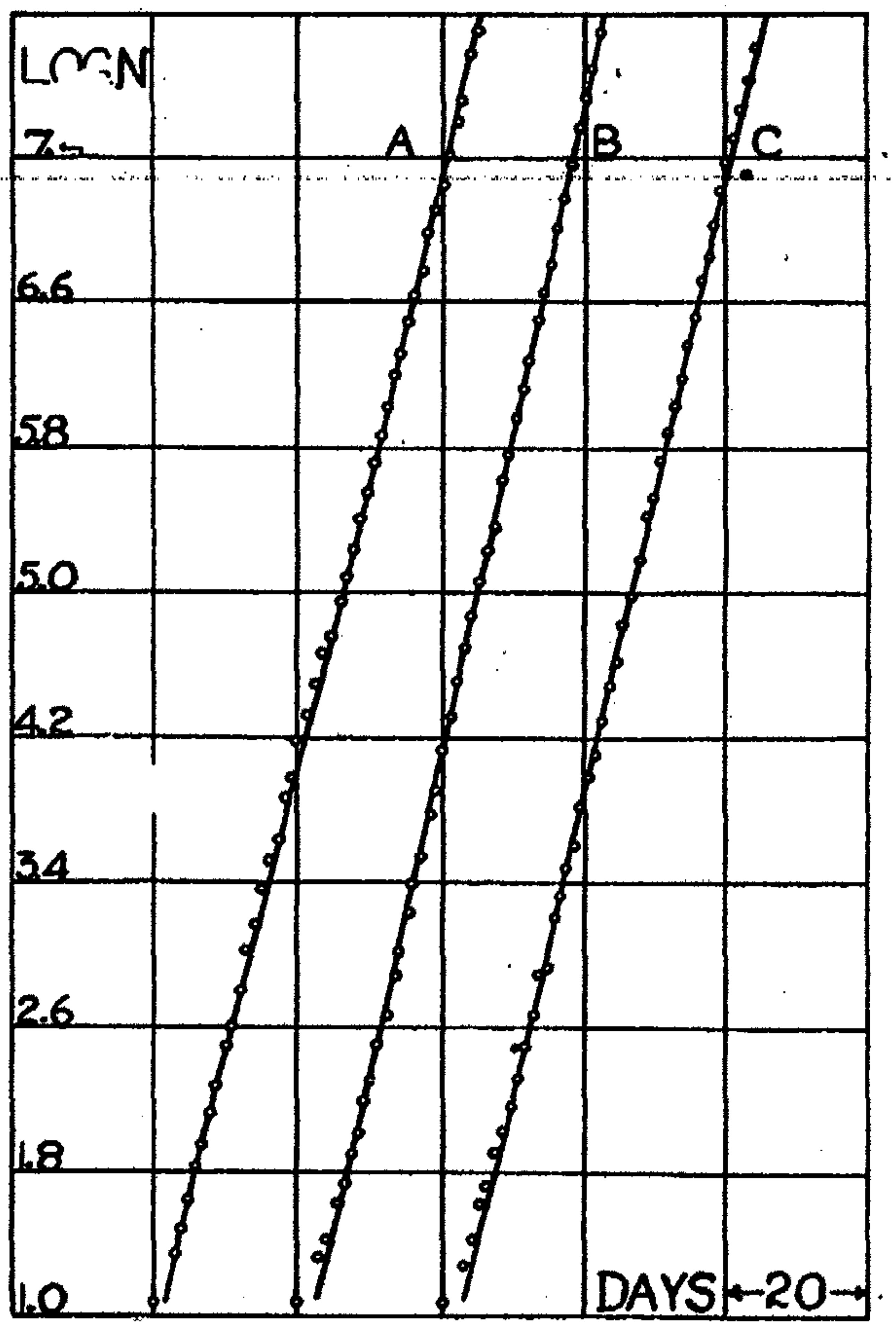

FIG. 3

Reproduction curves with continuous illumination.

Average intensity of light 900 footcandles. Log. of the number of plants against the number of days. Each square represents 20 days. A. Iron as phosphate—K 0.161. B. Iron as chloride—K 0.178. C. Iron as nitrate—K 0.167.

At the end of 8 weeks the rate had not varied and all plants were healthy. The cultures containing nitrate and phosphate showed an occasional brown tip, but the plants in the chloride solution were uniformly green, although not so dark as when grown with 15 hours light. The difference in the rate of growth is not large, but is confirmed by the fact that in all cases, however the length of day was varied or the intensity of light altered, the solution containing chloride produced plants which were slightly larger and showed distinctly a more healthy appearance than those without.

Given a medium suitable for the Lemna, growth and reproduction will take place under the 24 hours light with a much greater speed than when the exposure is for shorter periods, and health and vitality of plants will be maintained. It is possible, therefore, that the failure of some investigators to get reproduction with certain plants under 24 hours light may be due to the fact that the environment of the plant, with regard to food, reaction, etc., is not suited to the rapid growth attained with continuous illumination.

Summary

1. The reproduction rate of Lemna major has been determined in inorganic water culture under electric light from Mazda lamps, with average intensities of 400 and 900 foot candles at the surface of the solutions.

2. In both cases increased length of day up to continuous light increased the rate of reproduction—the rate being directly proportional to the time of illumination.

3. The plants under the 900 footcandles, at all lengths of day, reproduced more rapidly than those with the corresponding exposure under 400 footcandles: the spread became greater as the period of illumination increased.

4. With iron supplied as phosphate, the plants became unhealthy after three weeks under the 24 hours light when the solution was changed twice a week. With continuous light, a 12 hour change of solution and 900 footcandles intensity, the rate of reproduction was increased and the health of the plants maintained, whether the iron was supplied as chloride, phosphate or nitrate. The solution containing iron chloride proved slightly superior to the other two.

THE ADSORPTION OF SILVER SALTS BY SILVER IODIDE*

BY JOHN SHERMAN BEEKLEY AND HUGH STOTT TAYLOR

The literature of colloid chemistry is replete with examples of the adsorption from solution of a great variety of substances by adsorbents of a complex and rather ill-defined nature, such as charcoal, cotton, wool, silk, silica gel, hydrated oxides, etc. Very often the substance adsorbed is itself colloidal, or it may be that its behaviour in solution is little understood, or the solvent may be one whose deportment toward the solute has not been thoroughly studied. Impurities, and extraneous substances in the solution, certainly not without effect on the adsorption process, have frequently been omitted from consideration. However, these researches are extremely valuable since they display the conditions which are actually encountered in the action of adsorption in many chemical processes, and in natural phenomena. Any research which concerns itself with the adsorption of well-characterized substances, by substances of a simple and defined nature, such as solids having a definite and known crystal-lattice, is important and should shed some light upon the causes and mechanism of adsorption from solution.

Such a simple case is found in the study, by Marc[1], of the adsorption from aqueous solution by crystals. The crystals were found to adsorb those substances which were isomorphous (in reality, homoömorphous) with them; thus, calcite adsorbed sodium nitrate, with which it is isomorphous, but did not adsorb potassium nitrate, while aragonite adsorbed the isomorphous potassium nitrate but not sodium nitrate.

Another simple case is the adsorption of silver nitrate (also potassium iodide) by silver iodide, studied by Lottermoser and Rothe[2]. The adsorbent and the substance adsorbed have here a common ion, and this common ion is known to be preferentially adsorbed since the colloid particle acquires a charge of the same sign as it possesses. It is to be supposed that adsorption takes place because of the fact that this common ion fits into the crystal-lattice of the adsorbent. There are many additional examples of adsorption of a common ion[3]. The adsorption force is here identical with the cohesive force of the adsorbent, and the adsorption process is thus analogous to the growth of a crystal in a saturated solution.

Further attention to this analogy is drawn by the researches of Paneth, and Paneth and Horovitz[4], on the adsorption of radio-elements by crystalline adsorbents. Radium was found to be strongly adsorbed by barium sulphate and barium chromate, but not at all by silver chloride and chromic oxide. Now radium chloride and radium oxide are soluble compounds, while radium

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* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Z. physik. Chem., 75, 710 (1911); 81, 641 (1913).

[2] Z. physik. Chem., 62, 359 (1908).

[3] Cf. Mukherjee: Trans. Faraday Soc., 16, 103 (1921).

[4] Physik. Z., 15, 924 (1914); Z. physik. Chem., 89, 513 (1915).

sulphate and radium chromate are only difficultly soluble. As a consequence of this observation, Paneth enunciated his Adsorption Rule for radio-elements: Those ions whose compound with the oppositely charged ions of the ion-lattice is difficultly soluble, will be relatively strongly adsorbed.

These views have been elaborated by Fajans and Beckerath[1] and a summary of their exposition is pertinent. Adsorption of ions by a crystal is through the agency of the residual valencies of the surface ions of the crystal-lattice. The Ag-ion adsorbed by silver iodide, for example, is incorporated into the silver iodide lattice, and it must have lost, therefore, its hydration-shell, the dehydration being accompanied by a large energy change.[2]

In general, upon adding to a saturated solution of a salt BA_1, in contact with solid BA_1, a second salt BA_2, there takes place, in addition to the precipitation of BA_1 following the solubility-product law, a further removal of B-ion through adsorption. The degree of this adsorption should be greater, according to Paneth's rule, the less soluble is BA_1. That is, the more easily the neutral surface draws both of its ions to the surface, the more easily will it draw the ion present in excess. "Generally speaking, not only will one dehydrated ion, as here assumed for the sake of simplicity, be added to the lattice, but, to a greater or less degree, each ion of the solution tends to be so added. If such an ion is foreign to the crystal-lattice, the influence of the solubility of its compound with the oppositely charged ions of the lattice, which certainly plays a great part here, becomes complicated by other factors." The authors suggest that the solubility of analogous salts of the type BA may depend largely upon the relative sizes of the separated B and A ions, and accordingly the adsorption of an ion A_2 by a lattice BA_1, must depend not only upon the solubility of BA_2, that is, the relative sizes of the ions B and A_2, but also upon the relative sizes of the ions A_1 and A_2.

Fajans and Beckerath found that silver halide sols made positive through the adsorption of Ag-ions did not adsorb Thorium-B, while those made negative with adsorbed halogen-ion did adsorb Th-B and Pb. This is in agreement with Paneth's rule, since the Th-B and Pb halides are not easily soluble.

Further experiments on the adsorption of ions by silver halides have been conducted by Frankenburger[3], who determined the spectral sensitivity of silver bromide under various surface conditions consequential to adsorption, and by Fajans and Frankenburger[4], who found that, in equilibrium with a solution $1.8 \cdot 10^{-6}$ molar with respect to Ag-ion, from one-fourth to one-tenth of the bromide ions of a silver bromide surface had silver ions adsorbed upon them. They also suggested[5] a mechanism for the precipitation of a salt from

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[1] Z. physik. Chem., 97, 478 (1921).

[2] For every ion thus fixedly held through adsorption, there is, if course, an oppositely charged ion of the solution in close proximity, but still in the solution and undeprived of its hydration-shell. The adsorption of one ion is, therefore, equivalent to the effective removal of one "molecule" (in the case of a univalent salt) from the solution.

[3] Z. physik. Chem., 105, 273 (1923).

[4] Z. physik. Chem., 105, 255 (1923).

[5] Cf. Fajans and Beckerath, loc. cit.

its saturated solution by the addition of an excess of one ion. As a simple case, take a difficultly soluble salt both of whose ions are equally strongly adsorbed by the lattice, that is, in equilibrium with its saturated solution in pure water; both ions being present in equal concentration, there is no potential difference between the salt and its saturated solution. Add one ion, say the cation, to excess. The adsorption equilibrium is disturbed, and the cation must accumulate on the lattice, cover it in part, and give to it a positive charge. This destroys the equilibrium with the anion, since some of the anions of the lattice are prohibited further kinetic exchange with the anions of the solution. New anions must come to the surface from the solution and a new state of equilibrium is established with fewer anions in solution. This means only that the solubility of the salt has been lowered by the addition of the excess ion. No quantitative relationship between solubility-product and adsorption has been derived[1].

The ions have been arranged in many series following their coagulative powers, their peptizing tendencies, or their adsorbability by various adsorbents[2]. These orders do not seem to be dependent upon any one specific property of the ions.

In view of the analogy of the adsorption process in adsorption by a crystalline adsorbent of a salt containing a common ion, to the building up of a crystal from saturated solution, it seems that there should be some relation between the adsorbability and the solubility of the salt. Such a consideration is, in general, quite natural and, granted that the adsorbent has equal affinity for two adsorbable salts, we should expect the less soluble one to be the more strongly adsorbed of the two, simply because its lesser solubility is indicative of a lesser affinity of the solvent for it. No clear-cut relationship of exactly this nature has so far been found. Lundelius determined[3] the order of adsorption of iodine by charcoal from its solution in carbon tetrachloride, chloroform, and carbon disulphide and found it to be in the inverse order of the solubility of iodine in these solvents. Moravitz found[4] the adsorption of heavy metals by blood charcoal to be greater, the smaller the solution tendency and the greater the adhesive tendency of these metals.

The present research was undertaken to determine, if possible, the relation between the solubility of various silver salts and their adsorbability by silver iodide. Salts of the uni-univalent type were chosen so that the factors of varying electric charge and differing valence might be eliminated. These solubilities are known and their ionic concentrations in solution may be determined from their known conductance. The adsorbent, silver iodide, has

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[1] In this connection, see Butler: J. Phys. Chem., 28, 438 (1924).

[2] Freundlich: "Kapillarchemie," p. 272 (1922); Weiser: J. Phys. Chem., 23, 205 (1919); 24, 30, 630 (1920), and following papers: Odén and Anderson: J. Phys. Chem., 25, 311 (1921); Odén and Langelius: 25, 285 (1921).

[3] Kolloid-Z., 26, 145 (1920). Cf., also, Georgievics: Kolloid-Z. 28, 253 (1921).

[4] Kolloidchem. Beihefte, 1, 301 (1910).

a definite, known crystal-lattice[1], even in the spongy precipitate, in which form it was used. It was chosen in preference to silver chloride, or silver bromide, because of its insensitivity to light when prepared pure.

Experimental

The Preparation of Materials

Silver Iodide.[*] To an approximately tenth-normal solution of strongly ammoniacal potassium iodide was added, slowly and with constant stirring, a one per cent excess of ammoniacal silver nitrate of the same concentration. The precipitated silver iodide was first washed[*] (all washings were made by decantation) with dilute ammonium hydroxide until the acidified washings gave no test for silver ion. This was followed by washing with distilled water until Nessler's reagent gave no test for ammonia. Ammonia was, however, still present and was removed by washing with five per cent nitric acid until the washings, made alkaline, gave no test with Nessler's reagent. Washing with distilled water until the washings gave no further test for free nitric acid with diphenylamine did not leave the precipitate completely devoid of adsorbed salts, notably perhaps ammonium nitrate. The washing was continued with distilled water, followed by the use of conductivity water until no appreciable increase was to be noted in the conductance of the supernatant liquid over a period of one week. The product so obtained was considered to be free from adsorbed and occluded salts, and was quite insensitive to light, no darkening being detectable in a sample which was exposed to the ordinary daylight of the laboratory for days. Without doubt this preparation does not have the greatest adsorbability of any preparation of silver iodide obtainable; nevertheless, it was quite satisfactory in that it gave measureable amounts of adsorption and was, moreover, reproducible. Varying quantities were prepared at one time and were kept suspended in water until used. Over the period of about two weeks during which a preparation was used, it showed no deterioration of its adsorptive power. One sample, however, kept for a period of six months, did show more than a fifty per cent diminished adsorption capacity.

Silver Nitrate, Silver Nitrite, Silver Acetate, Silver Benzoate, Silver Bromate. These salts were prepared by careful recrystallization of stock laboratory products.

Silver Chlorate. Chloric acid was prepared by treating dilute sulphuric acid with the requisite quantity of a solution of barium chlorate. The acid was neutralized with freshly precipitated, well-washed silver oxide. The solid salt was obtained by a repeated recrystallization from hot water, and was dried at 110°.

Silver Perchlorate, Silver Ethylsulphate, Silver Benzenesulphonate, Silver β-Naphthalenesulphonate. Solutions of these salts were prepared by neutralizing the free acids with freshly precipitated, most thoroughly washed silver

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[1] Haber: Ber., 55, 1717 (1922); Wilsev: Phil. Mag., 42, 262 (1921); 46, 487 (1923).

[*] Cf. Lottermoser and Rothe: loc. cit.

oxide. The concentrations of these solutions were determined by Volhard titrations and the desired dilutions made.

Water. The water used in making up all solutions had been distilled from acid and alkaline permanganate and showed a conductivity never greater than $1.8.10^{-6}$.

Experimental Method

A solution of desired concentration of a given salt was made up, by weight, as were all solutions employed. A quantity of the silver iodide suspension was transferred by means of a pipette to a small weighed flask (of about 80 c. c. capacity and having a ground glass stopper), and its weight determined. The silver salt solution was now added and the weight of the whole determined. The head of the stoppered flask was coated with paraffin and the flask rotated in a thermostat at 25° for about twenty-four hours. It was then removed, the composition of the supernatant liquid determined, and the silver iodide weighed in a gooch crucible. Trial experiments showed that equilibrium was established in three to five hours, and it is likely that so long a time was required because of the slowness with which the water clinging to the silver iodide mixed with the solution.

The equilibrium composition of the solution was determined through the measurement of its electrical conductance. A conductivity cell, chosen of such resistance capacity as to show a resistance between 200 and 1500 ohms, was calibrated for the concentration-range to be studied with solutions made up from the original solution. (It is to be noted that the solutions used in this calibration and in the adsorption measurements were made up from the same solution.) To measure the resistance, alternating current was used, with a Wolff resistance-box, and a Leeds and Northrup 'Student Type', drum-wound, slide-wire resistance. The concentration of an unknown solution was determined from its conductance by interpolation between the values obtained in the calibration of the cell. Frequent checks by analytical methods showed that the concentration so fixed represented the true silver-salt content of the solution. At the concentrations used, no solubility of silver iodide in the silver-salt solution was detectable.

The amount of adsorption was calculated from the formula

$$a = \frac{M\,(c_0 - c)}{m}$$

where

a = the amount of adsorbed salt in millimols per gram of silver iodide.
M = the weight of the solution.
c_0 = the initial concentration in millimolls per gram of solution.
c = the equilibrium " " " " " " "
m = the weight of silver iodide.

In view of the accuracy with which the concentration of solutions made up by weight is known, and in view of the fact that the error in the determination of the conductance of the solutions was less than one tenth of one per cent, the maximum experimental error in the value of *a* can safely be assumed to be 0.0003 millimols per gram.

The method used is fully illustrated by the typical case which follows:

TABLE I

Calibration of Cell No. 2 for Silver Benzoate

Solution	R	1000/R	Temp. 25° Concentration
2	1508.	0.663	0.001100
3	819.4	1.220	0.002065
4	631.8	1.583	0.002706
5	399.7	2.502	0.004362
6	301.8	3.314	0.005858
7	264.8	3.777	0.006734
1	214.8	4.656	0.008413

Concentrations expressed in millimols per gram solution

Solutions 2-7 made up by dilution of solution 1.

TABLE II

Adsorption of Silver Benzoate by Silver Iodide (Preparation No. 5). Temp. 25°

Flask+Ag. I+Water+Soln. No. 1	104.266	109.816	106.341
Flask+Ag. I+Water	92.921	85.708	65.270
Flask	24.179	25.183	27.952
Solution No. 1	11.345	24.108	41.071
Ag. I+Total Solution	80.087	84.633	78.389
Crucible + Ag. I	21.421	19.417	20.724
Crucible	17.723	15.814	16.986
Ag. I = m	3.698	3.603	3.738
Total Solution = M	76.389	81.030	74.651
Initial concentration = c_o	0.001250	0.002503	0.004629
Resistance = R.	1524	746.8	406.8
1000/R	0.656	1.339	2.458
Equilibrium conc. = c	0.001088	0.002275	0.004283
Adsorption = a	0.0033	0.0051	0.0069

Flask+Ag. I+Water+Soln. No. 1	103.626	87.328	116.900
Flask+Ag. I+Water	57.021	35.998	54.013
Flask	28.217	16.670	41.193
Solution No. 1	46.605	51.330	62.887
Ag. I+Total Solution	75.409	70.658	75.707
Crucible + Ag. I	20.105	21.282	21.348
Crucible	17.125	17.949	17.622
Ag. I = M	2.980	3.333	3.726
Total solution = M	72.429	67.325	71.981
Initial concentration = c_o	0.005414	0.006414	0.007350
Resistance = R	343.6	294.2	257.6
1000/R	2.910	3.399	3.882
Equilibrium conc. = c	0.005113	0.006019	0.006935
Adsorption = a	0.0073	0.0080	0.0080

Statement of Results

The experimental results are set down in the tables which follow:

TABLE III

Ag. I. Preparation 4. Aged six months. Temp. 25°

M	c_0	c	m	a
		Silver Acetate		
78.275	0.000475	0.000449	3.161	0.0007
81.598	0.000910	0.000854	3.983	0.001$_1$
79.466	0.002494	0.002430	2.646	0.001$_9$
77.958	0.003873	0.003758	3.040	0.0029
81.792	0.006132	0.005992	3.401	0.0034
75.139	0.008294	0.008137	3.072	0.0038
81.948	0.01102	0.01085	3.264	0.0044
73.886	0.01183	0.01165	3.054	0.0044
73.671	0.01553	0.01531	3.531	0.0046
73.968	0.01728	0.01704	3.938	0.0048
		Silver Nitrate		
78.086	0.003245	0.003205	4.632	0.0007
80.618	0.006002	0.005951	3.587	0.0011
72.914	0.009532	0.009477	3.658	0.0011
72.314	0.014426	0.014320	5.072	0.0015
76.923	0.016033	0.015992	1.917	0.0016
72.660	0.016997	0.016902	4.693	0.0015
		Silver Chlorate		
74.564	0.016708	0.016676	2.208	0.0011
73.654	0.016969	0.016936	2.522	0.0010
74.808	0.016840	0.016793	2.640	0.0013

TABLE IV

Ag. I. Preparation 5. Temp. 25°

M	c_o	c	m	a
		Silver Benzoate		
76.389	0.001250	0.001088	3.698	0.0033
81.030	0.002503	0.002275	3.603	0.0051
74.561	0.004629	0.004283	3.738	0.0069
72.429	0.005414	0.005113	2.980	0.0073
67.325	0.006414	0.006019	3.333	0.0080
71.981	0.007350	0.006935	3.726	0.0080
		Silver Perchlorate		
77.347	0.000477	0.000471	3.468	0.0001
81.746	0.000816	0.000809	2.831	0.0002
75.298	0.001247	0.001230	2.395	0.0005
69.773	0.002207	0.002155	3.391	0.0011
75.278	0.002626	0.002582	3.632	0.0009
81.423	0.003943	0.003906	2.877	0.0010
74.981	0.009097	0.009028	3.136	0.0016
71.593	0.001474	0.01466	3.536	0.0018
75.559	0.02061	0.02051	3.822	0.0020
		Silver Acetate		
76.751	0.00685	0.00659	2.848	0.0070
79.177	0.00752	0.00724	3.034	0.0073
		Silver Chlorate		
71.840	0.010938	0.010811	3.638	0.0025
74.721	0.011403	0.011286	3.428	0.0025
		Silver Nitrate		
66.849	0.007834	0.007670	3.679	0.0029
74.205	0.008989	0.008818	3.970	0.0032
		Silver Bromate		
66.403	0.003171	0.003026	3.107	0.0031
74.795	0.005029	0.004909	2.170	0.0041

TABLE V

Ag. I. Preparation No. 6. Temp. 25°

M	c_0	c	m	a
Silver Nitrate				
73.239	0.008058	0.007944	2.874	0.0029
71.129	0.009787	0.009689	2.318	0.0030
Silver Bromate				
82.395	0.002415	0.002297	3.526	0.0028
75.739	0.004367	0.004227	2.682	0.0039
72.612	0.006193	0.005983	3.312	0.0046
Silver Nitrite				
78.418	0.001946	0.001828	2.692	0.0034
76.205	0.002656	0.002482	2.747	0.0049
82.220	0.006599	0.006389	2.669	0.0064
75.920	0.009572	0.009310	3.170	0.0063
Silver Ethylsulphate				
76.216	0.001004	0.000980	3.246	0.0006
79.029	0.002463	0.002402	4.151	0.0012
70.723	0.003851	0.003799	2.694	0.0016
73.989	0.004078	0.004015	3.276	0.0014
66.270	0.008555	0.008464	2.678	0.0022
69.627	0.01459	0.01451	2.238	0.0025
Silver Benzenesulphonate				
77.614	0.001163	0.001113	2.348	0.0016
73.996	0.001976	0.001926	2.317	0.0016
75.586	0.003074	0.002973	2.893	0.0026
78.465	0.006789	0.006657	3.656	0.0028
72.612	0.01422	0.01403	3.661	0.0038
Silver β-Napthalenesulphonate				
76.799	0.0009289	0.000874	2.316	0.0018
69.937	0.001795	0.001717	2.145	0.0025
79.958	0.002703	0.002635	1.971	0.0028
75.610	0.004170	0.004029	3.203	0.0033
79.233	0.009339	0.009188	2.591	0.0046
72.428	0.01288	0.01268	2.483	0.0058
64.136	0.01441	0.01415	2.794	0.0060

The relative adsorbability of the divers salts is clearly shown in Figure 1, where *a*, the amount adsorbed in millimols per g. Ag. I, is plotted against *c*, the equilibrium concentration of the salt in millimols per g. solution. The data for these curves are taken from Tables 4 and 5. The cross-checks on silver nitrate and silver bromate make the data of these two tables strictly comparable. The relative positions of the silver acetate and silver chlorate curves were fully established by measurements on other silver iodide preparations (see Table 3).

That extraneous electrolytes do have a pronounced effect on an adsorption process of the kind studied is demonstrated by the following data:

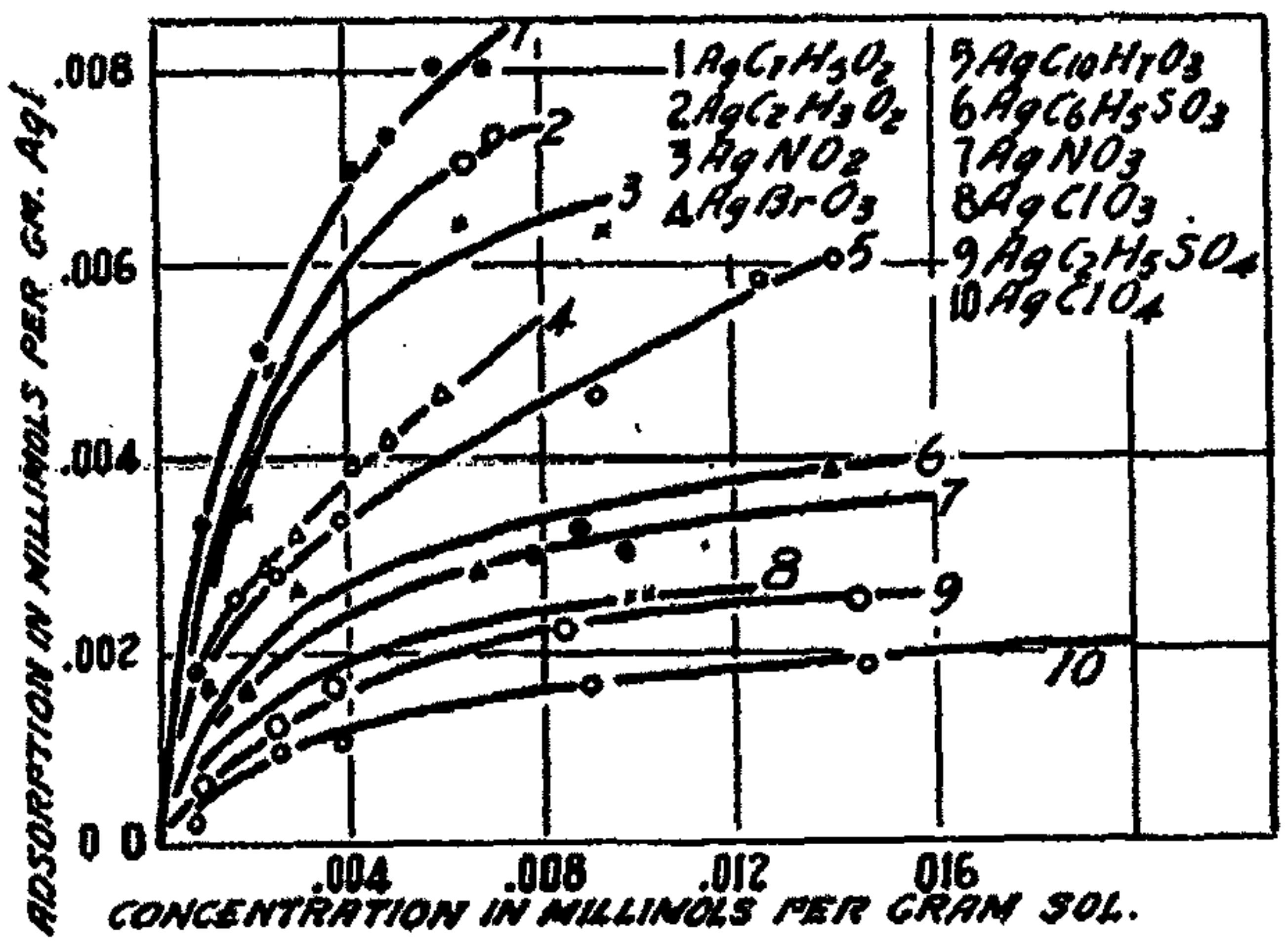

Fig. 1

TABLE VI

Effect of KNO_3 on adsorption of Ag NO_3. Temp. 25°.

M	C_0	C_{KNO_3}	C	$\frac{Mol_{KNO_3}}{Mol\ AgNO_3}$	m	a
72.31	0.01443	0	0.01429	0	5.07	0.0020
72.66	0.01700	0	0.01681	0	4.69	0.0028
71.94	0.01529	0.00984	0.01518	0.64	3.00	0.0026
78.52	0.01393	0.01963	0.01375	1.41	3.39	0.0042
83.19	0.01334	0.05050	0.01320	3.80	3.07	0.0038
66.34	0.01564	0.0880	0.01546	5.64	2.61	0.0046

The equilibrium concentration was determined by a method of electroanalysis, and the experimental error is correspondingly high. No pretense is made that any exact relation is shown between the molecular ratio of KNO_3 and Ag NO_3 and the variation in adsorption, but the data clearly show that the presence of KNO_3 increased the degree to which Ag NO_3 is adsorbed by Ag. I. This is in accordance with the observations of Michaelis and Rona[1] who found that HCl was more strongly adsorbed by charcoal when KCl also was present.

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[1] Biochem. Z., 97, 94 (1919).

Table VII shows results obtained with electrolytes other than silver salts.

TABLE VII

Electrolyte	c	a
HCl	0.011341	0.0004
	0.010292	0.0008
HNO_3	0.008922	0.0006
	0.009688	0.0004
KOH	0.007428	0.0003
	0.007640	0.0007
KNO_3	0.009795	0.0001
	0.009821	0.0003
$KClO_4$	0.010580	0.0001
	0.009833	0.0000

Discussion of Results

The silver salts studied may be arranged in the following order of decreasing adsorbability by silver iodide:

Benzoate > Acetate > Nitrite > Bromate > Napthalenesulphonate > Benzenesulphonate > Nitrate > Chlorate > Ethylsulphate > Perchlorate. In Table VIII the absolute and relative solubilities of these salts at 25° are set down.

TABLE VIII

Salt	Solubility at 25° millimols per g. H_2O	Relative solubility	Order of adsorbability
$AgBrO_3$	0.0081	1	4
$AgC_7H_5O_2$	0.0115	1.4	1
$AgNO_2$	0.0259	3.2	3
$AgC_{10}H_7SO_3$	0.039	4.8	5
$AgC_2H_3O_2$	0.0664	8.2	2
$AgClO_3$	0.8	100.	8
$AgC_6H_5SO_3$	1.38	170.	6
$AgC_2H_5SO_4$	12.9	1540.	9
$AgNO_3$	15.1	1860.	7
$AgClO_4$	26.3	3240.	10

While the two arrangements are not identical, it is to be observed that there is no very soluble salt which is strongly adsorbed, nor is there any slightly soluble salt which is weakly adsorbed. Thus, when the adsorption series is divided between the napthalenesulphonate and the benzenesulphonate, two groups are obtained which have the same members as the groups obtained by dividing the solubility series between the acetate and the chlorate.

Solubility is apparently, therefore, one determining factor in the relative masses of the silver salts adsorbed from solution by silver iodide.

The growth of a crystal in its solution is assuredly evidence of the attraction which the ions in the surface of the crystal have for the ions in solution. This chemical force may be assumed to be independent of the surroundings of the crystal and its effect to be dependent only upon the ability of the proper ions to reach the surface. A silver iodide surface exerts at certain discrete points the same attraction for silver-ions in solution whether these be yielded by the dissociation of silver iodide or by the dissociation of any silver salt of the type AgA. Two possibilities are presented in explanation of the variation in the amount of adsorption of salts of this type—that is, in the degree to which the Ag- and A-ions are removed as active components of the solution: (1) the anion may influence the amount of Ag-ion which is primarily adsorbed by the silver-iodide surface; (2) the anions themselves may be primarily adsorbed and to varying degrees, according to their individual characters.

In the first place, the greater, or less, affinity of the various anions *in solution* for the Ag-ion necessitates that more, or less, work be done to separate it from the solution. It is reasonable to assume that in any but a single crystal face all points of a surface where an ion can become attached do not possess equal attractive force for that ion. Therefore, in case the affinity of the anion in solution for the Ag-ion is great, the Ag-ion can be drawn to the silver-iodide surface only at those points where the force of attraction is greatest. Strong affinity is associated with high solubility, and, accordingly, high solubility, is to be associated with low adsorbability. Conversely, low solubility presages high adsorbability.

In the second place, there may result through the purely chemical adsorption of the silver-ions, followed by the usual electro-adsorption of the anion, a chemical adsorption of the anion A^-, strictly comparable to the building of an iodide-ion into the silver-iodide lattice, and to varying degrees, dependent upon the individual anion. Table III furnishes evidence that the anions themselves are not independently adsorbed. However, each adsorbed Ag-ion holds near itself, but in the solution, an anion, which may become adsorbed by the silver-iodide lattice in case a silver-ion of this lattice in immediate proximity is so situated as to possess a relatively large amount of residual valency. Since for every ion adsorbed, there is an oppositely charged ion held nearby, the operation of this process leads to a higher degree of adsorption than can be obtained through the primary adsorption of silver-ions alone.

Upon the basis of these considerations, the factors which may influence the degree of adsorption are: the hydration of the A-ion, the compatibility of the AgA crystal-lattice with the AgI lattice, and the affinity of the solvent for the ion-pair Ag A^-.

Low primary adsorption of the anion is consistent with a high degree of hydration of this ion, since the higher the degree of hydration of the ion, the more the work required to separate it from its hydration shell. Varying degrees of hydration of the anion may account for the fact that the order of adsorption of the salts is not the same as the order of their solubilities.

In accordance with Marc's observations, any silver salt which is isomorphous with silver iodide should be easily adsorbed. So far as is known, no one of the salts studied possesses the same crystal-symmetry as silver iodide. However, it is conceivable that even when the lattice of AgA differs in structure from that of AgI and the lattice constants are not the same, a single Ag-A linking may be affixed to the AgI lattice with little strain and relatively high stability. This is especially likely since one ion of the linking fits into the lattice of the adsorbent.

The chemical adsorption of A^- is most apt to take place when AgA is only slightly soluble, since low solubility implies relatively low affinity of the solvent for the salt. The constant attractive force exerted upon the anions of the solution by the Ag-ions of the AgI lattice is most effective of results when the salt AgA is little soluble.

A previous reference was made to the solubility of silver iodide in solutions of other silver salts. This phenomenon is exhibited by solutions of silver chlorate and of all the more soluble salts studied (see Table VIII) down to concentrations of about 0.1 mols per 100 mols of water, and is, of course, attended by complex-formation[1]. Just how this complex-formation is related to adsorption is not evident since solubility measurements showed the tendency to be greater in the case of silver chlorate than in the case of silver nitrate, yet the former is less adsorbed than the latter. It must be remembered that the double-salt phase was incapable of existence in the dilute solutions employed.

A study of the adsorption of the alkali-bromides by silver bromide would, it seems, yield results more tractable to theoretical treatment. The lithium, sodium, potassium, and rubidium salts possess the same crystal-symmetry (cubic) and the same type of arrangement of the atoms within the crystal, viz., the Na Cl type, as does silver bromide, while the crystal structure of caesium bromide is body-centered cubic. Important and relevant date for these salts are available—e. g., solubilities, heats of formation, lattice-constants[2] (AgBr, 5.78; LiBr, 5.48; NaBr, 5.95; K Br, 6.59; Rb Br, 6.93; CsBr, 4.30), etc. The determination of the temperature-coefficients of the adsorption would yield data from which the heats of adsorption could be calculated.

Summary

1. Silver salts have been found to be adsorbed by silver iodide in the following order.

Benzoate > Acetate > Nitrite > Bromate > Napthalenesulphonate
> Benzenesulphonate > Nitrate > Chlorate > Ethylsulphate
> Perchlorate.

2. While this is not exactly the reverse of the order of solubilities of these salts, the less soluble ones are strongly adsorbed, and the more soluble ones weakly adsorbed.

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[1] Hellwig: Z. anorg. Chem. **25**, 157 (1900).

[2] For a discussion of the relation of solubility to heats of solution of gaseous ions and lattice constants, see Butler: Z. physik. Chem., **113**, 279 (1924).

ADSORPTION AND SCHULZE'S LAW

BY HARRY B. WEISER

From an investigation of the coagulation by electrolytes of negative arsenious sulfide and antimony trisulfide sols, Schulze[1] concluded that the coagulating power of electrolytes is greater the higher the valence of the ion having a charge opposite to that on the colloidal particles. This conclusion has been supported by the later work of Prost[2], Linder and Picton[3], Hardy[4], Freundlich[5], and others; and has come to be known as Schulze's Law. Although this so-called law is little more than a qualitative rule[6], it cannot be doubted but that with most sols there is a tendency for the precipitation concentration of electrolytes to decrease with increasing valence of the precipitating ion. As a rule also, the precipitating power of electrolytes with multivalent precipitating ions is very much greater than with univalent precipitating ions.

The addition of electrolytes to a sol which owes its charge to preferential adsorption of ions, causes coagulation when the charge on the particles is reduced below a critical value by adsorption of ions of the electrolyte having a charge opposite to that on the sol. Since adsorption of the ions having the same charge as the sol, the stabilizing ions, cannot be disregarded, particularly with electrolytes that precipitate only in high concentrations, the precipitation value of an electrolyte for a sol is that concentration which results in sufficient adsorption of the precipitating ion to neutralize the combined adsorption of the original stabilizing ion and the stabilizing ion added with the electrolyte[7]. In so far as influences other than the adsorbability of the precipitating ion may be disregarded, one should expect the precipitating power of an electrolyte to be greater, the greater the adsorbability of the precipitating ion. Furthermore, one should expect an ion of high valence to be adsorbed more strongly than an ion of low valence to the extent that the precipitating power of an electrolyte increases with increasing valence of the precipitating ion in accord with Schulze's Law. This interpretation of Schulze's Law has recently been called in question by Dhar and his collaborators[8].

That adsorption of precipitating ions takes place during the coagulation of sols by electrolytes was demonstrated by Linder and Picton[9] in the course of their classic investigations on arsenious sulfide sol, thirty years ago. Sub-

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[1] J. prakt. Chem., (2) 25, 431 (1882); 27, 32 (1883).
[2] Bull. Acad. roy. Belg., (3) 14, 312 (1887).
[3] J. Chem. Soc., 67, 63 (1895).
[4] Z. physik. Chem., 33, 385 (1900).
[5] Z. physik. Chem., 73, 385 (1910).
[6] Bancroft: "Applied Colloid Chemistry," 213 (1921).
[7] Weiser: J. Phys. Chem., 28, 232 (1924).
[8] Dhar, Sen and Ghosh: J. Phys. Chem., 28, 457 (1924).
[9] Z. physik. Chem. 73, 385 (1910).

sequent investigations by Whitney and Ober[1] on adsorption of various cations during the precipitation of arsenious sulfide sol led them to conclude that equivalent amounts of all precipitating ions are carried down by a precipitated sol. This result was confirmed by Freundlich[2] who deduced therefrom that the most readily adsorbed ion will precipitate in the lowest concentration and vice-versa. In order to account for the marked influence of the valence of inorganic cations on the precipitation of a negative sol, Freundlich makes the further assumption that cations of different valence are equally adsorbed from equimolar solutions which would explain the well-known fact that the precipitation values (which correspond in the first instance to equivalent amounts) are very different.

Judging from the frequency with which the observations of Whitney and Ober and of Freundlich are referred to in text books of colloid chemistry, their conclusions appear to be generally recognized as quantitatively accurate. However, a closer survey of the experimental results throws some doubt on the accuracy of the deductions: the variation from equivalence in the adsorption values found by Whitney and Ober is more than 20 percent in certain cases; similar observations by Freundlich and Schucht[3] on adsorption by colloidal mercuric sulfide show much wider variations than this, all of which are attributed to experimental errors; some investigations made in my laboratory on adsorption of anions by hydrous oxide sols[4], disclose variations from equivalence that cannot be charged to experimental errors.

Recently Freundlich[5] has returned to this problem again; but instead of studying adsorption directly, he investigated the effect of salts with precipitating ions of variable valence on the cataphoretic migration velocity of colloidal particles of arsenious sulfide and hydrous ferric oxide sols. There was shown to be a close relationship between coagulation by electrolytes and the effect of the latter on electrokinetic processes. With univalent to quadrivalent cations derived from complex cobalt salts, the adsorption of equivalent amounts seems to have a similar coagulating effect on colloidal arsenious sulfide and the cations of different valence appear to be adsorbed equally from equimolar solutions[6]. However, with colloidal ferric oxide there appears to be a wide variation from equivalence in the adsorption from equimolar solutions of salts containing complex cyanide anions. Thus the precipitating power of $Au(CN)_4'$ appears to be twelve times as great as $Au(CN)_2'$ and $Fe(CN)_6'''$ twice as great as $Cu(CN)_4'''$. Moreover the precipitating action of bivalent $Pt(CN)_4''$ is but three times as great as univalent $Au(CN)_2'$.

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[1] J. Am. Chem. Soc., 23, 842 (1901).

[2] Kolloid-Z., 1, 321 (1907).

[3] Z. physik. Chem., 73, 385 (1910).

[4] Weiser and Middleton: J. Phys. Chem., 24, 30, 630 (1920).

[5] Freundlich and Zeh: Z. physik. Chem., 114, 65 (1924).

[6] Cf. Matsuno: J. Coll. Sci., Tokyo, 41, No. 11 (1921).

Experimental

In the light of Freundlich and Zeh's recent observations on colloidal arsenious sulfide, it might appear that the variation from equivalent adsorption in Whitney and Ober's early experiments was due entirely to experimental errors. Accordingly they have been repeated with the following results:

Adsorption of cations by arsenious sulfide sols. Arsenious sulfide sols of different concentration were prepared by allowing a solution of arsenious oxide to drop slowly into water through which was bubbled a stream of carefully washed hydrogen sulfide. The several sols were washed with hydrogen to remove excess hydrogen sulfide and were kept in an atmosphere of hydrogen until used. 100 cc portions of sol were precipitated in a mixing apparatus with

TABLE I

Adsorption by Arsenious Sulfide Sols

Metal	Concn. of Sol grams per l	Weight of ppt. obtained from 180 cc of solution 1	2	Metal adsorbed Millieq. per g	Observer
Barium	6.42	0.0765	0.0762	0.116	Weiser
Strontium	6.42	0.0606	0.0605	0.107	Weiser
Calcium	6.42	0.0188	0.0187	0.093	Weiser
Barium	11.80	0.0767	0.0768	0.060	Weiser
Strontium	11.80	0.0606	0.0608	0.056	Weiser
Calcium	11.80	0.0191	0.0188	0.043	Weiser
Barium	21.50	0.0676	0.0679	0.072	Weiser
Strontium	21.50	0.0541	0.0541	0.069	Weiser
Calcium	21.50	0.0163	0.0162	0.073	Weiser
Barium	19.00	0.0702	0.0703	0.049	Weiser
Strontium	29.00	0.0552	0.0554	0.046	Weiser
Calcium	29.00	0.0172	0.0170	0.050	Weiser
Barium	10.00			0.110	Whitney and Ober[1]
Strontium	10.00			0.082	Whitney and Ober
Calcium	10.00			0.100	Whitney and Ober
Potassium	10.00			0.082	Whitney and Ober
Anilin				0.074	Fruendlich[2]
Neufuchsin				0.076	Freundlich
Barium	3.33 (approx)			0.086	Linder and Picton[3]
UO_2	4.14			0.088	Freundlich[4]
Cerium	4.14			0.069	Freundlich

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[1] J. Am. Chem. Soc., 23, 842 (1902).

[2] Kolloid-Z., 1, 322 (1907).

[3] J. Chem. Soc., 67, 64 (1895).

[4] Z. physik. Chem., 73, 408 (1910).

40 cc of N/50 solutions of the chlorides of the respective metals, diluted to 100 cc. After standing two hours, the mixtures were centrifuged and 180 cc of the supernatant liquid were analyzed. Particular precautions were taken in all the procedures to make the observations as nearly accurate as possible. Barium and strontium were precipitated and weighed as sulfate; and calcium was precipitated as oxalate and weighed as oxide. The experiments were all done in duplicate and the adsorption values were calculated from the average of the two results. The observations are recorded in Table I together with similar observations by other investigators. It will be noted that the variation from equivalence in the adsorption of calcium, strontium and barium ions for each sol used by the author is somewhat less than in the oft-quoted observations of Whitney and Ober. While it may be that this is due to experimental errors inherent in the analytical procedures, it is more likely, in the light of observations to be recorded later on, that there is a real difference in the amounts of the several ions carried down, as the results seem to show. Thus barium seems to be adsorbed a bit more strongly than strontium in every case. The observations with calcium are more erratic; but the determination of small amounts of this element are relatively less accurate because of the relatively low molecular weight of calcium oxide and the high factor for calcium in this compound.

If, for the moment, the amounts of the several ion carried down by a given sol are admitted to be equivalent, it would seem hardly necessary to point out that the adsorption value of a trivalent ion *expressed in mols* will be only one-third and that of a bivalent ion one-half the adsorption value of a univalent ion. But the recognition of this obvious fact furnishes the basis of Dhar's novel interpretation of Schulze's Law to which we will return in a subsequent paragraph.

Contrary to Freundlich's belief[1] the adsorption expressed in equivalents per gram of arsenious sulfide varies widely with different sols. This results from the difference in purity, stability, and size of particles that obtain with different preparations. As an illustration of the influence of the purity of sol on the adsorption of precipitating ions, experiments were carried out on two sols, each containing 27.5 g per liter. The results are given in Table II. Sol No. 1, had the odor of hydrogen sulfide; while sol No. 2 was freed from excess hydrogen sulfide by thorough washing with hydrogen. As might be expected the adsorption of barium ion from barium chloride is less the smaller the excess of hydrogen sulfide in the sol.

TABLE II

Sol No.	N/50 $BaCl_2$ to effect coagulation Total volume 200 cc	$BaSO_4$ remaining in 180 cc		Ba adsorbed Millieq. per gram
		1	2	
1	35	0.0527	0.0529	0.069
2	35	0.0568	0.0569	0.056

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[1] Kolloid-Z., 1, 321 (1907).

Adsorption of anions by hydrous oxide sols. Although the amounts of barium, strontium, and calcium adsorbed by a given arsenious sulfide sol are not far from equivalent, this is by no means true in other cases. In Table III are recorded some earlier observations on adsorption of anions during the precipitation of colloidal alumina[1]. In addition to the anions listed, experiments with thiosulfate and phosphate were carried out but the values for these ions are omitted, the first because of contamination of the precipitating solution by sulfate; and the second because of the improbability that the precipitating anion is PO_4''' rather than a mixture of H_2PO_4' and HPO_4''. The adsorption values as recorded in the second column, are not even approximately equivalent. Since the variation noted cannot be due to experimental errors, it was necessary to inquire further into the mechanism of the precipitation process. While Whitney and Ober and Freundlich are doubtless right in concluding that adsorption of equivalent amounts of various ions will lower the charge below the critical value necessary for agglomeration, the actual amount of a given ion carried down is determined (a) by adsorption of ions by the electrically charged particles during neutralization and (b) by adsorption of salt by the electrically neutral particles during the process of agglomeration and settling. The amounts of (a) will be approximately equivalent but the amounts of (b) will vary with the nature and concentration of the electrolyte[2]. The marked effect of salt adsorption on the amount of an ion carried down by a sol is shown in a striking fashion by a study of adsorption of oxalate ion during the precipitation of a hydrous chromic oxide sol. The sol was prepared by prolonged dialysis in the hot of a sol formed by adding ammonia to a solution of chromium nitrate until the particles of precipitated oxide just failed to redissolve. The concentration of the purified sol was adjusted to two grams Cr_2O_3 per liter. Because of the instability of the preparation it was stored in a pyrex vessel and pyrex apparatus was used in all experiments. 100 cc portions of the sol were precipitated with the precipitation value of potassium oxalate and with several concentrations above the precipitation

TABLE III

Anion	Adsorption Milliequivalents per gram	Precipitation value potassium salts Milliequivalents per liter
Ferrocyanide	1.280	0.375
Ferricyanide	1.214	0.900
Sulfate	0.997	0.538
Oxalate	1.142	0.700
Chromate	0.870	1.300
Dithionate	0.657	1.625
Dichromate	0.629	1.775

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[1] Weiser and Middleton: Loc. cit.

[2] Weiser and Middleton: J. Phys. Chem., 24, 30, 630 (1920).

value. After standing one hour, the mixture was centrifuged and a portion of the supernatant liquid withdrawn and titrated with standard permanganate. The results are given in Table IV and shown graphically in Figure 1.

The lowest concentration was the precipitation value, at which all the electeolyte was adsorbed. The increased adsorption above the precipitation value was all due to adsorption by electrically neutral particles and it is altogether likely that a large part of the oxalate carried down at the precipitation value was adsorbed during agglomeration. For this reason Freundlich's conclusion that equivalent amounts are adsorbed at the precipitation concentration, cannot be generally true since this would mean either that the neutralized particles do not act as an adsorbent or adsorb all ions to the same extent. Moreover the variability of the precipitation concentration will necessarily result in variation in the degree of saturation of the adsorbent by the adsorbed phase. One should expect the adsorption values of various ions to approach equivalence more nearly the less the adsorption capacity of the

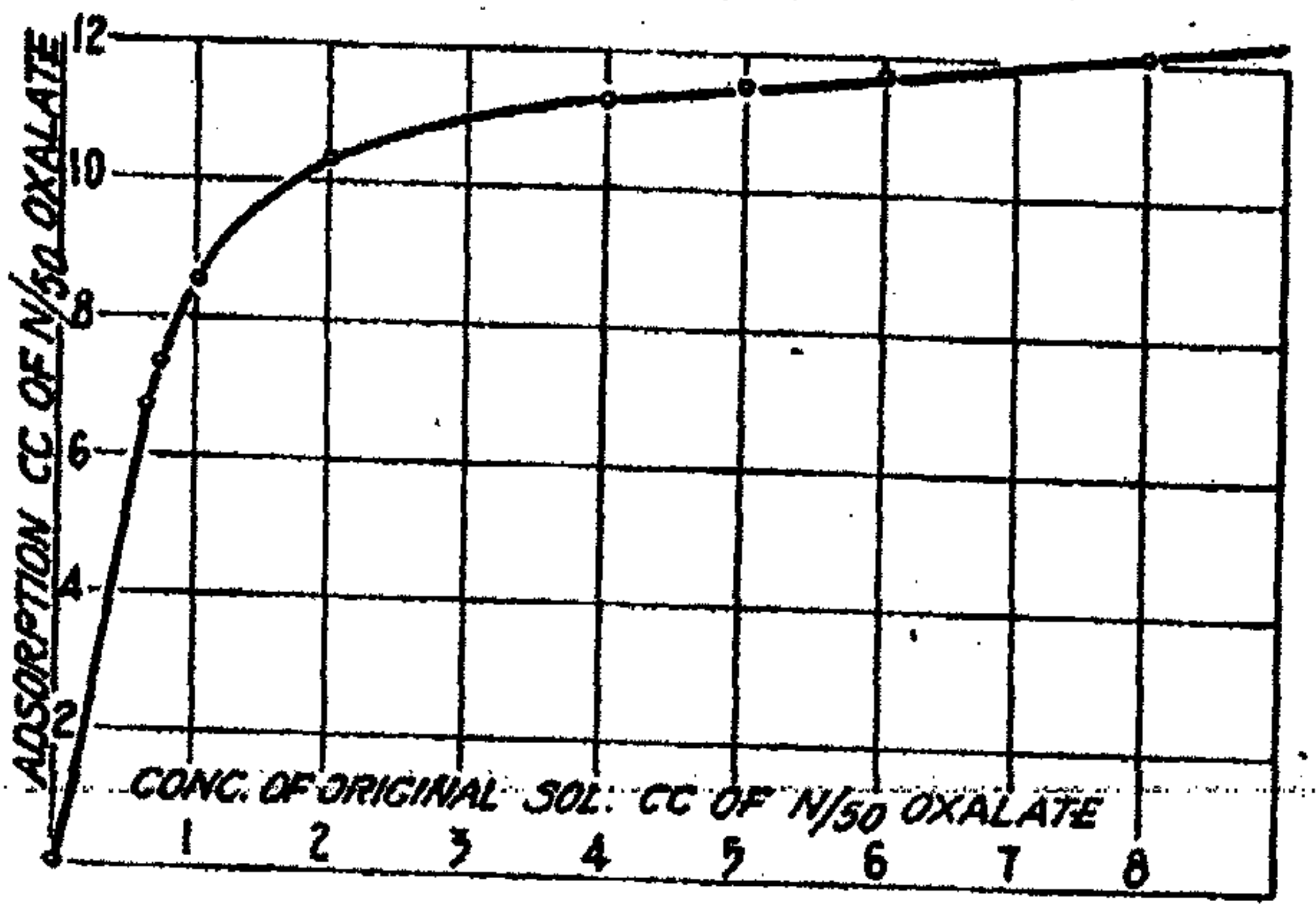

Fig. 1
Adsorption of Oxalate by Hydrous Chromic Oxide

Table IV

Adsorption of Oxalate by Hydrous Chromic Oxide

Volume of N/50 $K_2C_2O_4$ in 100 cc added to 100 cc of sol.	Adsorption of Oxalate cc N/50 solution	Milliequivalents per g
6.5	6.50	0.650
7.5	7.30	0.730
10.0	8.58	0.858
20.0	10.26	1.026
40.0	11.23	1.123
50.0	11.50	1.150
60.0	11.77	1.177
80.0	12.05	1.205
100.0	12.70	1.270

precipitated particles. This probably accounts for the values being more nearly equivalent with an arsenious sulfide sol than with a hydrous oxide sol having many times the adsorption capacity.

If the variation from equivalence arises from adsorption after neutralization, the adsorption values might appear, a priori, to give directly the order of adsorption of the anions. This is not necessarily true, however, because there are variable factors other than the adsorbability of the precipitating ions that determine the amount of salt adsorption after neutralization, for example: the nature and degree of ionization, and the degree of hydrolysis of the salt; the hydrogen ion concentration; the effect of different salts on the physical character of the precipitate, etc. From the observations recorded in Table III the order of adsorbability expressed in equivalents would appear to be as follows: ferrocyanide > ferricyanide > oxalate > sulfate > chromate > dithionate > dichromate. Considering the precipitation value of the several potassium salts, we find the order of precipitating power beginning at the greatest to be: ferrocyanide > ferricyanide > sulfate > oxalate > chromate > dithionate > dichromate. The order of adsorption determined directly is the same as the order deduced from precipitation data with the exception of oxalate and sulfate which are reversed. The cause of this exception is not known; but in this connection, attention may be called to some unpublished work of Everett E. Porter which disclosed that the order of precipitating power of oxalate and sulfate for chromic oxide sol is determined by the hydrogen ion concentration of the precipitating solution.

If the adsorption value is expressed in equivalents, as seems logical, since neutralization is determined by the number of adsorbed charges, the results given in Table III are in accord with the usual interpretation of Schulze's Law, that the ion of highest valence is most readily adsorbed. At the same time the data furnish evidence of the qualitative nature of this so-called law since a number of ions of the same valence show a wide variation in adsorption.

In a recent communication by Dhar, Sen and Ghosh[1] to which attention has already been called, the conclusion was reached that an ion which has a high precipitation value for a colloid is most adsorbed by the colloid and vice-versa. In support of this conclusion are cited some observations of the author and of Freundlich; but more especially the results of Dhar and his collaborators on adsorption during the precipitation of manganese dioxide. "Thus," it is pointed out, page 464, "the monovalent ions silver, sodium, lithium are more adsorbed (by manganese dioxide) than any of the bivalent, trivalent or tetravalent ions. These facts show that the ions of higher valence which in general have greater coagulating powers are adsorbed the least." Dhar's observations were not made during the precipitation of a purified sol but on manganese dioxide formed by mixing potassium permanganate and manganese sulfate in the presence of various electrolytes. In the solution from which the oxide separated there were the two reacting electrolytes; the salt whose adsorption was measured; together with the soluble products of

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[1] J. Phys. Chem., 28, 455 (1924).

the reaction potassium acid sulfate and sulfuric acid. This makes an almost hopelessly complicated system; and it seems unsafe to draw any conclusions whatsoever from the observations until we know more about the effect of the foreign electrolytes on the rate of precipitation and physical character of the precipitate and until something is known of the influence of the other salts in the system on the adsorption of the salt investigated. To cite but one example: aluminum nitrate is adsorbed about eight times as strongly as aluminum sulfate whereas the sulfates of cobalt, copper and cadmium are each adsorbed somewhat more than their respective nitrates. Aluminum is not "far less adsorbed" than strontium, nickel, cobalt, zinc, barium or cadmium ions if the values for the nitrates are compared.

Dhar, Sen and Ghosh are in entire agreement with the author's view that adsorption takes place in two steps on adding an electrolyte to a sol. To quote their own words: "In the coagulation of a colloid there are two distinct steps in which adsorption occurs. The first step is the electrical neutralisation of the charge on the colloidal particles through adsorption of an ion carrying a charge opposite to that on the sol and only here the Schulze-Hardy Law is applicable. The adsorption, however, does not stop there, but the coagulated particles further act as an adsorbent, taking up an additional amount of the electrolyte or ion. The amount of this second adsorption will depend on the adsorbability of the electrolytes or ions and the nature of the coagulated mass concerned and hence the final amount of adsorption may have any value depending on the above factors. The Schulze-Hardy Law cannot be rightly applied to these cases. If the adsorption by the neutral particles is not appreciable, then the Schulze-Hardy Law is likely to be followed; but if the neutral particles can adsorb the ion or the electrolyte appreciably, complications will arise and the Schulze-Hardy Law may not be applicable."

Dhar, Sen and Ghosh merely say that the Schulze Law applies only to the neutralization process which is accomplished by adsorption of equivalent amounts of precipitating ions. From this it is deduced, that if these equivalent values are expressed as gram mols, the adsorption value will be less the greater the valence of the ion and vice versa. Granting the premises, one can find no quarrel with the obvious deduction. However, few people will agree that Schulze's Law means only that neutralization of sols is accomplished by adsorption of equivalent amounts of ions of different valence.

While adsorption of equivalent amounts of precipitating ions will effect neutralization in case the adsorption of the stabilizing ion may be neglected, the important question is: why is the necessary adsorption obtained with *very low* concentrations of certain electrolytes and only with *very high* concentrations of others? Other things being equal one would expect neutralization by adsorption to be accomplished with the lowest concentration of electrolyte containing the most strongly adsorbed precipitating ion. In so far as Schulze's Law holds, the higher the valence of the ion the greater should be the adsorbability.

Investigations of the relationship between the precipitation value of electrolytes and the adsorption of the precipitating ions during the precipitation process have been carried out with multivalent ions chiefly. This is unfortunate, since with a series of such ions both the precipitation values and the adsorption values are likely to be so close together that it is hazardous to draw conclusions, particularly when the differences may be of the same order of magnitude as the errors inherent in the experimental procedure. It would be much better to study the relationship between precipitating power and adsorbability with univalent precipitating ions; but this has seemed impracticable heretofore, since the precipitation concentrations are usually so high that the change in concentration resulting from adsorption is too small to measure directly with any degree of accuracy. It is possible however to determine the relative adsorbability of univalent ions during the precipitation of sols by an indirect method that consists essentially in determining the effect of the presence of univalent precipitating ions on the adsorption of an easily estimated multivalent ion. Some experiments illustrating this method will be given in the subsequent paragraphs.

Adsorption by arsenious sulfide from mixtures of electrolytes. The precipitation values of barium chloride and of several chlorides containing univalent cations were determined for an arsenious sulfide sol containing 27.5 grams per liter. This was done by finding the smallest amount of the several solutions in 10 cc that will just cause complete coagulation of 10 cc of sol within two hours. The results expressed in milliequivalents per liter are given in Table V.

TABLE V

Precipitation of Colloidal Arsenious Sulfide.

Electrolyte	Precipitation value Milliequivalents per liter.
Barium chloride	2.74
Lithium chloride	88.7
Sodium chloride	73.5
Potassium chloride	63.7
Hydrochloric acid	52.5

The adsorption of barium ion during precipitation of the same sol was next determined from a solutions of barium chloride and from several mixtures of barium chloride with a chloride containing a univalent cation, as shown in the first column of Table VI. The adsorption values were determined on 100 cc portions of sol in the same manner as described in an earlier paragraph. From the observations it will be noted that univalent ions cut down the adsorption of barium in the order: lithium < sodium < potassium < hydrogen. Since, under otherwise constant conditions, one should expect the adsorption of a given cation to be cut down by the presence of a second cation in proportion to the adsorbability of the latter, it follows that the order of adsorbability of the univalent ions is: hydrogen > potassium > sodium > lithium. This is

TABLE VI

Adsorption of Barium Ion from Mixtures.

Electrolyte added to 100 cc sol Total volume 200 cc	BaSO$_4$ remaining in 180 cc		Barium adsorbed	
	1	2	Grams	Millieq. per gram As$_2$S$_3$
30 cc N/50 BaCl$_2$	0.0463	0.0464	0.0109	0.058
30 cc N/50 BaCl$_2$+30 cc N/50 LiCl	0.0466		0.0107	0.056
30 cc N/50 BaCl$_2$+30 cc N/2 LiCl	0.0572	0.0574	0.0037	0.019
30 cc N/50 BaCl$_2$+30 cc N/2 NaCl	0.0590	0.0592	0.0025	0.014
30 cc N/50 BaCl$_2$+30 cc N/2 KCl	0.0603	0.0602	0.0018	0.009
30 cc N/50 BaCl$_2$+30 cc N/2 HCl	0.0609	0.0609	0.0013	0.007

exactly the same as the order deduced from the precipitation values of salts, Table V, assuming that the salt containing the most readily adsorbed cation precipitates in lowest concentration.

Further, the results in Table VI furnish almost conclusive proof that the univalent ions are adsorbed more strongly than bivalent barium. For example the adsorption of barium is cut down but very little by the presence of an equivalent amount of lithium and 25 times the concentration of lithium cuts it down but two-thirds of the value in the absence of lithium. Similar results were obtained from a study of the relative effect of chloride and sulfate on the adsorption of oxalate by hydrous chromic oxide.

Adsorption by chromic oxide from mixtures. Precipitation and adsorption experiments were carried out on the hydrous chromic oxide sol used in earlier experiments. The results of the observations are given in Table VII which is self-explanatory. The slight effect of chloride as compared with sulfate on the adsorption of oxalate leaves no room to doubt but that the univalent ion is adsorbed much less than the divalent one. In the light of these observations, the conclusions of Dhar and his collaborators appear to be both theoretically and experimentally unsound.

TABLE VII

Adsorption of Oxalate Ion from Mixtures

Electrolyte added to 100 cc sol Total volume 200 cc	Oxalate adsorbed Millieq. per g	Precipitation values Millieq. per l	
50 cc N/50 Oxalate	1.149	K$_2$C$_2$O$_4$	0.650
50 cc N/50 Oxalate + 50 cc N/50 KCl	1.142	KCl	8.75
50 cc N/50 Oxalate + 50 cc N/2 KCl	1.118		
50 cc N/50 Oxalate + 50 cc N/50 K$_2$SO$_4$	0.990	K$_2$SO$_4$	0.620

Summary

1. Schulze's Law, that the precipitating power of an electrolyte is greater the higher the valence of the precipitating ion, is but little more than a qualitative rule.

2. In so far as Schulze's Law holds, the adsorbability of an ion is greater, the higher the valence.

3. The conclusion of Dhar and his collaborators that ions with the lowest precipitating power are adsorbed the most and vice-versa, is both theoretically and experimentally unsound.

4. An indirect method has been described for determining the relative adsorbability of weakly adsorbed univalent ions.

5. With strong electrolytes containing weakly adsorbed precipitating ions and the same stabilizing ion, there is a direct relationship between the relative adsorbability of the precipitating ions and the coagulating power of the electrolytes in the sense that the electrolyte containing the most readily adsorbed precipitating ion, coagulates a sol in lowest concentration.

6. The amounts of various precipitating ions carried down on precipitating a sol are determined by (a) adsorption by the electrically charged particles during neutralization and (b) adsorption by the electrically neutral particles during the process of agglomeration. The amounts of (a) will be equivalent in case the adsorption of the stabilizing ions of the several electrolytes is constant or is negligibly small; but the amounts of (b) will vary with the nature and concentration of the electrolyte.

7. From 6, one should expect the adsorption values of various ions to approach equivalence more nearly, the less the adsorption capacity of the precipitated particles. This probably accounts for the values being more nearly equivalent with arsenious sulfide sol than with hydrous oxide sols having many times the adsorption capacity.

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MOLECULAR WEIGHT AND SOLUTION

BY WILDER D. BANCROFT

There are two apparently contradictory conceptions of molecular weight in vogue at present. The chemist determines gram-molecular weight from the vapor density or from the change of the vapor pressure of a solution. For him molecular weights are specific and vary discontinuously. The gram-molecular weight of oxygen is 32, of nitrogen 28, and of hydrogen about 2.0. Even when gram-molecular weights appear to vary continuously, as they do in the case of nitrogen peroxide or of sulphur vapor, the chemist concludes, very properly, that he is dealing with a mixture of two or more substances. When the apparent gram molecular weight of nitrogen peroxide varies continuously between 92 and 46 as limits, the chemist accounts for this by postulating varying mixtures of N_2O_4 and NO_2. When the apparent gram-molecular weight of sulphur varies continuously from about 192 to about 64, the chemist postulates continuously varying mixtures of substances to which he assigns the formulas S_6, S_4 and S_2. To get the absolute molecular weight of a substance the chemist divides the gram-molecular weight by the Avogadro number, 6.1×10^{23} or thereabouts, for the number of molecules in one gram-molecular weight. The absolute weight of a molecule of oxygen gas is therefore something over 5×10^{-23} grams.

According to the physicists a particle suspended in a liquid behaves exactly like one dissolved, and may be considered a molecule.[1] Einstein "showed that, according to the molecular kinetic theory, the colloidal solutions should give osmotic pressure and diffusion just as ordinary solutions, that there is no difference between a suspended particle and a molecule." If we accept this, and the physicists do accept it, the molecular weight ceases to be specific because a suspended particle of platinum may weigh exactly the same, and therefore have the same molecular weight, as a suspended particle of quartz. Furthermore the molecular weight can vary continuously with the size of the suspended particle.

It is difficult to imagine any two conceptions that are more discordant than these two and yet they can be harmonized very easily if we wish to. The molecular weight of the physicist is the weight of, or is a function of the weight of, the actual suspended particle. The molecular weight of the chemist—the gram-molecular weight divided by the Avogadro number—is the weight of the single particle of the gas. In other words the molecular weight of the chemist is the lower limiting value of the molecular weight of the physicist and it is only at the limiting values that the specificity comes in.

This way of looking at things makes a result obtained by Perrin[2] a little less startling. "It may be interesting to observe that the largest of the

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[1] Svedberg: "Colloid Chemistry," 92 (1924).

[2] "Brownian Movement and Molecular Reality," 46 (1909).

granules [of gamboge] for which I have found the laws of perfect gases followed, are already visible in sunlight under a strong lens. They behave as the molecules of a perfect gas, of which the gram-molecule would weigh 200,000 tons." A perfect gas with a gram-molecular weight of 200,000 tons is a bit staggering to the chemist; but it is not so bad if one says that these suspended particles of gamboge behave as hydrogen gas would if the individual particles weighed, in round numbers, three ten-billionths of a milligram, taking a billion as a thousand million.

Einstein's point of view has the further advantage of enabling us to account for the behavior of certain colloidal solutions before it occurs to some of the people on the other side of the fence to cite these cases against us. If one is going to consider the suspended particles in a colloidal solution as forming a second phase in the ordinary sense of the word, they ought to act like a phase of constant concentration, whereas they don't. Tannin in water forms a colloidal solution without any question; but the amount of tannin adsorbed by a textile fiber from a colloidal solution of tannin varies continuously with the apparent concentration of the tannin. This is exactly what should happen if the suspended particles of tannin can be considered as equivalent in certain respects to a solution of tannin. The substantive dyes are all in colloidal solution; but the amount taken up by cotton varies continuously with the apparent concentration of the dye. In other words we get the same general form of isotherm for adsorption from a true solution and from a colloidal solution.

The difficulties about haemoglobin and oxygen now disappear. It is practically certain that haemoglobin and oxygen form a definite compound. The experimental data seem to show that this compound dissociates much as it should if the haemoglobin and the oxygen compound were both in true solution and yet we know they are not. Bayliss[1] has put the difficulty very clearly. "It may occur to the reader that there is one class of cases of which no mention has yet been made, namely, the taking up of gases by surfaces such as that of charcoal, adsorption, in which we certainly get a relation between the amount taken up and the pressure. This was in fact suggested by Wolfgang Ostwald[2] as applying to the haemoglobin-oxygen system. But it is obvious that it is very difficult to reconcile the fact that one molecule of haemoglobin, when saturated, combines with one molecule of oxygen and no more, with anything but a chemical compound as the final result. The key to the puzzle will probably be found in a combination of the two processes. The amount of oxyhaemoglobin would be determined by the amount of oxygen adsorbed on the surface of the haemoglobin under a given pressure. At the same time, there are difficulties in the treatment of the problem from this point of view; but it has, as yet, received little attention. It seems clear that it is not permissible to use either the law of mass action or the phase rule as applying to the case, until it has been proved that they do or do not

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[1] "Principles of General Physiology", 619 (1915).

[2] Kolloid-Z. 2, 264, 294 (1908).

hold in the case of colloidal solutions, where there must be surface phenomena intervening, although these phenomena may not be as simple as when larger and flatter surfaces are concerned."

If we adopt the Einstein point of view, the mass law does apply to colloidal solutions, so that difficulty disappears. On the other hand the molecular weight of haemoglobin, as defined by Einstein, will vary with the state of aggregation and may therefore vary with the nature and amount of electrolyte. It is quite probable, though not yet proved, that this may account for the peculiar changes in the dissociation equation[1]. "The form of the dissociation curve is very sensitive to the concentration of hydrogen ions, so that it can be used as an indicator for changes in this direction occurring in the blood either as the result of muscular work, of want of oxygen, or in pathological states of acidosis.

"Now what are the equations to the curves obtained in the presence of acid or of salts? Since haemoglobin is in colloidal solution and, as we have seen, electrolytes have a powerful effect in causing aggregation of colloidal particles, this phenomenon would naturally be looked for as the explanation. A. V. Hill, on the hypothesis of the aggregation of molecules of haemoglobin causing the reaction to become of a higher order than unimolecular, arrived at an expression of the form:—

$$y = 100\frac{kx^n}{1+kx^n}$$

where y is the percentage saturation of haemoglobin with oxygen, x the oxygen pressure. This formula, by proper choice of the constants, K and n, was found to apply to the experimental data of several cases taken.

"In attempting to understand the meaning of this equation, it is well to point out that Hill himself did not profess to attach any direct physical meaning to the constants, although Barcroft regards K as the equilibrium constant and n as the average number of molecules of haemoglobin in each aggregate. Hill subsequently adopts this view to a large extent . . .

"The constancy of n with a particular acid leads Bancroft to make the statement that the action of acid does not lead to change in the number of molecules in the aggregates, but to a change of the equilibrium constant. But, as we have seen, it is not satisfactorily shown that n refers to the number of molecules in the aggregates, and I might venture to point out that constancy of the exponent is also a characteristic of adsorption."

While it is clearly useful to treat a colloidal solution as having some of the properties of a true solution, it would be a serious mistake not to distinguish between the two at other times. There is nothing inconsistent about this. So far as the effect on the partial pressure of water vapor is concerned, we may consider the alcohol in a dilute aqueous solution as behaving like a gas; but, if we consider the density of the solution or its solvent action for sodium chloride, sugar, or naphthalene, we have to treat the alcohol as a liquid. In

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[1] Bayliss: "Principles of General Physiology," 623 (1915).

fact, if we consider the effect of the water on the partial pressure of the alcohol we treat the alcohol as a liquid and the water as a gas. When we say that a solute behaves in certain respects like an ideal gas, we do not mean either that it behaves in all respects like an ideal gas or that it is an ideal gas. The fact that many physical chemists do commit this error does not make it any less an error.

If we shake up clean carbon black with water, we get a suspension and everybody knows that the carbon black is not dissolved in the water. The problem is to determine at what point of dispersity, a sol changes to a solution. So far, nobody has tried to draw the line sharply; but it can be done if we make one assumption, the accuracy of which will have to be left to the future.

The simpler cases can be decided without making any assumption, by harking back to Gibbs. According to Gibbs the properties of a phase containing any number of components are dependent only on the temperature, pressure, and the concentrations, provided we are working under conditions under which we can ignore effects due to gravity, surface tension, electromotive forces, etc. Conversely, any apparent phase in which the properties depend on something other than the temperature, pressure, and concentrations is not a phase in the sense in which Gibbs uses the term. According to this definition a colloidal gold sol is not a one-phase system because we can fix the temperature, pressure and concentration, and yet the color may be either blue or red by transmitted light. It does not help to talk about surface tension effects because they would not be an important factor in case we were dealing with a true solution.

By the application of the Gibbs criterion in one form or another we can show that most of the colloidal solutions are two-phase systems; and yet we encounter no difficulty with mixtures of gases, a case which bothers a person who tries to define a phase as being either chemically or physically homogeneous. In the last analysis a mixture of two gases is physically and chemically heterogeneous; but everybody knows it is a one-phase system and that is the way it comes out if we apply the criterion of Gibbs.

The difficulty comes with strictly reversible sols of such substances as tannin and soaps. So far as I know now, they satisfy the criterion of Gibbs and yet are two-phase systems. The only way I see now of handling these cases is to make a definite and explicit assumption as to the properties of gases, leaving it to the future to determine whether the guess is a good one or not.

We know that hydrogen will pass through hot platinum while other gases will not. We know that helium will pass through hot quartz while hydrogen will not. We know that carbon monoxide will pass through hot iron while many other gases do not. We know that hydrogen passes through rubber much more readily than does helium, and that carbon dioxide passes through more rapidly than either. We know that there is no apparent relation between the molecular weights of the substances which pass through rubber and those which do not, whereas there is a very distinct relation between the chemical properties. Practically everybody will agree that these are cases in which the gases pass through the diaphragm or membrane because of solubility and not because of a porous structure. I am making the explicit assumption—for which I have no experimental evidence—that any pore which will let one gas or liquid through will let another gas or liquid through. In other words, there is no such thing as a molecular sieve for gases or vapors.

If this postulate be granted, then any substance which can be filtered out by an ultra-filter is in suspension. This criterion enables us to handle the cases of tannin and of soap. Bechhold[1] was not able to construct an ultra-filter which was permeable to water and which stopped any substances which all of us agree are in true solution.

When one makes the suggestion that inability to pass through an ultra-filter is a proof of a suspension, the usual answer is that a copper ferrocyanide membrane stops sugar, magnesium sulphate, etc. To meet this difficulty it is necessary to point out the theoretical difference between an ultra-filter and a semipermeable membrane. This is the more important because I myself have not been entirely free from error in regard to the semipermeable membrane.

We can have two types of semipermeable membrane, one with a continuous film and the other with a porous one. In the case of a continuous film it is essential that the solvent shall dissolve in the membrane and that the solute does not. With a porous film we shall have a semipermeable membrane only in case we have strong negative adsorption—adsorption of the solvent and not the solute—and in case the diameter of the pores is so small that the adsorbed liquid fills the pores completely leaving no central channel, through which the solution can diffuse. I had assumed previously[2] that the copper ferrocyanide membrane was probably a continuous film; but that seems to have been a mistake. With our present views in regard to gelatinous precipitates, a copper ferrocyanide membrane must consist of particles of copper ferrocyanide with adsorbed water films, which means that it must be a granular membrane showing strong negative adsorption for many aqueous solutions, notably sugar solutions.

An ultra-filter is essentially a porous membrane which will, by hypothesis, never become a semipermeable membrane unless there is strong negative adsorption. It was a most fortunate accident that Bechhold worked with a material which gave no appreciable negative adsorption and consequently did not change to a semipermeable membrane as the pores were made smaller and smaller. If he had worked with materials having the properties of those used by Bigelow[3] and by Bartell,[4] it might have been a long time before we realized the fundamental difference between a semipermeable membrane and an ultra-filter.

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[1] Z. physik. Chem. 60, 257 (1907); 64, 328 (1908).

[2] Bancroft: "Applied Colloid Chemistry," 110 (1921).

[3] J. Am. Chem. Soc., 29, 1576, 1675 (1907); 31, 1194 (1909).

[4] J. Phys. Chem., 15, 659 (1911); 16, 318 (1912); J. Am. Chem. Soc., 36, 646 (1914); 38, 1029, 1036 (1916).

The conclusion that a substance which can be filtered out through an ultra-filter is in colloidal solution and not in true solution rests on the explicit assumption that any gas or vapor will go through any pore through which any other gas or vapor will go. It is not known whether this is true or not; but it seems plausible and it gives a definite mark to shoot at, whereas one great trouble in the past has been that people were not willing to put forward any definite criterion which would enable us to decide whether we were dealing with a true solution or a colloidal one.

For instance, Mellor[1] says that "while a solution in equilibrium can be said to have the same composition in all its parts, so that it cannot be separated by mechanical or physical operations into different individual parts, yet, according to the molecular theory, there must be a limit to the subdivision beyond which the solution can no longer be regarded as homogeneous. Consequently, there is no clearly defined line of demarcation between heterogeneous and homogeneous mixtures. A so-called homogeneous solution, for instance, can sometimes be separated into its component parts by certain membranes, just as a mixture of gases can sometimes be separated into its constituent parts by atmolysis. A homogeneous solution, or a mixture of gases, however, is considered to be a homogeneous one-phase system because diffusion maintains one uniform concentration throughout its mass."

The converse of the general proposition is not necessarily true that any apparent solution which will pass through the finest ultra-filter is necessarily a true solution. It seems conceivable that an electrically-stabilized emulsion might pass through any ultra-filter. Such a case need not bother us, because it would not satisfy the criterion of Gibbs.

The general results of this article may be summarized as follows:—

1. The molecular weight of the chemist is a function of the vapor density of a gas or of the osmotic pressure of a solution.

2. The molecular weight of the chemist is specific and varies discontinuously.

3. A suspended particle behaves in some respects like a substance in true solution. The molecular weight of the physicist is a function of the weight of the suspended particle.

4. The molecular weight of the physicist is, or may be, non-specific and varies continuously.

5. The two conceptions of molecular weight are not inconsistent if we remember that the molecular weight of the chemist is a function of the weight of the ultimate particle and that the specificity shows only when we get down to this value in any given case.

6. The conception that a colloidal solution may behave in some respects like a true solution enables us to account for the adsorption isotherms with tannin sols or with sols of the substantive dyes. The suspended particles do not behave like a phase of constant concentration.

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[1] "Treatise on Inorganic and Theoretical Chemistry" 1, 515 (1922).

7. In certain respects a colloidal solution is fundamentally different from a true solution.

8. According to the criterion of Gibbs an apparent phase is not a one-phase system if the properties are not defined absolutely when the temperature, pressure, and concentrations are fixed.

9. An ultra-filter is a porous membrane showing no marked negative adsorption—preferential adsorption of the solvent.

10. An ultra-filter, as defined, differs fundamentally from a semipermeable membrane.

11. The explicit assumption is made that any gas or vapor will pass through any pore through which any other gas or vapor will pass.

12. A substance which can be filtered out by means of an ultra-filter is not in true solution.

Cornell University

THE CONDUCTIVITY OF ELECTROLYTES
II. THE MOBILITY OF THE HYDROGEN ION AT 25°.

BY CECIL W. DAVIES

In investigations on the electrochemistry of dilute solutions it is a matter of the first importance that the value of Λ_∞, the equivalent conductivity at infinite dilution, should be accurately known; whether or not the expression $\frac{\Lambda^2.C}{\Lambda_\infty(\Lambda_\infty - \Lambda)}$ will give a constant over ranges of concentration will depend entirely, except for the very weakest electrolytes, on the value of Λ_∞ used. Unfortunately this quantity cannot, at the present time, be determined with precision by even the most accurate experimental work, and recourse is therefore had to some method of extrapolation.

For strong electrolytes the empirical method of Kohlrausch appears to be reliable. If the conductivity values below 0.002 N are plotted against the square root of the concentration a straight line is obtained, and a production of this line to the axis gives Λ_∞. The truth of this linear relationship is borne out by the more recent accurate work of Weiland[1] whose data for KCl extend down to a concentration of 0.000025 N, and it also finds support in another direction: it has recently been shown[2] that the conductivity of a uni-univalent electrolyte is given within experimental error by the empirical equation

$$\Lambda = \Lambda_\infty - 2.12.\ 10^{-7}.\ T^3.\ \sqrt{c}\,(\sqrt{\Lambda^{\cdot}_\infty} + \sqrt{\Lambda'_\infty}) \qquad (1)$$

where $\Lambda^{\cdot}_\infty$, Λ'_∞ are the mobilities of the ions concerned; it is evident that the general applicability of such an equation affords strong support for Kohlrausch's method of extrapolation.

The linear relationship between the conductivity and the root of the concentration holds only for the strong electrolytes—those substances which may be regarded as completely dissociated. For weaker electrolytes the $\Lambda - \sqrt{c}$ curve is more or less curved, being concave to the axis of concentration. In these cases it is reasonable to suppose that equation (1) will give the slope of the tangent (for $C = 0$) of the experimental curve.

Use may therefore be made of this equation in the extrapolation of conductivity data. If $\Lambda^{\cdot}_\infty$ and Λ'_∞ are approximately known, then the slope of the $\Lambda - \sqrt{c}$ line for a strong electrolyte may be predicted and the extrapolation checked to some extent, in that close agreement between the predicted and the experimentally found slopes will afford some evidence for the accuracy of both equation and data. For a weaker electrolyte the equation may be expected to give the limiting slope at infinite dilution. In the following sections the equation is applied to the conductivity data for acids.

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[1] J. Am. Chem. Soc., 40, 131 (1918).

[2] J. Phys. Chem., 29, 473 (1925).

Until the last year or so the value 347 was usually accepted as the mobility of the hydrogen ion at 25°. This value depended chiefly on the work of Kendall[1] upon organic acids. More recently the results of Kraus and Parker[2] on iodic acid and of Parker[3] on hydrochloric acid have led to the value 349.9. These authors in the course of their experiments have investigated the effects both of impurities in the water and of the glass of the cell on the conductivities of acids, and have shown that the presence of these sources of error in Kendall's work is sufficient to account for his much lower value. As Kraus and Parker[2] point out, the method of extrapolation used by them will give a minimum value for Λ_∞, and the value 349.9 for the hydrogen ion must be regarded as such. By applying the method described in this paper the higher value 351.3 is obtained.

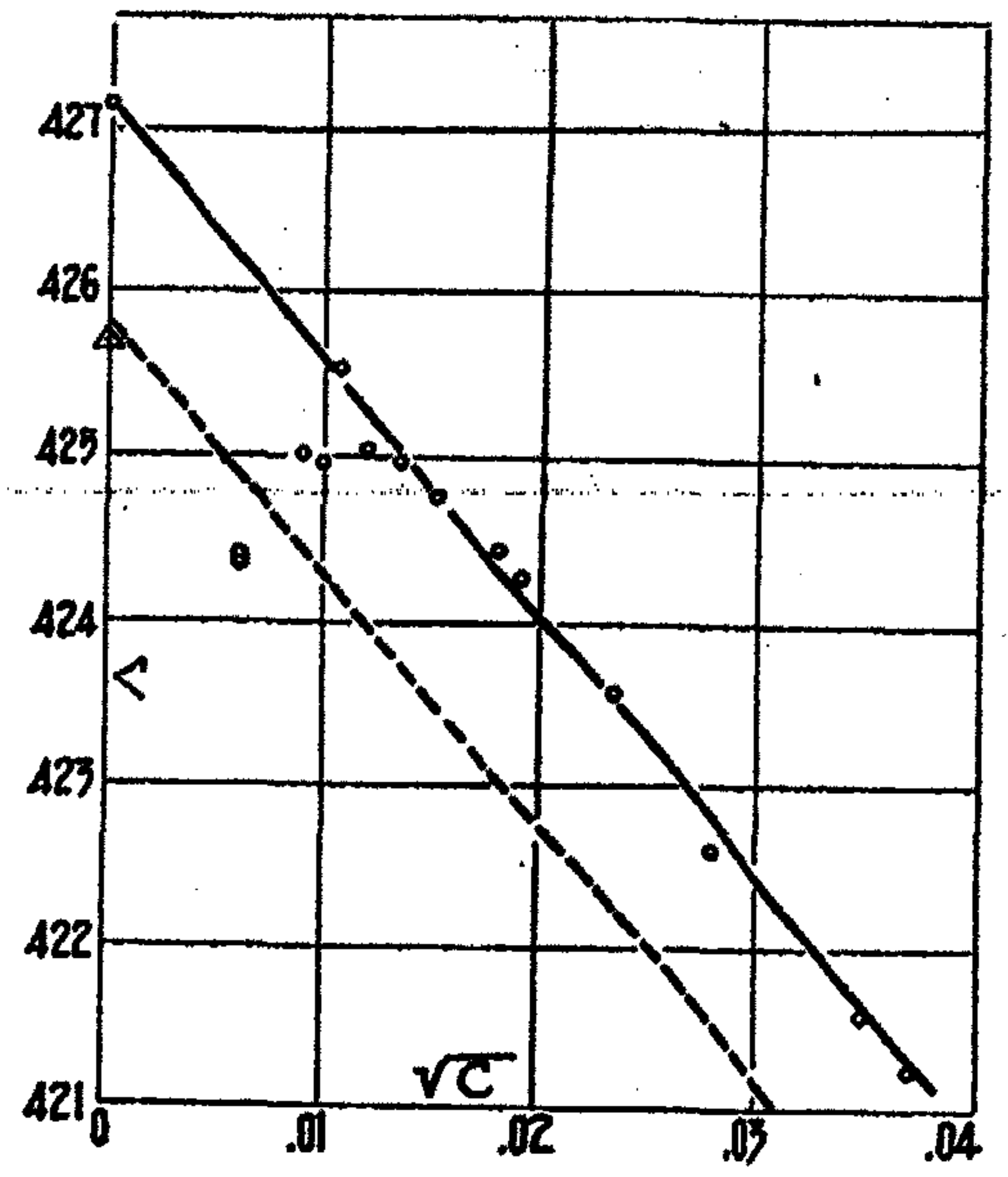

FIG. 1

Fig. 1 shows the data of Parker on HCl plotted against $\sqrt{c}$. The last four points were rejected by Parker as definitely showing contamination of the acid from some source. With the exception of these the experimental points lie satisfactorily on a straight line—in agreement with Kohlrausch's conclusions for other strong electrolytes,—and give the value $\Lambda_\infty = 427.1$.

Now if $\Lambda'_{Cl} = 75.8$, $\Lambda'_{H} = 350$ be taken as approximate values for the mobilities of the ions, equation 1 gives for the slope of this line:

$$\frac{\Lambda_\infty - \Lambda}{\sqrt{c}} = 5.61. (8.71 + 18.71) = 154,$$

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[1] J. Chem. Soc., **101**, 1275, (1912).

[2] J. Am. Chem. Soc., **44**, 2429, (1922).

[3] J. Am. Chem. Soc., **45**, 2017 (1923).

a number which may be in error by 1% owing to uncertainty in the value of the constant 5.61. This slope is shown in Fig. 1 by a dotted line, and this is very nearly parallel to that drawn through the experimental points. Not only then do the data obey Kohlrausch's law, but they also conform with the general equation deduced for other strong electrolytes, and the value Λ_∞ = 427.1 can be accepted with some confidence. If Λ'_{Cl} be taken as 75.8 this gives Λ'_H = 351.3. For comparison, Parker's value Λ_∞ = 425.7 is also shown in Fig. 1, denoted by a triangle.

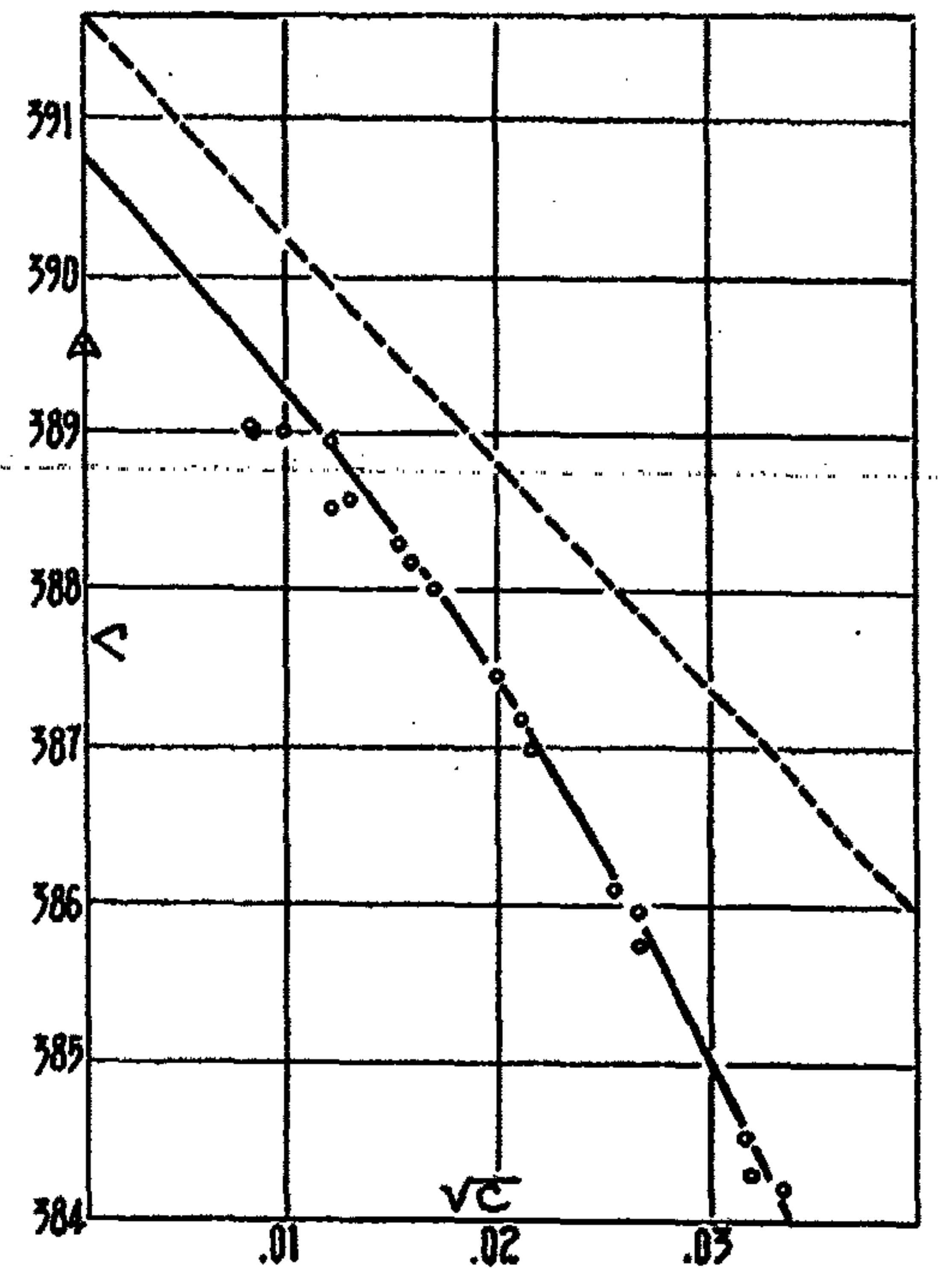

Fig. 2

In Fig. 2 the data of Kraus and Parker on iodic acid are shown on the same scale. In this case the experimental points do not lie on a straight line, which suggests that in concentrations greater than 0.0001 N. iodic acid cannot be considered as completely dissociated. If Λ_{IO_3} = 39.6, equation 1 gives $\frac{\Lambda_\infty - \Lambda}{\sqrt{c}} = 5.61\ (6.29 + 18.71) = 140$, and this number should represent the limiting slope of the conductivity curve at dilutions so great that dissociation can be considered complete. In Fig. 2 this slope is shown as a dotted line, and an unbroken line shows the extrapolation of the experimental data carried out so as to conform with this limiting slope. This extrapolation gives Λ_∞ = 390.8 and taking Λ_{IO_3} = 39.6, Λ'_H becomes 351.2. As before, the experimental points suggest that even the accurate work of Kraus and Parker was unsuccessful in entirely eliminating at great dilutions all errors due to the presence of impurities.

The two series of data of Kraus and Parker therefore lead to the value 351.3 ± 0.1 as the probable mobility of hydrogen ion at 25°.

A consequence of accepting this value is that the expression $\frac{\Lambda^2.C}{\Lambda_\alpha(\Lambda_\alpha - \Lambda)}$ will be found not to give a constant for HCl or HIO_3, nor for the transition acids investigated by Kendall[1].

It is also interesting to find in the form of the conductivity curve of iodic acid a clear indication that this acid is not so highly dissociated as HCl or the greater number of uni-univalent salts. It is more comparable in strength with the stronger transition acids such as trichlorobutyric acid; the truth of the statement of Kraus and Parker that iodic acid is a much stronger electrolyte than KCl is very doubtful.

These points will be discussed in a later paper[2], in which the true equilibrium constants for several electrolytes will be derived.

Summary

1. A new criterion is proposed for use in the extrapolation of conductivity data.

2. The value 351.3 is derived for the mobility of hydrogen ion at 25° from a consideration of the data of Kraus and Parker on HIO_3 and HCl.

3. At 25° HCl can be regarded as completely dissociated at concentrations below 0.002 N, while the dissociation of HIO_3 is not virtually complete at concentrations above 0.0001 N. Neither acid appears to give a constant for the expression $\Lambda^2.c / \Lambda_\alpha . (\Lambda_\alpha - \Lambda)$ at great dilutions.

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[1] The dissociation constants found by Kendall are just as incompatible with the Kraus and Parker value $\Lambda'_H = 349.9$.

[2] Part III, J. Phys. Chem. 29, 977 (1925).

THE CONDUCTIVITY OF ELECTROLYTES.
III. THE CORRELATION OF STRONG AND WEAK ELECTROLYTES

BY CECIL W. DAVIES

In considering the conductivities of solutions it is customary to classify electrolytes into two groups. The "weak electrolytes" give a constant for the expression $\Lambda^2.c/\Lambda_\infty.(\Lambda_\infty - \Lambda)$, so that for these electrolytes the Arrhenius theory of partial ionisation is satisfactory. The second group consists of the "strong electrolytes" for which the theory of Arrhenius appears to fail.

It seems most unlikely that this classification corresponds to any actual fundamental distinction, for the typically "strong" and "weak" electrolytes in water are connected by an extensive and unbroken series of electrolytes intermediate in strength, and in some non-aqueous solvents most of the electrolytes investigated would have to be classed as "transition" electrolytes. This being so, a satisfactory theory of solutions will be impossible until the arbitrary distinction has been removed and the behaviour of the two groups reconciled.

Unfortunately the tendency of much modern research has been to make such a reconciliation more remote, owing to the development of the "complete dissociation theory," which is regarded by many chemists[1] as the only satisfactory explanation yet advanced for the behaviour of strong electrolytes in dilute solution. According to this theory the decrease in conductivity of a strong electrolyte, at any rate in very dilute solutions, is to be attributed to a diminution in the mobilities of the ions concerned rather than to a decrease in their number. Much recent work on strong electrolytes is interpreted with the aid of this theory, while conductivity changes in weak electrolytes on the other hand are explained by the unmodified Arrhenius theory, in which no account is taken of possible changes in the mobilities of the ions. The defects of this position are evident, especially when we find that for transition electrolytes neither theory affords a satisfactory basis[2].

On the other hand, reference should be made to the attempts to reconcile the behaviour of strong and weak electrolytes on the basis of the original Arrhenius theory; many chemists hold the view that the strong as well as the weak electrolytes "obey the mass action law," that is, that they do give a constant in the expression $\Lambda^2.c/\Lambda_\infty.(\Lambda_\infty - \Lambda) = K$, at sufficiently low concentrations. Evidence for this belief is found in the more recent conductivity

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[1] See A. A. Noyes [J. Am. Chem. Soc., 46, 1080 (1924)] and the authors referred to in reference 5 of that article.

[2] The dissociation constants found by Kendall [J. Chem. Soc., 101, 1275 (1912)] for several acids of "transitional" strength were obtained by choosing an appropriate value for the mobility of the hydrogen ion. This value, Λ_H = 347.2 has since been shown to be too low [Kraus and Parker: J. Am. Chem. Soc., 44, 2446-8 (1922), and see Davies: J. Phys. Chem., 29, 973 (1925)].

work of Kendall[1] on many organic acids, of Weiland[2] on KCl, of Kraus and Parker[3] on HIO_3 and of Parker[4] on HCl.

This view is open to much criticism. In the first place, the constancy of K in "the mass action expression" depends entirely on the value taken for Λ_∞, and this in turn on the method of extrapolation adopted. In the cases of KCl, HIO_3 and HCl a method of extrapolation, different from those used by the authors mentioned but just as consistent with the experimental results, will lead to quite different values[5] in each case for Λ_∞; and in the case of the organic acids investigated by Kendall the mobility of the hydrogen ion was taken as 347.2, a value which is quite incompatible with the results of Kraus and Parker on other acids. Direct evidence for the view that the mass action law is obeyed is therefore of a very uncertain character.

Again, many consequences of the theory are difficult to explain. For instance, KCl is stated to obey the law of mass action at low concentrations, the value of the ionisation constant being $K = 0.02$; for HIO_3, $K = 0.07$ which leads Kraus and Parker to state that it is a much stronger electrolyte than KCl; yet, at a concentration of 0.05N, the value[6] of Λ/Λ_∞ for HIO_3 is only 0.80, while the corresponding value[7] for KCl is 0.89. Further, taking again the case of KCl, the figures of Weiland lead one to suppose that the mass action expression gives a constant K at concentrations under 0.0001 N, but that at 0.0005 N the value of K has already increased by 100%. The presence of very considerable disturbing influences must therefore be admitted even at such great dilutions as this, and there seems to be no *a priori* reason for expecting, just as there is little evidence for proving, that at 0.0001 N all such influences have entirely disappeared whereas dissociation into ions is still incomplete.

The opposite view seems more probable and more consistent with the facts. Thus from the standpoint of the complete dissociation theory these disturbing influences are attributed to the electrical charges on the ions and to the effect their presence has on ionic mobilities, and this will persist even at dilutions so great that dissociation can be regarded as complete. The behaviour of aqueous solutions of strong electrolytes seems to support this view[8]. The object of the present paper is to show that this factor must be recognised in discussing the conductivity of any electrolyte except the very weakest ones; and that the theory of Arrhenius must be modified so as to take account of these changes in ionic mobilities. In any electrolyte in any solvent the change in conductivity with increasing concentration is to be

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[1] Kendall: J. Chem. Soc., **101**, 1275, (1912); Medd. k. Vetenskapsakad. Nobelinst. **2**, 38 (1913).

[2] Weiland: J. Am. Chem. Soc., **40**, 131 (1918).

[3] Kraus and Parker: J. Am. Chem. Soc., **44**, 2429 (1922).

[4] Parker: J. Am. Chem. Soc., **45**, 2017 (1923).

[5] Davies: J. Phys. Chem. **29**, 000 (1925).

[6] Groschuff: Z. Anorg. Chem. **47**, 331 (1905).

[7] Abegg's Handbuch: 2, I, 349 (1908).

[8] Davies: J. Phys. Chem. **29**, 473 (1925).

attributed to two causes: in part, to changes in the mobilities of the ions, and partly to a decrease in their number on account of their combination to form neutral molecules.[1]

In tracing the magnitudes of these two effects the strong electrolytes will be discussed first, for they comprise an extreme case in which the first of these two contributory causes alone is present in very dilute solutions.

Strong Electrolytes

It has been shown[2] that in aqueous solutions of uni-univalent strong electrolytes at concentrations below 0.002 N, the conductance of any ion can be represented by the equation

$$\dot{\Lambda}_c = \dot{\Lambda}_\infty - 2.12.\ 10^{-7}.\ T^3.\ \sqrt{c}.\sqrt{\dot{\Lambda}_\infty} \qquad (1)$$

where $\dot{\Lambda}_\infty$ is the conductance of the ion at infinite dilution and $\dot{\Lambda}_c$ its conductance at the concentration considered. This empirical equation is supported by conductivity data (the conductivity of a uni-univalent salt being given by the sum of two such expressions) and by the transport number data.

The behaviour of such solutions can also be studied in other ways such as by the freezing point and E. M. F. methods, from the results of which the activities of the ions can be derived; the activity-concentration ratio in dilute solutions is then invariably found to show a regular decrease with increasing concentration. It is not difficult to reconcile this fact with a complete dissociation theory; the activity of an ion depends not only upon its concentration but upon such factors as the resistance offered to the passage of the ion by the medium. Any factor which affects the mobility of an ion will also be expected to affect its activity. From the standpoint of the Kinetic Theory, the activities of two reactants depend on the number of impacts occurring, and this in turn depends both on the speed of the molecules or ions and on their concentrations. Now the decrease in the mobility of an ion with increasing concentration is governed by the simple relationship expressed in equation (1). It seems reasonable to suggest that the decrease in the activity coefficient of an ion will be due to the same cause and may be calculated in the same way: that is, that the activity of each ion of a strong electrolyte will be given by an expression such as $a = c.\ \dfrac{\dot{\Lambda}_\infty - \kappa\sqrt{c}\sqrt{\dot{\Lambda}_\infty}}{\dot{\Lambda}_\infty}$ (2) (where $k = 2.12.\ 10^{-7}.T^3 = 5.61$ at 25°C.), and that the mean activity coefficient for a strong electrolyte will be expressed by the equation:

$$\gamma = \frac{a_\pm}{c_\pm}\sqrt{\frac{\dot{\Lambda}_\infty - \kappa\sqrt{c}\sqrt{\dot{\Lambda}_\infty}}{\dot{\Lambda}_\infty} \cdot \frac{\Lambda'_\infty - \kappa\sqrt{c}\sqrt{\Lambda'_\infty}}{\Lambda'_\infty}} \qquad (3)$$

This suggestion is easily tested. In Table I the activity coefficients for several ions are calculated by equation (2), and in Table II the mean activity coeffi-

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[1] In interpreting work at higher concentrations than are dealt with in this paper other influences may have to be recognised, such as the complex ion formation postulated by Schneider and Bradley: [J. Am. Chem. Soc. 45, 1121 (1923)] and others.

[2] Davies: J. Phys. Chem. 29, 473 (1925).

cients calculated in the same way from equation (3) are compared with experimental results[1].

TABLE I

			c =				
Ion.	Λ_∞	$\sqrt{\Lambda_\infty}$.	.0001	.0002	.0005	.001	.002
Cl	75.8	8.71	.9936	.9908	.9856	.9795	.9712
IO_3	39.6	6.29	.9910	.9877	.9800	.9716	.9601
H	351.3	18.74	.9970	.9956	.9931	.9906	.9868
K	74.0	8.60	.9936	.9908	.9854	.9792	.9707
Na	51.0	7.14	.9922	.9888	.9826	.9752	.9649

TABLE II

c	.0001	.0002	.0005	.001	.002
HCl (calc.)	.9954	.9931	.9895	.9851	.9788
HCl (obs.)	——	——	.991	.984	.971
KCl (calc.)	.9936	.9908	.9855	.9793	.9709
NaCl (calc.)	.9928	.9900	.9842	.9772	.9681
KCl NaCl } (obs.)	.993	.990	.984	.977	.967
KIO_3 (calc.)	.9924	.9893	.9826	.9754	.9654
$NaIO_3$ (")	.9917	.9883	.9813	.9734	.9625
KIO_3 $NaIO_3$ } (obs.)	.988	.982	.972	.961	.946

Having regard to the degree of accuracy of the experimental results at these low concentrations (they are all based on some empirical extrapolation of experimental results to zero concentration) it is difficult to criticize the agreement shown in Table II. But it may be said that all experimental results, as far as they go at the present time, support the view that the whole behavior of these electrolytes can be explained by a regular diminution in the mobilities of the ions with increasing concentration. The table also shows that activity coefficients calculated by equation (2) can be employed in mass-action expressions in place of experimentally determined values without introducing serious errors.

Weak and Transition Electrolytes

Here it is necessary to distinguish between two effects: changes in the degree of dissociation, and changes in the ion mobilities. For this purpose it seems reasonable to suppose that the presence of neutral molecules of the electrolyte will not affect the mobilities of the ions except in so far as it modifies, at fairly high concentrations, the viscosity of the medium. If this is so, the mobility of each ion will be given at any concentration by the equation: $\Lambda' = \Lambda'_\infty - 5.61\sqrt{c_i}\sqrt{\Lambda'_\infty}$ where c_i is the ionic concentration.

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[1] Taken from Lewis and Randall: "Thermodynamics," pp. 336, 344.

TABLE III. ACETIC ACID

	1	2	3	4	5	6	7	8	9	10	11	12	13
	C	Λ	η_0	$\Lambda.\frac{\eta_c}{\eta_0}$	$\frac{\Lambda}{\Lambda_\infty}.\frac{\eta_c}{\eta_0}$	$\frac{\Lambda^2.c}{\Lambda_\infty(\Lambda_\infty - \Lambda)} = K_1(\times 10^4)$	K_2 $(\times 10^4)$	c_i	c_i/C	$c_i^2/c_u = K_3(\times 10^4)$	f_H	f_{Ac}	$\frac{f_H.f_{Ac}.c_i^2}{c_u} = K_4(\times 10^4)$
1.	.2529	3.221	1.0291	3.314	.00845	.1722	.1823	.002174	.008598	.1886	.9860	.9590	.1782
2.	.1265	4.618	1.0146	4.684	.01195	.1776	.1828	.001533	.01212	.1880	.9883	.9649	.1793
3.	.07369	6.086	1.0085	6.138	.01566	.1804	.1835	.001168	.01585	.1882	.9897	.9701	.1807
4.	.06320	6.561	1.0073	6.609	.01686	.1801	.1827	.001078	.01706	.1872	.9902	.9709	.1799
5.	.03685	8.591	1.0042	8.628	.02201	.1809	.1825	.0008198	.02225	.1865	.9915	.9747	.1803
6.	.01842	12.091	1.0021	12.12	.03091	.1807	.1818	.0005741	.03117	.1847	.9928	.9788	.1795
7.	.009208	16.98	1.0011	17.00	.04301	.1807	.1810	.0004022	.04367	.1837	.9940	.9824	.1794
8.	.004606	23.81	1.0005	23.82	.06077	.1810	.1811	.0002817	.06115	.1835	.9949	.9851	.1799
9.	.002303	33.22	1.0002	33.23	.08476	.1807	.1807	.0001962	.08519	.1827	.9956	.9877	.1797
10.	.001151	46.12	1.0001	46.12	.1177	.1806	.1806	.0001360	.1181	.1823	.9965	.9897	.1797
11.	.0005757	63.58	—	—	.1622	.1807	.1807	.00009370	.1628	.1822	.9972	.9913	.1801
12.	.0002879	86.67	—	—	.2211	.1807	.1807	.00006386	.2218	.1821	.9977	.9928	.1803
13.	.0001439	116.62	—	—	.2976	.1813	.1813	.00004290	.2982	.1823	.9979	.9942	.1808
						Mean (Nos. 7 - 12)	.1808					Mean:	.1799

Now the equivalent conductivity of the solution is given by the equation $\Lambda = c_i/C . (\Lambda^{\cdot} + \Lambda')$, where C is the total concentration and c_i/C represents the degree of ionisation. If κ is the specific conductivity of the solution, this equation may be put in the form

$$\kappa = \Lambda.C = c_i \left\{ \Lambda_\alpha - 5.61.\sqrt{c_i} \left(\sqrt{\Lambda^{\cdot}_\alpha} + \sqrt{\Lambda'_\alpha} \right) \right\} \qquad (4)$$

and from this we can, for each value of C, the total concentration, calculate the corresponding ion-concentration c_i, and $C - c_i = c_u$, the concentration of undissociated molecules.

The calculation is applied to acetic acid at 25°C in Table III. The first two columns show total concentration and equivalent conductivity taken from the data of Kendall[1]; column 3 shows the viscosity (taking the mean of the values of Reyher[2] and of Rivett and Sidgwick[3]), and the corrected conductivity values, $\Lambda\eta_c/\eta_o$ are given in column 4. Column 5 gives the degree of ionisation calculated by the Arrhenius method, $\alpha = \Lambda/\Lambda_\alpha \ . \ \eta_c/\eta_o$, Λ_α being taken as 351.3[4] + 40.7[5] = 392.0, and columns 6 and 7 give the mass-action constants K_1 and K_2, calculated according to the Ostwald dilution law using in the first case the uncorrected and in the second case the corrected conductivity values. The remainder of Table III shows the results of applying the methods described in this paper. Column 8 gives the ion-concentration obtained by means of equation (4), where the constants have in this case the values: $\kappa = c_i . (392.0 - 140.9\sqrt{c_i})$; column 9 gives the degree of dissociation, and column 10 gives values for $c_i^2/c_u = K_3$, where K_3 will be seen to increase steadily with increasing concentration.

In order to obtain the true mass-action constant for the dissociation of acetic acid, the activities and not the concentrations must be employed. For the neutral molecules at these low concentrations it may be assumed that the two are proportional, but in the cases of the ions this is no longer true, and the ionic concentration must be multiplied by appropriate activity coefficients as shown in equation (2). These are given in columns 11 and 12, calculated by means of the formulae

$$f_H = \frac{351.3 - 5.61\sqrt{c_i}.\sqrt{351.3}}{351.3} \qquad f_{Ac} = \frac{40.7 - 5.61\sqrt{c_i}.\sqrt{40.7}}{40.7}$$

Finally, column 13 shows the true mass-action constant $K_4 = \frac{f_H . c_i . f_{Ac} . c_i.}{c_u}$

It will be seen that K_4 shows a very satisfactory constancy. In finding the mean value for the series, the figure at the lowest concentration is excluded as the experimental data seem less trustworthy in this case, and the value at the greatest concentration is also neglected as the ionic concentration here

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[1] J. Chem. Soc., **101**, 1275 (1912).

[2] Reyher: Z. physik. Chem., **2**, 744 (1888).

[3] Rivett and Sidgwick: J. Chem. Soc., **97**, 736 (1910).

[4] Davies: J. Phys. Chem. **29**,

[5] Bredig: Z. physik. Chem. **13**, 218 (1894).

is rather greater than those for which the relationships used in the calculation are found to hold[1]. The mean of the remainder is $K = 0.1799 \cdot 10^{-4}$.

When the values of K_4 are compared with the values that one obtains when no allowance is made for changes of ionic mobility, as shown in columns 6 and 7 of the table, it is found that K_4 is on the whole much more constant than K_1 and K_2. At the same time, however, K_1 and K_2 are both satisfactorily constant up to concentrations of 0.01 N, and a comparison of columns 6 and 7 shows that the variations of K in the stronger solutions might conceivably be attributed to inadequacies of the viscosity correction. In the stronger acids shortly to be discussed, however, there is no room for doubt that the true dissociation constant K_4 is satisfactory and that the Ostwald K is not.

Another point of interest in Table III is the fact that although the calculated degree of dissociation differs considerably at the higher concentrations from that given by the Arrhenius formula, yet the new value for the constant K differs by only 0.5% from the K_2 obtained by Ostwald's dilution law. The reason for this is that in calculating K_2 two factors are neglected, and the weaker the acid the more nearly do these counterbalance one another. In the first place, by assuming constant mobilities for the ions one obtains values for the concentration of the ions that are too low; but by using these concentrations in the mass-action expression instead of the lower activities one arrives at a value for the mass-action constant which is not greatly in error.

In Table IV are shown the results of applying the same method of calculation to the transition acids investigated by Kendall, and to Iodic acid. The table shows clearly that K_1, calculated by the Ostwald dilution law, is not constant but increases steadily with increasing concentration; but that the "true dissociation constant" K_4 remains satisfactorily constant except at the greatest dilutions, where it shows a falling off. This effect at low concentrations is only to be expected since the conductivity values at these extreme dilutions are known to be too low[2]. The effect on K_4 of a slight change in the accepted conductivity value for the lowest concentration is illustrated in Table IV for the case of cyanoacetic acid, an arbitrary conductivity value being employed in calculating row 10.

In the case of iodic acid the data used are those of Kraus and Parker[3]. This is a much stronger acid than those previously discussed, and at the concentrations considered in Table IV less than half of the conductivity diminution, $\Lambda_\infty - \Lambda$, is to be attributed to the effect of incomplete dissociation, the greater part of it being due to the diminution in the ion-mobilities Yet it will be seen that when allowance is made as before for the second of these causes a satisfactory mass action constant $k = 0.173$ is obtained.

Iodic acid is especially interesting since it seems to occupy a position midway between the typical "strong" electrolytes and transition electrolytes

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[1] Davies: J. Phys. Chem. 29, 473 (1925).

[2] Kraus and Parker: J. Am. Chem. Soc., 44, 2446 (1922).

[3] J. Am. Chem. Soc., 44, 2249 (1922).

TABLE IV

	1	2	3	4	5	6	7	8
	C	Λ	$\frac{\Lambda}{\alpha}$	(100x) $\frac{\Lambda^2.c}{\Lambda_\alpha.(\Lambda_\alpha - \Lambda)} = K_1$	c_i	c_i/C	(100x) $c_i^2/c_u = K_3$	(100x) $\frac{f_u.f_{Cv}.c_i^2}{c_u} = K_4$
CYANOACETIC ACID. $\Lambda_\alpha = 351.3 + 38.9 = 390.2$								
1.	.003716	238.7	.6117	.3583	.002313	.6224	.3815	.3596
2.	.003005	252.4	.6469	.3559	.001975	.6573	.3787	.3588
3.	.001858	282.6	.7241	.3533	.001364	.7340	.3766	.3599
4.	.001503	294.9	.7556	.3514	.001150	.7652	.3746	.3593
5.	.0009287	320.0	.8200	.3470	.0007691	.8283	.3706	.3583
6.	.0007515	329.2	.8437	.3423	.0006399	.8515	.3669	.3558
7.	.0004644	347.1	.8894	.3326	.0004161	.8960	.3585	.3497
8.	.0003757	353.2	.9051	.3245	.0003421	.9105	.3482	.3406
9.	.0002322	364.8	.9350	.3119	.0002183	.9401	.3430	.3368
10.	.0002322	366.0	.9380	.3295	.0002191	.9432	.3662	.3596
o-NITROBENZOIC ACID. $\Lambda_\alpha = 351.3 + 32.2 = 383.5$								
1.	.003906	265.0	.6908	.6034	.002751	.7042	.6552	.6113
2.	.001953	303.6	.7916	.5875	.001568	.8030	.6387	.6064
3.	.0009765	333.5	.8694	.5659	.0008578	.8786	.6198	.5968
4.	.0004883	353.6	.9217	.5323	.0004536	.9290	.5930	.5768
5.	.0002441	365.3	.9526	.4668	.0002338	.9579	.5309	.5204

TABLE IV (continued)

o-CHLOROBENZOIC ACID. $\Lambda_\infty = 351.3 + 32.8 = 384.1$.

	1	2	3	4	5	6	7	8
1.	.006663	134.6	.3504	.1260	.002376	.3567	.1317	.1236
2.	.003331	174.0	.4530	.1249	.001530	.4594	.1300	.1235
3.	.001666	218.0	.5676	.1242	.0009565	.5741	.1290	.1239
4.	.0008327	262.6	.6837	.1231	.0005742	.6896	.1276	.1237
5.	.0004163	302.1	.7865	.1206	.0003295	.7916	.1251	.1223
6.	.0002081	333.0	.8670	.1176	.0001813	.8712	.1227	.1205
7.	.0001041	353.7	.9210	.1115	.00009623	.9245	.1177	.1161

3.5 DI-NITROBENZOIC ACID. $\Lambda_\infty = 351.3 + 29.1 = 380.4$.

1.	.003929	175.7	.4618	.1558	.001843	.4690	.1628	.1535
2.	.001965	219.0	.5755	.1535	.001145	.5828	.1600	.1527
3.	.0009825	262.7	.6904	.1514	.0006847	.6969	.1574	.1519
4.	.0004912	301.5	.7925	.1488	.0003922	.7984	.1553	.1512
5.	.0002456	330.9	.8698	.1429	.0002148	.8744	.1497	.1469
6.	.0001228	350.7	.9219	.1337	.0001137	.9255	.1420	.1400

IODIC ACID. $\Lambda_\infty = 351.3 + 39.62 = 390.92$.

1.	.002	380.48	.9733	7.09	.0019781	.9891	17.9	16.9
2.	.0015	382.37	.9782	6.56	.0014878	.9919	18.1	17.3
3.	.001	384.43	.9834	5.82	.00099465	.9947	18.5	17.8

such as cyanoacetic acid. Thus its conductivity curve suggests[1] that at concentrations below 0.0001 N it can be treated—like the strong electrolytes—as completely dissociated, and this is in keeping with its dissociation constant k = 0.173 which requires a degree of ionisation of 99.94% at 0.0001 N. It seems natural to infer that the "strong" electrolytes themselves differ from weak and transition electrolytes only in their degree of ionisation which must be much greater even than that of iodic acid. Thus, for example, an electrolyte with a dissociation constant k = 1.0 would be 99.99% ionised at 0.0001 N, and 99.0% ionised at 0.01 N.

Summary

In the following paragraphs a summary is given of the conclusions reached in this paper and the preceding papers of this series.

I. In considering dilute solutions of electrolytes whether strong or weak the change of conductivity with increasing concentration is to be attributed partly to changes in the mobilities of the ions and partly to a decrease in the degree of ionisation.

II. With strong electrolytes at concentrations of 0.002 N or less the first of these causes alone is present. Evidence for this is found in the facts that (a) the conductivities of salts at these concentrations are additive, i. e., the sum of the ionic mobilities at the concentration considered, (b) the ionic mobilities so calculated vary with the concentration according to a general relationship: $\dot{\Lambda}_{\infty} - \Lambda = 2.12 . 10^{-7} . T^{3}\sqrt{c}\sqrt{\dot{\Lambda}_{\infty}}$, (c) the activity coefficients of the ions when calculated thermodynamically show the same proportionate decrease as do the mobilities, and probably from the same cause.

III. It follows from the equation quoted above that the conductivity of an electrolyte at sufficiently low concentrations is directly proportional to the square root of the concentration. This provides a satisfactory method of extrapolation.

IV. With weak and transition electrolytes the changes in the ionic mobilities are again given by the equation quoted, c in this case being the ionic concentration. These changes are only negligible when dealing with the very weakest electrolytes.

V. If allowance is made for these mobility changes the true degree of dissociation of a weak electrolyte can be calculated; and if the product of the ionic activities is then divided by the calculated concentration of unionised molecules the true dissociation constant is obtained.

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[1] Davies: J. Phys. Chem. 29, 973 (1925).

THE SORPTION OF IODINE AND CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTION, BY NORIT CHARCOALS. A COMPARISON OF THE SORPTION AND CATALYTIC ACTIVITIES.

BY J. B. FIRTH AND F. S. WATSON

In the present investigation the sorptive capacity and catalytic activity of several grades of the well known commercial decolourising charcoal Norit have been studied. Lemoine[1] found that charcoal obtained on the decomposition of wood, cocoanut, and sugar are efficient catalysts of hydrogen peroxide; the catalytic effect being apparently *correlative* with their sorptive power for gases.

The sorptive capacity and catalytic activity of a large number of charcoals have already been determined (see appendix) and no definite relationship between these two factors has been discerned.

The objects of the present investigation were firstly to determine for Norit, the sorptive capacity for iodine and catalytic activity towards hydrogen peroxide solution and secondly to determine whether these two factors were interdependent.

Experimental

Norit of grades 1, 2, 3 and 7, was used throughout the experiments herein described. The percentage ash is given in Table I. This ash consisted mainly of silica associated with a little phosphate and calcium. The ash itself in all four cases was similar and showed only a negligible sorption of iodine and catalytic activity towards hydrogen peroxide solution.

Purification and Activation of the Charcoal.

The Norit as supplied was digested with hot distilled water, filtered and thoroughly washed with hot distilled water until the washings showed no appreciable residue on evaporation. The resulting charcoal was then subjected to one of the following treatments.

I. The charcoal was dried in an air oven at 120°C.

II. The charcoal was heated in a vacuum in a quartz flask at 600°C, for two hours and then allowed to cool in a vacuum.

III. As in II except that the temperature was 900°C.

IV. A quantity of the charcoal activated as in II was treated with N/10 iodine solution in chloroform, in the proportion of 25 cc of the solution per gram of charcoal, for 24 hours. The charcoal was then filtered off, transferred to a silica evaporating dish and gently heated until iodine vapours were no longer evolved. The charcoal was then digested with alcoholic potassium hydroxide, filtered off and washed with boiling distilled water until the filtrate showed no opalescence with silver nitrate solution. The resulting

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[1] Compt. rend. **162**, 725 (1916).

charcoal was finally heated in a quartz flask in a vacuum at 600°C, for two hours and the required quantity of the charcoal weighed out after cooling to room temperature.

V. The charcoal was first treated as in III then as in IV except that the final heating was carried out at 900°C.

In some experiments the charcoal was subjected to further iodine or treatment by repeating processes IV or V two or, in some cases, three times.

Relative Bulks of the Charcoals.

The volume occupied by one gram of the charcoal, dried at 120°C was determined for each charcoal, and also after each of the treatments II to V. The charcoal was introduced into a weighed graduated tube, the tube being tapped until a constant reading was obtained, the volume was observed and the tube plus charcoal reweighed. From these observations the volume in cc. of one gram of the charcoal was calculated. The results are given in Table I.

TABLE I

Charcoal.	Percentage Ash.	Volume in c.c. occupied by one gram of charcoal after treatment.				
		I	II	III	IV	V
Norit No. 1	1.887	3.533	3.558	3.563	3.545	3.584
" " 2	8.424	2.262	2.415	2.386	2.463	2.571
" " 3	6.718	2.325	2.427	2.398	2.487	2.519
" " 7	10.561	2.053	2.179	2.257	2.261	2.358

Sorption of Iodine from Solution in Chloroform

N/10 solutions of iodine in chloroform were used throughout. The charcoal after being subjected to one of the above treatments and cooling to room temperature was brought into contact with the iodine solution as rapidly as possible. One gram of the charcoal was used in each case and treated with 25 c.c. of the N/10 iodine solution. The experimental details were very similar to those already stated in previous researches. The temperature of experiments was 18°C. The results are expressed in terms of 100 c.c. of solution; the mass of the carbon, $m = 4$ grams; x/m = grams of iodine sorbed by 1 gram of carbon; $a - x$ = the final concentration of the solution in grams per 100 c.c.

From previous researches (loc. cit.) it is evident that in the case of an active charcoal the sorption is very rapid during the first few minutes whilst after 24 hours the rate of sorption is very slow hence in the present case it is considered sufficient to determine the amount of iodine sorbed after 30 minutes and 24 hours respectively. Experiments were also carried out in the charcoal which had previously been subjected to iodine treatment (i.e. method IV or V) and in several experiments the iodine treatment was repeated a second time. The results are given in Table II.

TABLE II

Time.	Treatment I.		Treatment II.		Treatment IV.		Treatment IV. repeated.		Treatment III.		Treatment V.		Treatment V. repeated.	
	x/m	a-x	x/m	a-x	x/m	a-x	x/m	a-x	x/m	a-x	x/m	a-x	x/m	a-x
							Norit 1							
30 mins.	0.2996	0.0716	0.3069	0.0424	0.3075	0.0400			0.3133	0.0168	0.3138	0.0148	—	—
24 hours	0.3044	0.0524	0.3103	0.0288	0.3113	0.0248	0.3120	0.0220	0.3139	0.0144	0.3139	0.0144	—	—
							Norit 2							
30 mins.	0.3028	0.0588	0.3115	0.0239	0.3125	0.0200			0.3120	0.0220	0.3132	0.0172	—	—
24 hours	0.3075	0.0400	0.3119	0.0223	0.3128	0.0188	0.3142	0.0122	0.3139	0.0144	0.3130	0.0220	0.3086	0.0246
							Norit 3							
30 mins.	0.2991	0.0735	0.3110	0.0260	—	—	—	—	0.3144	0.0124	—	—	—	—
24 hours	0.3048	0.0508	0.3129	0.0184	—	—	—	—	0.3149	0.0103	—	—	—	—
							Norit 7							
30 mins.	0.2971	0.0816	0.3105	0.0261	—	—	—	—	0.3137	0.0150	—	—	—	—
24 hours	0.3040	0.0540	0.3126	0.0196	—	—	—	—	0.3137	0.0150	—	—	—	—

Catalytic Decomposition of Hydrogen Peroxide Solution

The catalytic activity of each of the Norit charcoals was determined. Five series of experiments were carried out in which the carbon prior to treatment with hydrogen peroxide solution was activated by one of the five methods already described. The experimental details were as already described in previous researches (loc. cit).

Aqueous solution of hydrogen peroxide containing 212.5 c.c. of available oxygen per 25 c.c. of solution (measured at N. T. P. was employed in all cases. All experiments were carried out at 18°C.

The volumes of oxygen liberated were recorded at intervals ranging from thirty seconds to half an hour according to the velocity and stage of the reaction.

A series of blank experiments with hydrogen peroxide solution alone gave an average yield of 0.25 c.c. of oxygen in 3 hours. The volumes of oxygen recorded were corrected to N. T. P. Typical results for each charcoal are given in Table III. whilst the complete results are shown graphically for each charcoal in Figs 1 and 2. The results for Norit 3 and 7 after treatments II and IV, and after III and V respectively are very similar; hence only the results for treatments II and III are shown graphically.

TABLE III

Time in Minutes	Treatment I. Volume of Oxygen (c.c.)	Treatment II. Volume of Oxygen (c.c.)	Treatment III. Volume of Oxygen (c.c.)	Treatment IV. Volume of Oxygen (c.c.)	Treatment V. Volume of Oxygen (c.c.)
			Norit 1		
1	0.4	0.4	2.3	2.0	7.9
2	0.8	0.9	2.7	2.5	9.1
3	0.9	1.3	3.0	3.1	10.0
6	1.0	2.2	3.7	4.5	11.9
9	1.1	2.8	4.3	5.7	12.1
30	3.2	7.1	8.0	10.8	19.2
60	6.5	11.6	11.8	16.6	26.2
120	11.1	16.4	18.7	23.0	35.0
180	14.0	18.5	22.6	25.1	38.2
240	15.1	19.8	25.9	26.2	39.6
			Norit 2		
1	0.4	0.8	2.2	4.9	5.4
2	0.8	1.0	2.4	5.2	7.1
3	1.2	1.1	2.6	5.4	8.3
6	2.3	1.3	2.9	6.2	10.7
9	3.1	1.5	3.1	7.0	12.9
30	6.7	3.6	4.5	11.4	22.9
60	9.1	5.5	6.7	17.1	31.0
120	13.8	10.4	11.2	25.2	40.8
180	16.8	11.1	13.8	32.0	47.0
240	18.5	11.5	15.6	36.5	52.1

TABLE III (Continued)

Time in Minutes	Treatment I. Volume of Oxygen (c.c.)	Treatment II. Volume of Oxygen (c.c.)	Treatment III. Volume of Oxygen (c.c.)	Treatment IV. Volume of Oxygen (c.c.)	Treatment V. Volume of Oxygen (c.c.)
			Norit 3		
1	5.0	13.4	19.6	15.1	19.2
2	8.2	21.6	31.5	22.7	29.5
3	10.9	29.5	41.5	29.8	39.1
6	17.4	45.9	65.7	47.4	65.4
9	23.0	58.0	82.8	59.0	83.1
30	49.7	105.6	136.5	107.2	137.6
60	74.9	138.8	166.0	140.1	168.0
120	106.2	159.2	189.8	160.4	189.4
180	125.2	172.0	191.2	173.1	190.8
240	139.5	182.6	193.3	184.1	192.9
			Norit 7		
1	7.2	15.8	17.5	15.2	19.2
2	10.4	25.0	27.0	22.9	28.5
3	12.5	31.6	35.0	30.0	36.7
6	17.8	46.2	53.7	47.2	55.5
9	22.8	58.2	67.8	59.1	70.2
30	47.2	106.0	123.7	89.5	123.5
60	71.5	139.1	159.0	125.4	157.2
120	102.8	161.2	190.0	153.6	188.5
180	121.3	172.5	198.1	173.6	200.4
240	134.4	183.1	207.2	192.8	208.2

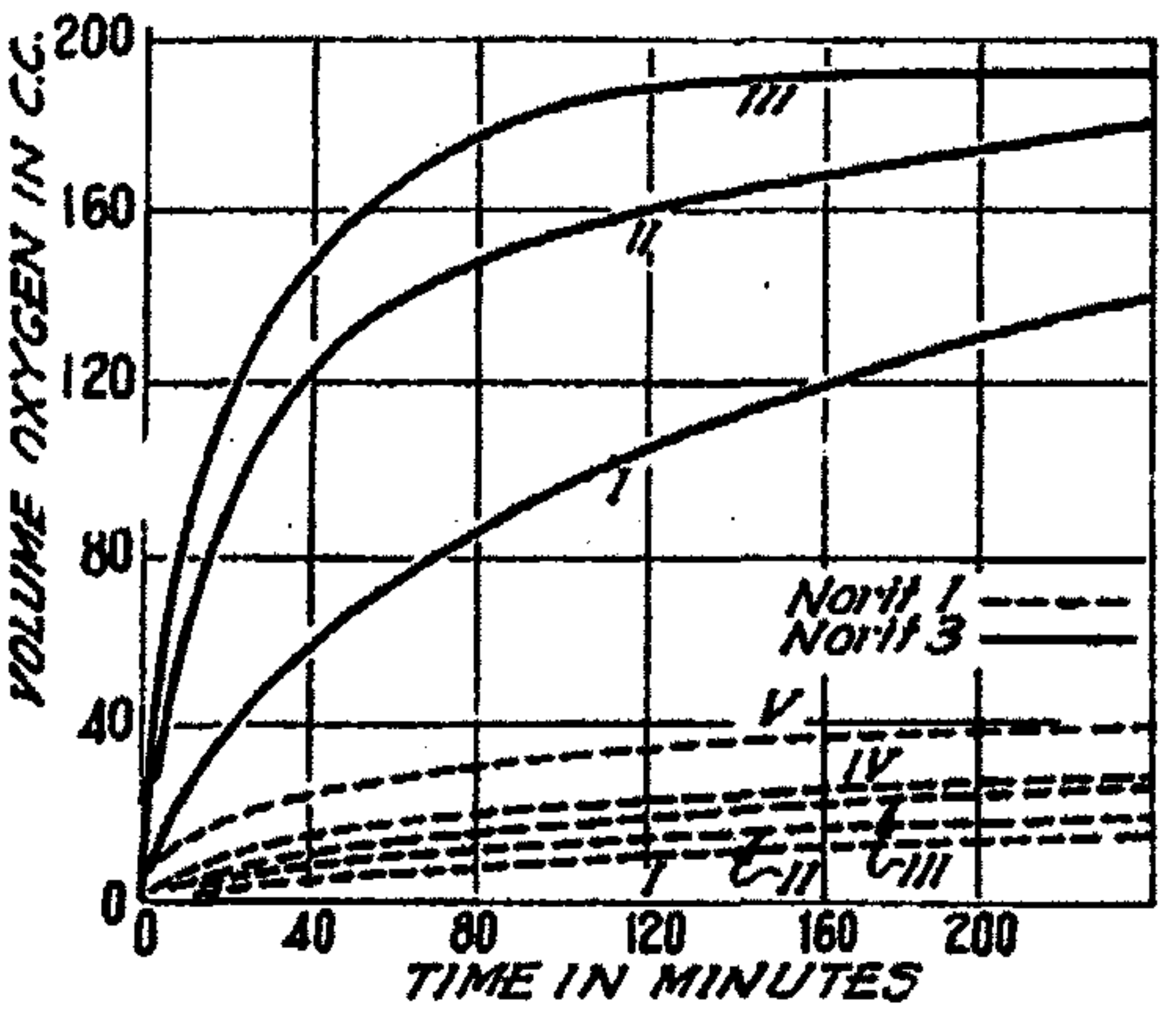

FIG. 1

Discussion of Results

It will be observed from Table I that the percentage ash varies considerably in the different grades. Heat treatment and also subsequent iodine treatment, produces in general an increase in the volume occupied by one gram of the charcoal; the change however is very slight in the case of the purer charcoal Norit 1, but is quite appreciable in the case of Norit 7. in which, treatment V produces an increase in volume of about 15 per cent. In the case of Norit 2 and 3 a slight decrease in volume was observed after heat treatment[1] at 900°C.

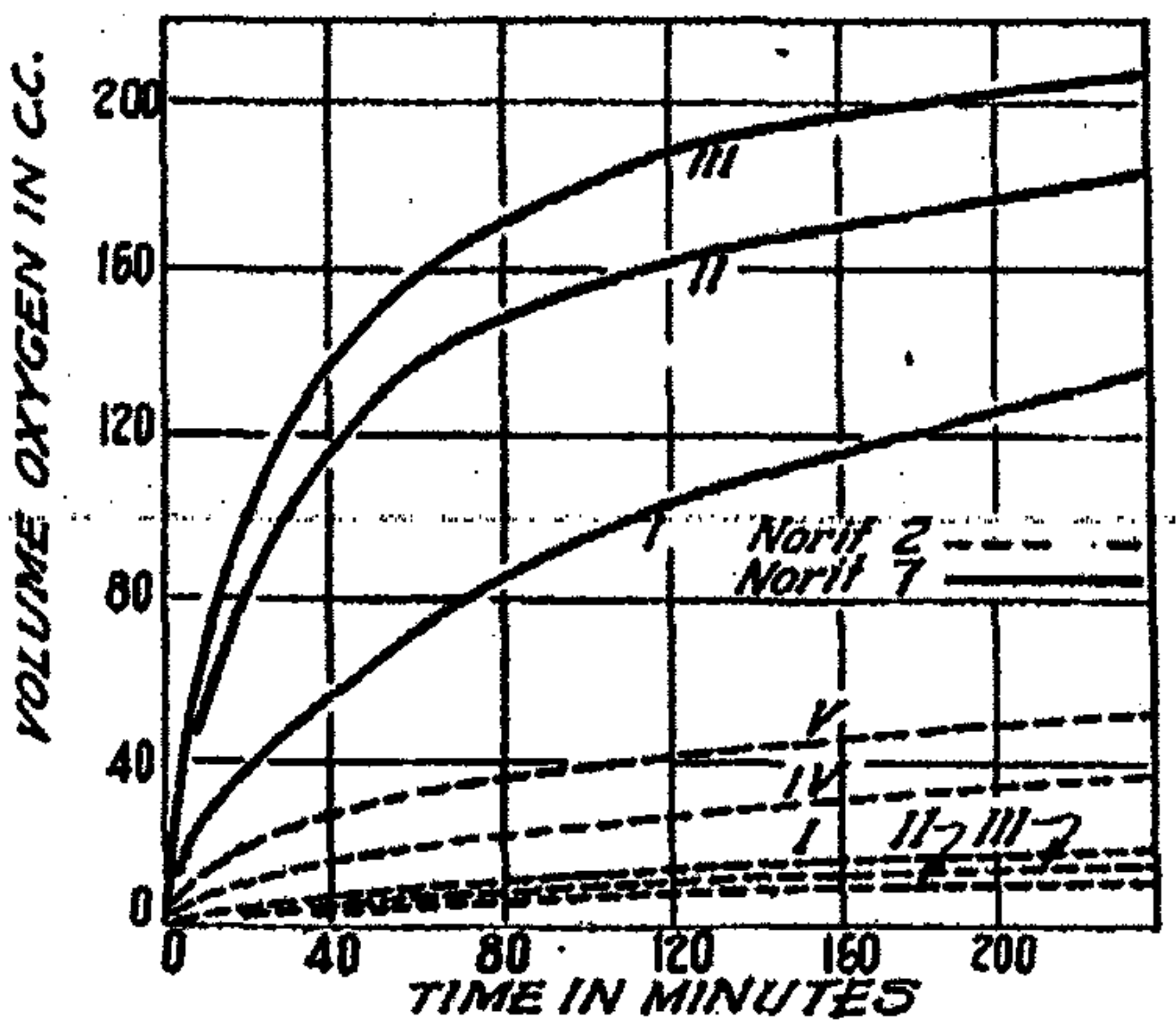

FIG. 2

Table II shows that all four grades of Norit have high sorptive power. Norit 7 which gives the lowest result adsorbs as much as 93.5 per cent of the total iodine present, in thirty minutes and 95.7 per cent in twenty-four hours. The general effect of the various treatments is to increase slightly the amount of iodine sorbed; the maximum sorption being obtained with Norit 3 after treatment III, in which case after contact with the iodine solution for twenty-four hours removed over 99 per cent of the iodine present. It should be noticed that within the limits of the experiments herein described, the percentage ash does not appear to materially affect the sorptive capacity of the charcoal.

In previous researches (see appendix) the sorptive activity of a large number of charcoals prepared from pure chemical substances has been examined. The activity of these charcoals varied over a wide range; the most active charcoals being derived from cane sugar, glucose, cellulose and rice starch. The results of the present experiments show that the various grades of Norit possess an activity which is at least comparable with that of the above mentioned charcoals.

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[1] Cf. Firth; J. Chem. Soc. 119, 926 (1921).

In the series of experiments on the catalytic decomposition of hydrogen peroxide solution by the several grades of Norit after the various treatments, the results indicate a very marked difference in the catalytic activity of the charcoals. Although all four grades of Norit showed high sorption activity after treatment I, the corresponding catalytic activity is only very slight in the cases of Norit 1 and 2, whilst in the cases of Norit 3 and 7 it is only moderate, 65.6 and 63.3 per cent respectively of the available oxygen being liberated in four hours. In all cases the activity is increased by subsequent heat treatment, in the cases of Norits 1 and 2 the maximum percentage of available oxygen liberated is only 18.6 and 24.5 respectively, after a period of four hours, whilst for Norits 3 and 7 the corresponding values were 90.7 and 98.4 percent respectively.

The results obtained at 600°C., with and without iodine treatment are similar, and also those at 900°C. In previous researches (see appendix) treatment with iodine at 900°C has markedly increased the activity, in the present case it would appear that the maximum activity had been attained without the previous sorption of iodine. A comparison of the results for the sorptive capacity and catalytic activity of the charcoals does not reveal any close relationship between the two factors. A charcoal of high sorption capacity is not necessarily highly catalytic towards hydrogen peroxide. A consideration of the results previously obtained with other charcoals leads to a similar conclusion, for example, potato starch charcoal shows high sorption activity but shows a much less catalytic activity towards hydrogen peroxide solution, than charcoals of much lower soprtion activity e.g. inulin charcoal[1]. The figures show clearly the absence of the marked *initial* activity (α activity) which is a characteristic feature of a highly catalytic charcoal.

Summary

Under the conditions of the experiments herein described the results of the present investigation may be summarised as follows:—

1. Norit charcoals 1, 2, 3, and 7 show very high sorption activity towards iodine in chloroform solution.
2. Norit charcoals 1 and 2 show feeble catalytic activity towards hydrogen peroxide solutions, whilst 3 and 7 show only moderate catalytic activity.
3. The sorption activity is not materially increased by previous heating in vacuo at temperatures higher than 100°C.
4. The catalytic activity is substantially increased by previous heating in vacuo at temperatures 600°-900°C.
5. The catalytic activity of a charcoal is not correlative with its sorptive capacity for iodine from chloroform solution.

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May 25, 1925.

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[1] J. Chem. Soc. 123, 326; J. Soc. Chem. Ind. 42, 37T (1923).

Appendix

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SOME CONSIDERATIONS ON HYDRATION AND SOLUTION[1]

BY H. AUSTIN TAYLOR

Since the time when the properties of solutions were regarded as being caused by general hydration, as an alternative to the ionic theory, chemical literature has been inundated at intervals with attempts to apply either one or other or both of these ideas, purporting to explain many and varied phenomena, while at the same time no adequate theories of the mechanism or cause of solution have been suggested. As a result therefore many of the so-called explanations are stated in terms which give no physical concept of the underlying idea, and as a consequence lack the definiteness which they should carry.

From the early investigations of Mendeléef[2] concerning the hydration of substances in aqueous solution there grew up numerous applications of this idea to solution properties in general. H. E. Armstrong[3] attempted to explain the mechanism and velocities of inversion of sugars and esters on the view of mutual hydration of the participants in the reactions, to the complete exclusion of any ionic dissociation ideas[4]. Later H. C. Jones amplified these ideas to general solvation.[5]

Regarding these theories of hydration one point has been emphasised repeatedly, apparently as a necessary consequence of any view of hydration of a solute in solution. The exact form which this consequence takes, seems to have varied in different cases although it would appear that such was the result merely of terminology on a phenomenon about which we have no practical conception. Thus Jones (loc. cit.) concludes "that in solution a part of the solvent is combined with the dissolved substance and *no longer plays the role of solvent.*"[6]

Among the facts which led to this result two cases may be cited. Ordeman[7] made determinations of the specific conductivity of solutions of potassium chloride and of calcium chloride, to which various amounts of other chlorides were added. It was found that the increase in conductivity was greater with potassium than with calcium chloride. Since however, the solutions had the same chloride ion concentration the shift of the dissociation due to the anions was the same in both cases and it was suggested that "the combined water in the solution of the hydrated salts is less associated than the free water, in which case the added salts would be less dissociated since the dissociating power changes with its own association, and further, this effect would be

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[1] Contribution from the Havemeyer Chemical Laboratory. New York University.

[2] Z. physik. Chem., 1, 273 (1887).

[3] J. Chem. Soc., (1890) et seq.

[4] Cf. Nature, 55, 78 (1896).

[5] Inter alia. "Hydrates in Aqueous Solution." Carnegie Inst. Pub. No. 60.

[6] Author's italics.

[7] Carnegie Inst. Pub. Nos. 230, 161 (1915); 260, 119 (1918).

greater the greater the concentration, since more combined water would then be present in the solution of calcium chloride."[1] The other example may be taken from the observations of Jones and Guy[2] who found that "combined water has less power to absorb in the region 1.05-1.2μ than free or uncombined water," a fact confirmed later by Jones, Shaeffer and Paulus[3] namely that "in some cases aqueous solutions of hydrated salts were forty percent more transparent than a comparable quantity of pure water."

Again, Lapworth[4] as a result of reaction velocity measurements in hydrogen ion catalysis concludes "that water added to acids in less basic solvents reduces the concentration of the hydrogen ions, or on a less hypothetical basis, diminishes the availability of the acid for salt formation." This fact he correlates with a previous, more general, observation by Armstrong (loc. cit.) "that substances which act as dehydrants will have a concentrating effect on others which are hydrated in aqueous solutions." Jones and Lapworth[5] also compare their results of the action of hydrochloric acid in ester hydrolysis in removing water from the system, with an earlier experiment by Berthelot and Péan de Saint-Gilles[6] showing that the presence of barium chloride affects to a marked extent the proportion of benzoic ester hydrolysed by water, Berthelot adding "due perhaps to the affinity of barium chloride for water."

More recently Harned[7] points out "that the activity coefficient of hydrochloric acid is greater in solutions of electrolytes which have higher hydration values or which when alone in aqueous solutions have higher activity coefficients," although he concludes later[8] that neutral salt effect is probably due to the large decrease in the heat content of transfer and not to high hydration of the hydrogen ion, since it was found that neutral salt action is a function of the total ion activity and not that of the catalysing ion alone, a fact in opposition to the suggestion of Poma[9] and Bjerrum[10] who would account for it solely on a basis of hydration.

Finally Corran and Lewis[11] find that the activity of the chloride ion rises in presence of sucrose, which rise can be accounted for by a decrease in the total amount of water present, but that the amount of water of hydration need not be deducted, leading to the observation that the chloride ion "is soluble in the water of hydration of sucrose." This and other observations

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[1] This explanation of the results would seem particularly interesting in view of the recent results of Harned: J. Am. Chem. Soc., 47, 930 (1925) who has shown indisputably, that the actual dissociation of water is increased very rapidly at first by salt addition; the effect of sodium chloride being somewhat greater than that of potassium chloride.

[2] Carnegie Inst. Pub. No. 190 (1913).

[3] Carnegie Inst. Pub. No. 210 (1915).

[4] J. Chem. Soc., 93, 2203 (1908).

[5] J. Chem. Soc., 99, 1429 (1911).

[6] Ann. Chim. Phys., 68, 225 (1863).

[7] Taylor: "Treatise on Physical Chemistry," p. 767 (1924).

[8] J. Am. Chem. Soc., 42, 1808 (1920).

[9] Z. physik. Chem., 87, 197 (1914).

[10] Z. anorg. Chem., 109, 295 (1920); cf. also Thomas and Baldwin: J. Am. Chem. Soc., 41, 1981 (1919).

[11] J. Am. Chem. Soc., 44, 1673 (1922).

in Lewis' laboratory have led to the interesting conclusions summarised by Garrett and Lewis[1], "that (1) the water of hydration of sucrose is *not* free to act as solvent for the hydroxy (valeric) acid molecule; (2) the water of hydration of potassium and lithium chlorides *is* available as solvent for the hydroxy acid molecule; (3) hydrogen ion is *insoluble* in the water of hydration of sucrose and also *insoluble* in the water of hydration of potassium and lithium chlorides; (4) potassium and chloride ions, both of which are hydrated, are soluble in the water of hydration of sucrose; (5) sucrose tetrahydrate is soluble in the water of hydration of acetic acid." More generally they suggest that the solvent power of water of hydration cannot be related simply to the electric charge in the case of molecules but is apparently specific of both colliding individuals, so that when both colliding individuals are hydrated, mutual solubility occurs.

From such a varied collection of observations, but one result can be drawn. However unjustifiable some of the conclusions may be in the light of more recent work, one point would seem certain, namely, that if hydration does occur, there is some difference between the combined water and that in the free state. Whether this difference may be expressed either as dissociating power, light absorbing power, activity or solvent power would not appear certain. Some of the facts are based on various theories and mechanisms of reaction which if incorrect would vitiate the conclusions. Thus in ion catalysis Rice[2] would account for all mechanisms solely on the basis of unhydrated ions, a theory which will account for the observed facts and which does not necessitate a consideration of the possibility even, of solvent power of the water of hydration.

Regarding these results solely in the light of their practical significance and attempting to visualise the various points suggested, one is forced to fall back on some theory of solution, a problem about which our knowledge is most meagre. The major portion of the advance in the theories of solution has been made on the assumption that bodies in solution behave in many respects like the same body in the gaseous state. Now the dynamical condition of a molecule in solution is utterly different from that in the gaseous state, in that, in solution a molecule is never outside the range of attraction of its neighbours but is continually passing from one neighbour to another by collision. If we consider that the molecules in a solution move with velocities comparable with those in the gaseous state, which is probable, since the solvent molecules at least, escape into the surrounding vapour, then it would seem that from the rate of diffusion of a substance in solution the molecules do not progress as though they were capable of passing freely through the solvent molecules, however possible such a passage might be on the Bohr theory. We are led therefore to consider a solution as composed of solvent molecules, between the interstices of which, the solute is continually moving. Nevertheless it appears that the solute molecules, at least in so far as they produce osmotic pressure, may be regarded as occupying the whole volume

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[1] J. Am. Chem. Soc., 45, 1101 (1923).

[2] J. Am. Chem. Soc., 45, 2808 (1923); 46, 2405 (1924).

of the solution, since this pressure may be calculated from the gaseous pressure which they produce when alone in such a volume.

Such a simple view however, leads to difficulties when we come to consider a saturated solution. Obviously a saturated solution is not one in which all the interspaces between the solvent molecules are occupied by solute, since a saturated solution of one substance can still dissolve a certain amount of a second substance, irrespective of the absolute size of the molecules of the two substances, and independent therefore, of any question of packing of the solute molecules in the solvent interspaces. Furthermore in osmotic phenomena it seems reasonable to ascribe attractive forces, whether they be "capillary" forces or electrostatic, to the solvent and solute molecules to account for the movement of the solvent molecules through the membrane. The solvation theory of osmosis would, on this basis, be a special case, in which permanent chemical combination occurred between the solvent and solute. Now from our knowledge of the hydration values of various substances in aqueous solutions[1] and their solubilities, it is not conceivable that any hydration theory can account for the cause of solution and solubility and there remains only the view of attractive forces between the molecules, definite in magnitude for every pair of solvent and solute molecules. When these attractive forces are satisfied the solvent is said to be saturated with the solute, yet at the same time there still remain these forces between the solvent for a second solute, the neutralising of which will be modified somewhat by the secondary influence of the solute molecules of both kinds on one another. The condition would therefore seem parallel again to that in gaseous mixtures in so far as attractive forces between the molecules exist. On the simplest theory then, it is evident that the effect of addition of a solute to a solvent must take into consideration the relative attractions, magnitudes and possibly to some extent the change in available spacing of the molecules.

Such a view of solution processes is in agreement with the more recent ideas of Born and Landé[2] and of Fajans[3]. It was shown that quantitative relationships hold between gaseous ions and ions in solution, when the change in electrical field outside the ion, due merely to change in the dielectric capacity of the medium, is taken into account. The actual process of solution of a gaseous ion is regarded[4] as the condensation of an unknown number of water molecules around the ion comparable with electrostriction. It is supposed that by means of the charge on the ion, the oppositely charged parts of the polar water molecules in the immediate neighbourhood are oriented towards the ion, the similarly charged parts of the water molecules being repelled from the ion, these in turn repelling other molecules in their vicinity. A solution of an electrolyte in water would therefore be an electrically polarised system, the solubility depending on the extent to which this polarisation

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[1] Cf. Washburn: J. Am. Chem. Soc., 31, 322 (1909).

[2] Ber. deutsch physik. Ges., 1918 et seq; Z. Physik, 1920 et seq.

[3] Ber. deutsch. physik. Ges., 21, 542 (1919); Compare also Debye and Hückel: Physik. Z., 24, 185; and Debye: 24, 334 (1923).

[4] Fajans: loc. cit.

may proceed. Further this would depend on the size of the ions (as shown by Born[1] which governs the distances through which the electrical forces are operating.

There remains one other theory which offers a suggestion as to the fundamental cause of solution, namely, that due to Kruger[2], which indicates that radiation, usually of the infra-red region, plays a rôle in these processes. Kruger deduced a relationship between the dilution of the solution and the dielectric constant of the solvent, which, qualitatively at least, agrees with known observations; for example, water with a high dielectric constant is our best known solvent. The application of these ideas to the kinetics of solution has not however received as yet the attention of the proponents of the radiation theory of chemical reaction[3], although following the same line of reasoning as they employ, namely a quantisation of the energy change involved, and using data on the rate of solution obtained in Nernst's laboratory[4] the calculated wave lengths fall in the infra-red region. Temperature coefficients of the order of 1.5 to 1.8 per 10°C rise were obtained for such substances as benzoic acid and lead chloride dissolving in water. The wave lengths calculated from these temperature coefficients are 3.0μ and 2.7μ respectively, both of which are in the infra-red region where the radiation density is greatest at room temperatures. That the rate of solution could be affected however, by exposure to infra-red radiation seems well nigh impossible, especially if the Nernst-Noyes-Whitney view of the rate of solution being the rate of diffusion of the saturated solution away from the solute, is true. One point nevertheless, suggests itself, namely, that of an interpretation of the above calculated critical increments or energies of activation (which are of the order of 7,000 to 10,000 calories) being a measure of the statistical attractive forces between the solvent and solute molecules, for it is evident that the rate of diffusion must depend to a large extent on these forces.

With these theories of solution in mind, attempts to picture some of the statements made previously with regard to water of hydration, such for example as its ability to act as solvent, do not lead very far. It is difficult in fact, on any theory, to see how the few molecules of water attached to an ion or a molecule can act as a solvent for another molecule. On the electrical view apparently, an ion or a molecule becomes 'hydrated' (in the Born sense), that is, goes into solution, when an electrical polarisation is effected. No suggestions are available of the number of water molecules necessary to complete this 'hydration,' although comparison of the data on the heat of hydration of a gaseous ion with those on the heat quantities usually attributed to the formation of ion hydrates of definite stoichiometric composition would seem to point to a much larger number of molecules being involved in the former case. It would be improbable therefore, that the few molecules of

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[1] Ber. deutsch. physik. Ges., 21, 679 (1919). Compare also forth-coming publication by Hückel on change in dielectric constant with concentration.

[2] Z. Elektrochem., 17, 453 (1911).

[3] Cf. Lewis' "System of Physical Chemistry," 3rd. Ed. Vol. II. p. 232.

[4] Brunner and St. Tolloczko: Z. physik. Chem., 35, 283 (1900).

water of hydration of an ion or a molecule in aqueous solution, which molecules are already bound and probably therefore oriented in a definite manner, could ever satisfy the requirements of a solvent for another ion or molecule. The confirmation which the electrical treatment of Born and Fajans has received up to the present seems to have proved its reliability and utility.

An attempt therefore, was made to confirm the facts by a totally different method[1]. Consider the system benzene: water with hydrogen chloride distributed between the two phases. In the aqueous layer there is an equilibrium which may be expressed by the equation:

$$HCl \rightleftarrows H^{\cdot} + Cl'$$

According to Moran and Lewis (loc. cit.) hydrogen ion is insoluble in the water of hydration of various electrolytes. On adding these electrolytes therefore to the aqueous layer one should remove water capable of dissolving hydrogen ion. The concentration of the hydrogen ion would thereby be increased in the remaining water. This would cause an increase in the concentration of undissociated hydrochloric acid, or on the complete dissociation theory, would increase the probability that a hydrogen and a chloride ion were under mutual electrostatic influences. The disturbance of the equilibrium obtaining in the aqueous layer would be reflected in the benzene layer, the effect being measurable by a change in the distribution ratio of the hydrogen chloride between the two solvents.

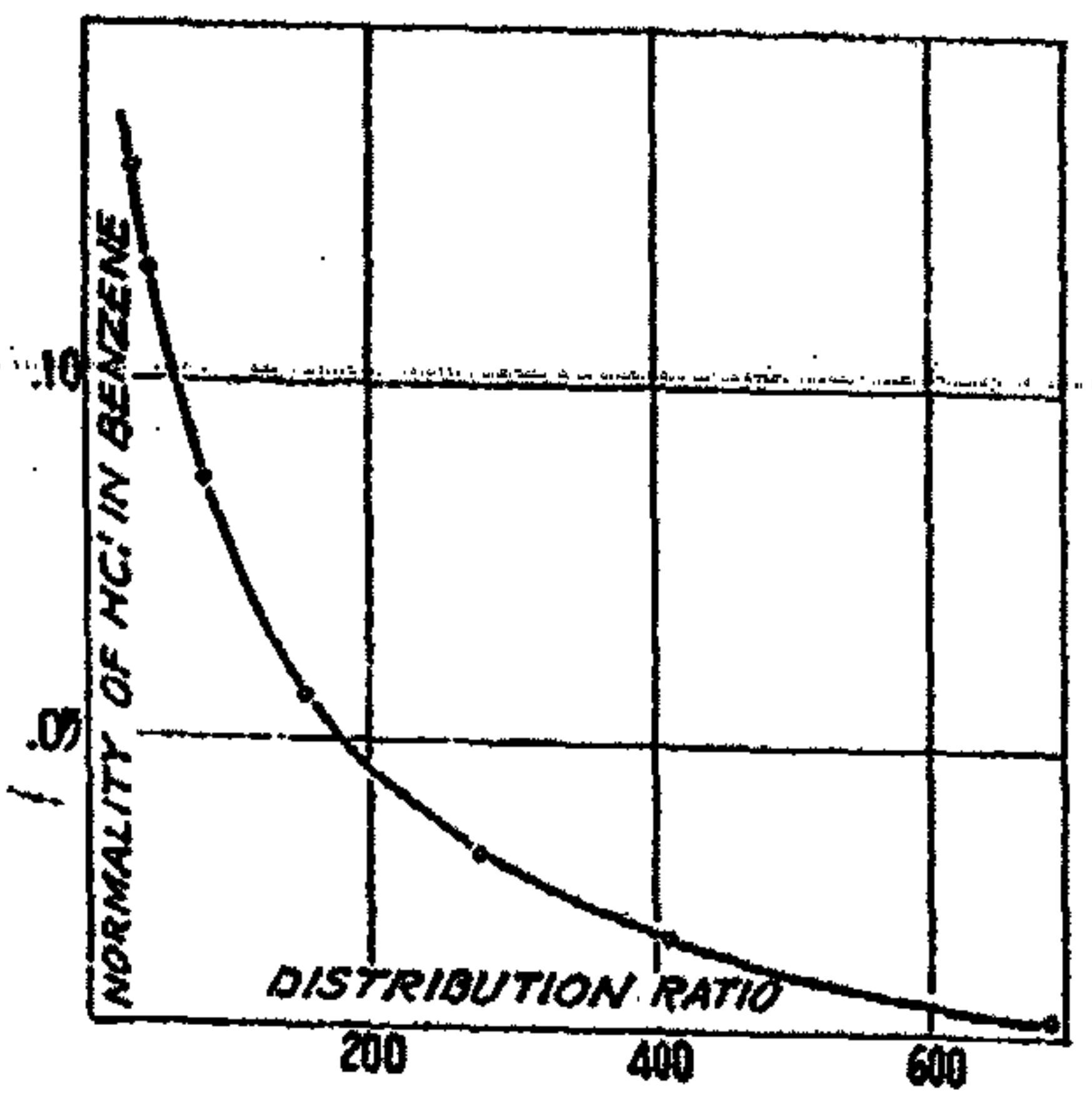

Fig. 1

Hydrogen Chloride in Benzene and Aqueous Solutions

A number of solutions were made up of concentrated hydrochloric acid containing several electrolytes and glycerol, all being more or less hydrated in solution. These solutions were allowed to attain equilibrium with benzene by repeatedly shaking over a period of several days, and their distribution constants found by titration of the two layers in each case with standard sodium hydroxide.

Beckmann[2] finds that the greater the normality of hydrogen chloride in the benzene layer under such circumstances, the more nearly does the hydrogen chloride tend to form single molecules. The distribution ratio calculated directly from the titre of each layer does not, therefore, yield a constant. For our purpose however, it does not seem necessary to obtain one. The difficulty is most easily overcome by finding the value of the 'constant' for different

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[1] Much work along the same line has been carried out by Szyszkowski using in all cases however, weak acids only. Cf. Meddel. från. K. Vet. Akad: s. Nobelinstitut. 3, Nos. 2, 3, 4, 5, 9, 10, 11 (1915-1918).

[2] Z. physik. Chem., 60, 385 (1907).

concentrations of hydrogen chloride in the benzene layer. To this end a series of solutions of aqueous hydrochloric acid of different strengths were taken and their partition coefficients obtained with benzene.

The ratio calculated from the observed titrations of the two layers is shown in Fig. 1 plotted against normality of hydrogen chloride in the benzene layer.

From the slope of the curve, it can be seen that the value of the ratio changes rapidly with a small change in the hydrogen chloride concentration of the benzene.

The results obtained in the distribution experiments using aqueous solutions of hydrogen chloride together with the hydrated bodies are given in Table I, the concentrations of added substance being approximately normal in each case.

TABLE I

Added Compound (Approx. 1N)	Phase	Normality of HCl	Ratio	Ratio for pure HCl
NaCl	Benzene	0.072	161.4	158
	Water	11.63		
KCl	Benzene	0.0716	160.4	160
	Water	11.49		
LiCl	Benzene	0.130	83.9	85
	Water	10.92		
RbCl	Benzene	0.0714	157.2	160
	Water	11.22		
$CaCl_2$	Benzene	0.1161	98.2	95
	Water	11.40		
$BaCl_2$	Benzene	0.0698	166.5	165
	Water	11.61		
Glycerol	Benzene	0.0740	153.8	153
	Water	11.37		

The third column gives the normality of hydrogen chloride in the two layers taken directly from the titrations with standard sodium hydroxide. Column 4 is the direct ratio of these, namely, water: benzene. In column 5 is added the ratio observed in the previous case using pure aqueous hydrochloric acid and benzene; the ratio given being taken from the graph when the concentration of hydrogen chloride in the benzene layer in the two cases is the same. In this way a true comparison of the aqueous solutions can be made, that is, of pure hydrochloric acid on the one hand and a hydrochloric acid solution containing a hydrated substance on the other. That the actual value of the ratio is different in the different salt solutions is to be expected when it is observed that the total hydrogen chloride concentration varies slightly from case to case, a variation magnified greatly in the value of the ratio owing to the smallness of the benzene concentration.

The remarkable result however, is the agreement between the last two columns shown. Since the observed ratio in the case of the different solutions, agrees with that for pure hydrochloric acid when the concentration in the benzene layer is the same in each case, it follows that the concentration in the aqueous layer must also be the same in the two cases. In other words the neutral salt or glycerol solution of hydrogen chloride is behaving in exactly the same manner as a pure aqueous solution of hydrogen chloride, and the presence of the added compound whether largely or slightly hydrated is without effect on the distribution.

At first sight such a result would appear to deny many of the facts stated earlier in the paper. The possibility of interpreting the statement specifically, however, in any one regard is not obvious. It might appear for example that the activity of hydrochloric acid in neutral salt solution was the same as that in pure aqueous solution (a fact denied by Harned), if we regard the distribution law from the point of view of the activity concept namely, that the ratio of the activity of the distributed species in the two phases is constant. It can nevertheless be argued that the concentration of the hydrogen chloride in the aqueous layer is so great that even the activity concept fails to hold rigidly in this case, as in others dealing with strong electrolytes, which by its failure would vitiate the observation made. Or again, to take another example relative to the ability of water of hydration to act as a solvent, although such an effect is noticeable with more dilute acid solutions it would in all probability be negligibly small with such concentrated ones.

The apparent fact that the neutral salt solution was behaving in the same manner as a pure aqueous hydrogen chloride solution having the same concentration of HCl suggested at once that confirmation might be obtained from a determination of the vapour pressure of the hydrogen chloride over the two solutions. Absolute data on the vapour pressures of hydrogen chloride over its aqueous solution, especially at such concentrations as were used in this work, are scanty and unconvincing. The reason becomes obvious on analysing the data at lower concentrations. Dobson and Masson[1] give the partial pressure of hydrogen chloride over 10.52 N HCl as between 35 and 40 mms., but state that no stress may be laid on these values. Bates and Kirschman[2] give a value of 4.20 mms. for 10 N HCl, both these values being given at 25°C. Now according to the solubility date of Roscoe and Ditmar the maximum strength of an HCl solution at 25°C is about 19 N, so that the increase in partial pressure of hydrogen chloride over solutions from 10 to 19 N must be extremely rapid and hence the accuracy of individual determinations uncertain. It was considered doubtful therefore, whether the effect of neutral salt would be noticeable on the partial pressure of 12 N HCl, the strength used in the previous work, since the concentration of salt is small even in the saturated solution, and the partial pressure of the hydrogen chloride increasing rapidly.

A few comparative tests however, were made by bubbling a fixed volume of dry air through the hydrogen chloride solutions and absorbing the acid carried over in standard sodium hydroxide. Care was taken to avoid any

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[1] J. Chem. Soc., 125, 668 (1924).

[2] J. Am. Chem. Soc., 41, 1991 (1919).

spray being carried over by passing the air from the hydrogen chloride bottle through a small column containing glass wool which was previously saturated with hydrogen chloride vapour, the whole apparatus being completely immersed in a thermostat at 25°C. Table II gives the results obtained in cubic centimetres of the standard alkali used.

TABLE II

Solution	Vapour Pressure in ccs. Alkali.
12 N HCl	61.85
	61.27
12 N HCl + N NaCl	61.50
	60.87
12 N HCl + N KCl	61.58
	(59.40)

The results although only comparative would appear to show that the vapour pressure of the hydrogen chloride was not appreciably affected by the presence of this quantity of added salt in such concentrated solutions of acid. What the effect would be on more dilute solutions cannot be foretold but the two effects herein observed for concentrated solutions are mutually confirmatory.

It seems definite therefore that the many facts quoted earlier in the paper are not proven generally and that doubt must be cast on the various explanations offered. Recent work by Linderström-Lang[1] on the influence of neutral substances on the solubility of succinic and boric acids leads to the view that hydration as playing the leading part in the salting out process must be rejected. The causes of variation in the solubility may be explained on the basis of Debye's views on the nature of the cohesive forces between the ions the specificity of an ion being due not to hydration but to these forces which will depend on their structure, size and polarisability.

Further work along these lines is at present in progress using smaller concentrations of acid and with other acids also towards a more definite elucidation of the problem.

Summary

(1) Numerous cases have been quoted where evidence is suggested that the water combined as water of hydration, differs from ordinary water in many of its properties.

(2) The interpretation of these examples from the point of view of modern theories of solution is discussed and criticisms offered.

(3) From a study of the effect of various hydrated bodies on the distribution of hydrogen chloride between benzene and water it is suggested that aqueous solutions of such bodies behave precisely as does pure water, indicating no dissimilarity between the so-called combined and free water.

(4) This fact appears also to be confirmed by a study of the effect of neutral salts on the partial pressure of hydrogen chloride over concentrated hydrochloric acid solutions. Further work is in progress.

New York, N. Y.

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[1] Compt. rend. Trav. Lab. Carlsberg, 15, 1 (1924).

THE NATURE OF SOAP IN ALCOHOL*

BY WALTER A. PATRICK, WILLIAM L. HYDEN AND EDWARD F. MILAN

It has been assumed that soaps in aqueous solution are colloidal while in alcohols they exhibit simple crystalloid properties. For this reason it has been thought that in water soap is a colloidal electrolyte whose molecular weight cannot be determined by the colligative properties of the solution. In alcohol, however, the crystalloid has been found to exhibit its true molecular weight. Upon this point there has been some controversy. Krafft[1] obtained contradictory results from two separate investigations. A. Smits[2], in his work on sodium palmitate solutions in water, found that the molal boiling point rise rapidly decreased with the concentration. This work demonstrated that soap solutions in water are colloidal—especially in concentrations as high as 0.3 normal. M. E. Laing[3] found potassium oleate solutions gave closely agreeing values for the molecular weight by the boiling point method. An average value of 304.9 was obtained while the theory requires 320.5. Miss Laing also measured the conductivity of 40° and 60° and from these results calculated the dissociation. This amounted to as much as 30% in case of dilute solutions (.03 N.) at 60°.

The nature of non-aqueous solutions is not fully understood and we are confronted with the question: Can we employ the ordinary methods of aqueous solutions for the determination of the various properties of non-aqueous solutions? Views have been expressed but it is generally conceded that the ionizing power of the solvent is definitely related to its dielectric constant, the electrical conductance of the solution, the lowering of the freezing point, as well as the rise of the boiling point, the osmotic pressure, and other colligative properties.

It is very surprising therefore that soap in alcohol which gives a dissociation of some 30%, according to Miss Laing, should give a normal rise in the boiling point. In order to further the evidence for the nature of solutions of soaps in alcohols the present investigation was undertaken. Sodium oleate was selected as the soap because it is readily soluble in alcohol and gives clear solutions.

Apparatus

The differential thermometer and ebullioscopic apparatus of Menzies and Wright[4] was employed. It is superior to the Beckmann apparatus since it is more convenient, less fragile, more sensitive; and also errors due to superheating, changes in barometric pressure, etc, are eliminated. The several advantages of this apparatus make the results obtained by its use more trustworthy than those by the older Beckmann apparatus.

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*Contribution from the Chemistry Laboratory of Johns Hopkins University.

[1] Ber. 29, 1328 (1896); 32, 1584 (1899).

[2] Z. physik. Chem. 45, 608 (1903).

[3] J. Chem. Soc. 113, 435 (1918).

[4] J. Am. Chem. Soc. 43, 2309 (1921).

The molal boiling point rise was checked for this instrument over a range of concentrations using C. P. urea as a standard. Concordant results were obtained whose maximum deviation from the mean varied only by a few percent.

Materials

Ethyl alcohol which was practically free from water and also alcohol of commerce were used as solvents. The dry alcohol was prepared by distillation from a mixture of sodium ethylate and ordinary 95% alcohol observing the usual precautions. A fraction boiling at 78.1° at 752 mm. was selected as the solvent. This alcohol possessed a density of .7899 at 20°. The commercial alcohol, which had a density of .8043 at 20°, was pure except for the usual amount of water and its boiling point was slightly different from that of the dry alcohol.

Pure sodium oleate amorphous powder was kept in a desiccator over anhydrous calcium chloride. This material was made into pastilles, weighed and immediately transferred to the boiling point apparatus. Clear solutions resulted which possessed a faint yellowish cast only at the highest concentrations used. The solutions were neutral to phenol-phthalein.

Results

The following tables give the data from the experiments.

Table I

The B. P. constant for ethyl alcohol was taken as 15.6 when the concentration is one mole of solute per 100 cc. of solvent.

Series 1

Pure Alcohol — B. P. 78.0°C. Press. 751.0 mm.

Wt. Sample	Rise mm.	Conv. Factor	Rise Obs. °C.	Rise Cal. °C.	Mol. Wt. Cal.	Ratio obs/cal	Conc. M/1000 cc.	Working Vol. cc.
0.0560	3.1	0.005328	0.0169	0.0089	164.3	1.853	0.0057	32.2
0.0679	3.5	0.005328	0.0186	0.0112	183.2	1.661	0.0073	31.0
0.1335	6.2	0.005326	0.0328	0.0212	195.9	1.554	0.0136	32.2
0.2264	9.3	0.005323	0.0495	0.0352	221.1	1.377	0.0231	32.2
0.3696	14.0	0.005319	0.0755	0.0576	237.0	1.264	0.0377	32.2
0.3862	14.4	0.005303	0.0764	0.0626	249.6	1.219	0.0402	31.6
0.5696	20.3	0.005296	0.1075	0.0924	261.5	1.164	0.0592	31.6
0.8113	27.8	0.005291	0.1471	0.1316	272.3	1.118	0.0844	31.6
1.1471	37.6	0.005282	0.1986	0.1865	285.1	1.067	0.1193	31.6
				Series 2				
0.0674	3.5	0.005328	0.0186	0.0105	171.9	1.771	0.0068	32.8
0.1210	5.5	0.005325	0.0292	0.0192	199.5	1.525	0.0123	32.3
0.1505	6.6	0.005325	0.0357	0.0235	216.8	1.494	0.0151	32.8
0.2492	10.0	0.005320	0.0532	0.0395	226.2	1.345	0.0254	32.3
0.3161	12.1	0.005325	0.0644	0.0514	242.4	1.256	0.0330	31.5
0.6814	24.3	0.005315	0.1292	0.1109	261.3	1.165	0.0695	31.5
0.8492	28.4	0.005310	0.1508	0.1348	272.0	1.119	0.0864	32.3
1.3288	42.0	0.005301	0.2226	0.2162	295.6	1.030	0.1386	31.5

TABLE II

Series 1

95% Alcohol – B. P. 78.2° (corr). Press. 751.6

Wt. Sample	Rise mm.	Conv. Factor	Rise Obs. °C.	Rise Cal. °C.	Mol. Wt. Cal.	Ratio obs/cal	Conc. M/1000 cc.	Working Vol. cc.
0.1435	6.4	0.005291	0.0339	0.0244	218.9	1.390	0.0156	30.2
0.3863	14.7	0.005285	0.0777	0.0656	256.8	1.185	0.0420	30.2
0.5833	21.5	0.005277	0.1134	0.0990	265.6	1.146	0.0635	30.2
0.8157	29.1	0.005271	0.1534	0.1384	274.7	1.108	0.0887	30.2
1.1568	39.4	0.005264	0.2074	0.1963	288.0	1.057	0.1259	30.2

Series 2

Press 751.0

0.0475	2.8	0.005291	0.0148	0.0081	166.2	1.832	0.0052	30.1
0.1002	5.3	0.005288	0.0287	0.0171	181.0	1.643	0.0109	30.1
0.1608	7.2	0.005285	0.0380	0.0274	219.0	1.390	0.0176	30.1
0.2255	9.6	0.005283	0.0507	0.0384	230.4	1.321	0.0246	30.1
0.2975	12.0	0.005281	0.0633	0.0507	243.3	1.251	0.0325	30.1
0.3817	15.0	0.005278	0.0792	0.0650	249.9	1.218	0.0417	30.1
0.4812	18.0	0.005257	0.0949	0.0819	262.7	1.159	0.0525	30.1
0.6282	23.0	0.005273	0.1213	0.1070	268.4	1.134	0.0702	30.1
0.8073	28.4	0.005269	0.1496	0.1375	279.6	1.090	0.0883	30.1

Series 3

0.0500	2.9	0.005291	0.0153	0.0083	164.0	1.856	0.0053	31.0
0.1490	6.5	0.005288	0.0344	0.0246	218.2	1.395	0.0158	31.0
0.3170	12.7	0.005285	0.0671	0.0524	237.7	1.281	0.0336	31.0
0.4920	18.4	0.005299	0.0971	0.0813	255.5	1.194	0.0522	31.0
0.6885	24.9	0.005273	0.1313	0.1138	263.9	1.153	0.0730	31.0
1.0277	35.4	0.005268	0.1865	0.1700	277.3	1.097	0.1089	31.0

M. W. Sodium Oleate = 304.36

The value of the ratio of the observed rise to the calculated rise is the degree of dissociation plus one i.e.

$$\alpha = (\text{Ratio obs/calc}) - 1$$

Discussion of Results

The determinations given above all show substantially the same result; as the concentration increases the boiling point rise approaches normality. This proves that sodium oleate in alcohol is highly ionized at the boiling point, in dilute solutions.

The relation of ionization and concentration is exhibited in Figure 1.

This curve represents the type of curve obtained by a study of the oleate in both moist and pure alcohol. It is seen that, even at the highest concentration used, there was appreciable dissociation. This is not strictly contradictory to the work of Laing since the value obtained by her (304.9) differed from the theoretical by some 5%. In her work no concentration lower than .14 normal was used, for the boiling point work, and at this concentration the ionization is fairly small. In our investigation, however, the molecular weight was found to alter with the concentration which was not the case in Laing's work.

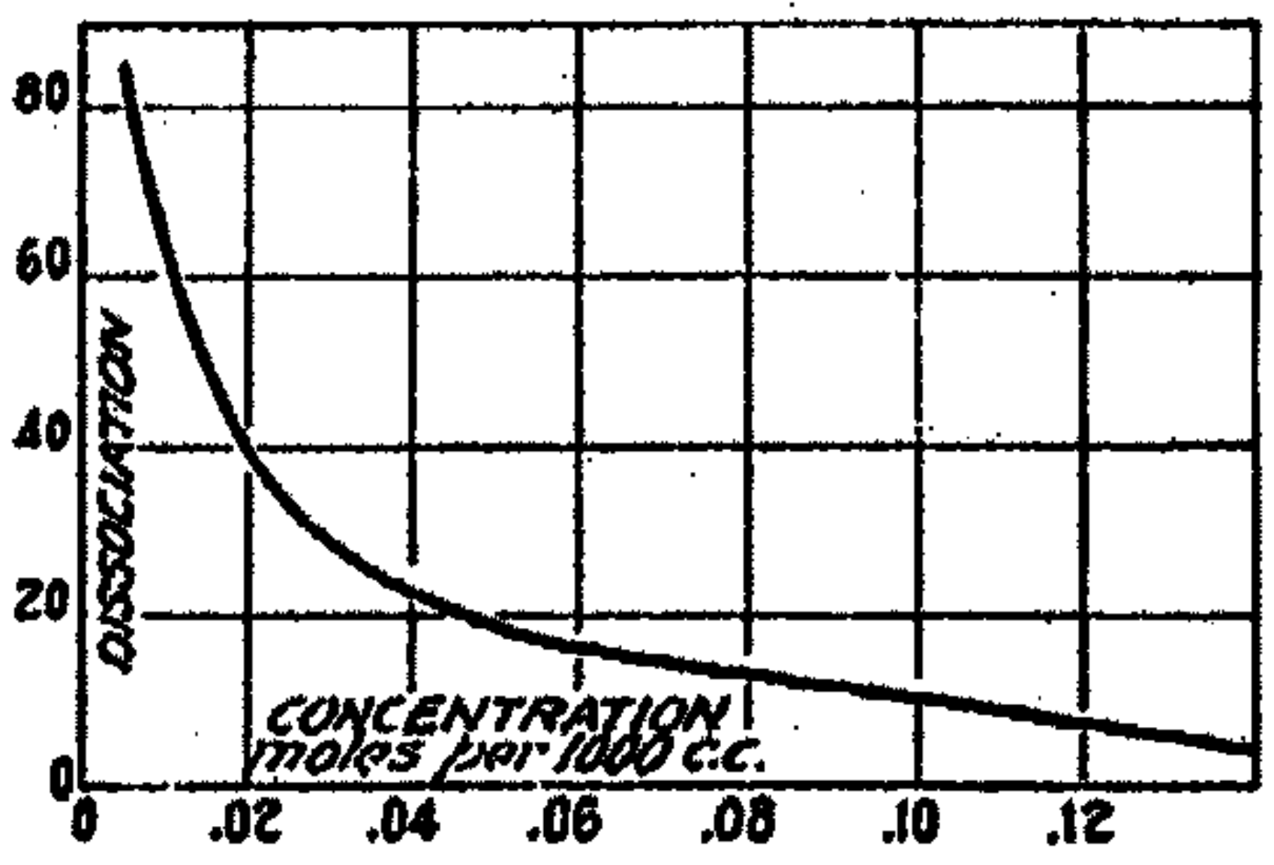

Fig. 1

The fact that the values found by us differed with concentration of the soap is in harmony with the conductivity work of Laing on dry alcoholic solutions of potassium oleate. Below are given ionization values calculated from her work taking the value of the conductivity at infinite dilution at 60° as 60 mhos.

Volume Normality	Specific Conductance	Ionization
.68	.001927	4.6%
.49	.001812	6.1
.38	.001694	7.3
.31	.001566	8.4
.27	.001452	9.1
.22	.001285	9.9
.16	.001187	11.7
.11	.000891	13.5
.02	.000381	32.0

It is recognized that the conductivity method of obtaining the dissociation is of doubtful applicability when alcohol is employed as a solvent. The value of Λ_∞ cannot be determined directly, with any degree of accuracy. At comparable concentrations the ionization of the potassium soap, as determined by Laing, agrees in magnitude, at least, with the results obtained by the boiling point method for the sodium soap.

The boiling point method for the determination of dissociation is not free from objections.[1]

A slight error in the reading of the temperature, especially at the higher dilutions, causes a large error in the dissociation. The difficult portion of the curve to obtain is below .02 normal. Probably the most accurate results were obtained above .02 normality.

Similar results were obtained from the two alcohols used; indeed the results are almost identical. In other words, a small amount of water has but little, if any, effect upon the dissociation.

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[1] Jones: Z. physik. Chem. 31, 114 (1899).

Alcoholic solutions of sodium oleate behave very differently from aqueous solutions for in water the boiling point rise does not indicate the true molecular weight. In alcohol, on the other hand, the soap is a simple electrolyte which is dissociated to a large extent. Thus, when the concentration of the soap falls below .15N the ebullioscopic method cannot be used to find the molecular weight.

A calculation for the constant in Ostwald's dilution law showed that in this case the law is not obeyed. Cohen has emphasized the fact that the laws of Rudolphi and Ostwald do not hold when applied to solutions of electrolytes in alcohols.

Summary

The rise in the boiling point of sodium oleate in pure and moist alcohols has been measured over a range of concentrations.

Sodium oleate has been shown to be dissociated in alcohols at the boiling temperature.

The true molecular weight of sodium oleate in alcohol cannot be evaluated by the ebullioscopic method since the dissociation increases enormously above .15 normal, becoming greater than 50%.

Baltimore, Md.

THE ELASTICITY OF GELATIN IN RELATION TO pH AND SWELLING*

BY G. W. SCARTH

The method here followed in investigating the relation of the elasticity of a gelatin jelly to H-ion concentration is such that the results bear directly on two theoretical questions. The first is physical and concerns the theory of swelling. Does the force which opposes and limits imbibition in gelatin, namely, its cohesion, measured by the modulus of bulk elasticity, remain a constant throughout the range of H-ion concentration as assumed for example in the Procter-Wilson-Loeb theory of swelling and viscosity; or if not, how will its variations affect these other properties? The second question is physiological and deals with the mechanism of protoplasmic contraction. Do any changes in elasticity occur in a gelatin jelly when subjected to acid, comparable to those occurring in contractile protoplasm during the liberation of acid, which is probably not confined to muscle merely as the chemical cause of contraction? If so, which phase of the response in gelatin, that of shrinkage up to pH 4.7, or of swelling beyond that point corresponds as regards elasticity, to the contraction phase in protoplasm.

Previous work on the relation of H-ion concentration to the elasticity of gelatin does not allow us to draw conclusions as to these questions. The only systematic investigations are those of Sheppard and Sweet (1922, 1924). In their experiments sols of various concentrations both of gelatin and of acid or alkali were allowed to set to jellies and the elasticity of the latter was measured in air or in oil. But in the case of both the specific problems mentioned above, the gels concerned are surrounded by a watery medium and free to imbibe water until they are at equilibrium with that medium whatever H-ion concentration it may assume. Elasticity as well as volume is affected by imbibition. Moreover, in all experiments on physical swelling and shrinkage, and in some cases at least of protoplasmic contraction also, the acid acts upon a preformed gel and not on its formation from the sol. The distinction is important in view of the profound influence that mode of formation exerts on the physical properties of gels.

In the following research therefore the variations in elasticity were measured in preformed and originally uniform jellies when brought to approximate equilibrium with media of varied H-ion concentration.

I. Relation to pH Effect in General

Isotropic gelatin.

Gelatin melted and cast into cylinders is designated *isotropic*, swelling being equal in all directions. Sheets of commercial 'leaf' gelatin, which swell

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*Research assisted by a Grant from the Honorary Advisory Council for Scientific and Industrial Research of Canada.

unequally, are signified when the term '*aeolotropic*' is used. Sheets of Coignet's "gelatin A" were washed for 48 hours in 3 changes of ice cold water, acidified to a pH of 4.6 originally, falling to 4.9 eventually. The gelatin was then melted below 60° C in its own water of imbibition and kept warm but below 40° for several hours. A small quantity of toluene was added to the above and to all subsequent solutions. The concentration of gelatin at this stage was 12.7%.

The solution was poured into a series of test tubes of 1 cm. diameter. Before it set two celluloid discs, each pierced by a bent pin, were inserted, one sinking to the bottom, the other buoyed near the top. After two days the tubes were slightly heated, and gently broken, and the pieces stripped off leaving smooth cylinders of gelatin. These were trimmed at each end so that a portion of the bent pin emerged as a means of attachment. They were suspended in a medium of pH 4.8 ±·1, temperature about 15°C, for 18 hours (or longer) at the end of which time they had imbibed water sufficient to reduce the concentration of gelatin to about 11%. The average volume of the cylinders was 8.5 c.c. the average length from disc to disc 7 cm. and the diameter of each approximated 1.1 cm. At the end of 18 hours at the isoelectric point, volume is nearly at an equilibrium, and extensibility will remain constant if temperature does not vary. Volume was determined by displacement. The measurements of extensibility were made by a system of amplifying levers permitting great delicacy of reading. These levers were used also for applying the stretching force, the equivalent of 14 grams weight in the first set of experiments.

The cylinders of gelatin having been standardized as regards dimensions and extensibility, were transferred to various concentrations of acid and alkali for 24 hours. Measurements were repeated and the pH of the medium at the end determined electrometrically. 24 hours was found necessary to approximate maximum change in extensibility with small additions of acid and alkali. In high concentrations a longer period causes excessive disintegration due to uneven swelling. Pieces flake off with conchoidal fracture. This was partially obviated by a graded increase in the concentration of acid or alkali. But beyond the pH limits of the curves in Fig. 1, no reliable measurements could be made, while the extreme readings even there are probably rather lower than they would be but for fracture.

Even slight fluctuations in temperature may have a greater effect on elasticity than a considerable change in pH (the temperature coefficient being negative). All the measurements recorded below were made at the same temperature (15°C) but this does not obviate the persistent effect of fluctuations in the interval. The latter were not eliminated entirely but their resultant effect was found from variation in the control at pH 4.8, the extensibility of which, as shown by trial, would at constant temperature have remained constant. The necessary correction (1 to 7%) is made in the results given.

Results: In Fig. 1 are plotted, in percentages, the variations in volume, resistance to stretch (reciprocal of stretch) and Young's Modulus of stretch. The actual value of Young's Modulus (E) at pH 4.7 was about 6 grams per square millimeter, slightly higher at pH 7. It was calculated from the formula below—a close enough approximation for small stretches.

$$E = \frac{\text{Stress}}{\text{Strain}} = \frac{P}{S} \div \frac{l}{L}$$

where P = the force applied
S = the cross section (stretched)
l = the increase in length
L = the length (stretched)

S varies as L^2 in the swelling of this isotropic gelatin.

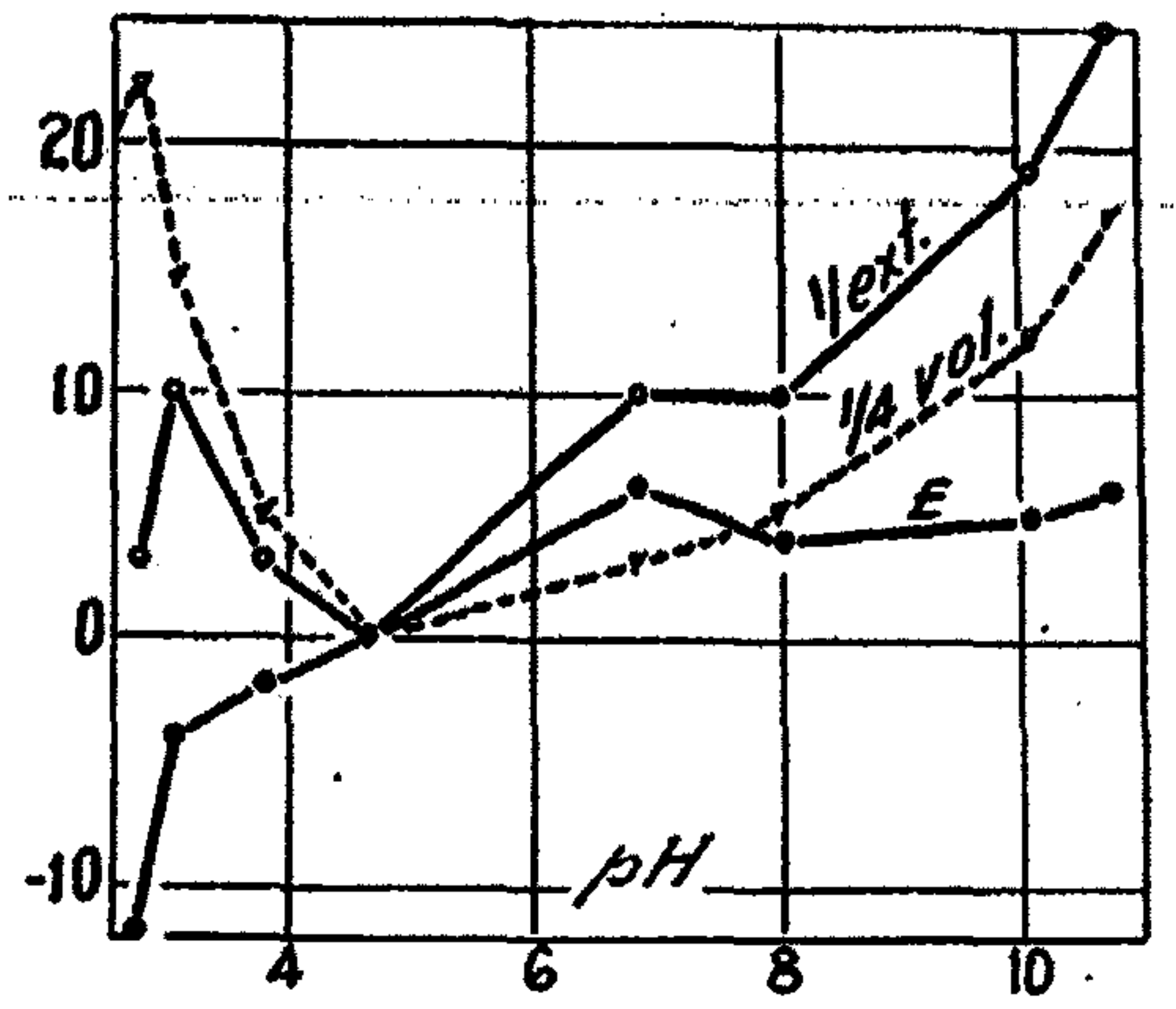

FIG. 1

Elasticity and Swelling of isotropic cylinders of gelatin in relation to pH of medium. E = Young's Modulus, 1/ext = reciprocal of extension under a constant stress.

Under the conditions of the above experiment when we think of elasticity in terms of Young's Modulus we regard each combination of gelatin, water and acid or alkali as a new substance of which we wish to know the modulus of elasticity, i.e. calculated for unit length and cross section. When we consider how the concentration of gelatin varies (namely inversely as the volume) the uniformity of Young's Modulus is remarkable. A discussion of the results is deferred until other experiments have been recorded.

Aeolotropic gelatin.

More extensive experiments were performed on strips simply cut from sheets of the same commercial gelatin as was employed above. In virtue of their thinness they come to equilibrium much more speedily, but, since swelling is greater at right angles to their greater extension than in the same plane, the cross section increases at a relatively greater rate than the length of the strip; consequently resistance to stretch, as we might expect, increases more rapidly in proportion to swelling than it does in isotropic gelatin. The relative difference in resistance to stretch falls far short, however, of the difference in cross section in the two cases. With an increase in cross section (at pH 3.1 as compared with pH 4.7) five times greater in aeolotropic than in isotropic gelatin (300% v. 60%) the increase in resistance to stretch was barely doubled (65% v. 35%).

Strips of Coignet's Gelatin A (7 × 2 cm. more or less) were clamped loosely at each end by a cork clamp and suspended vertically in a fluid medium; the lower end, being weighted, rested on the bottom of the vessel, and the other was attached to an auxonometer as before. In this case, about 2 grams weight was the stretching force used. Extensibility, dimensions, and pH were first determined in distilled water after 24 hours exposure. Subsequently acid or alkali was added to the same medium and on the elapse of four to five hours the measurements were repeated. Temperature was not recorded. It probably varied but little in the few hours that matter. Each plotted point was determined on a separate strip and is expressed as a percentage of the value in distilled water. In this set of experiments lactic was the acid used in order to strengthen the analogy to the conditions in active muscle. The results are the same with HCl over the greater part of the curve.

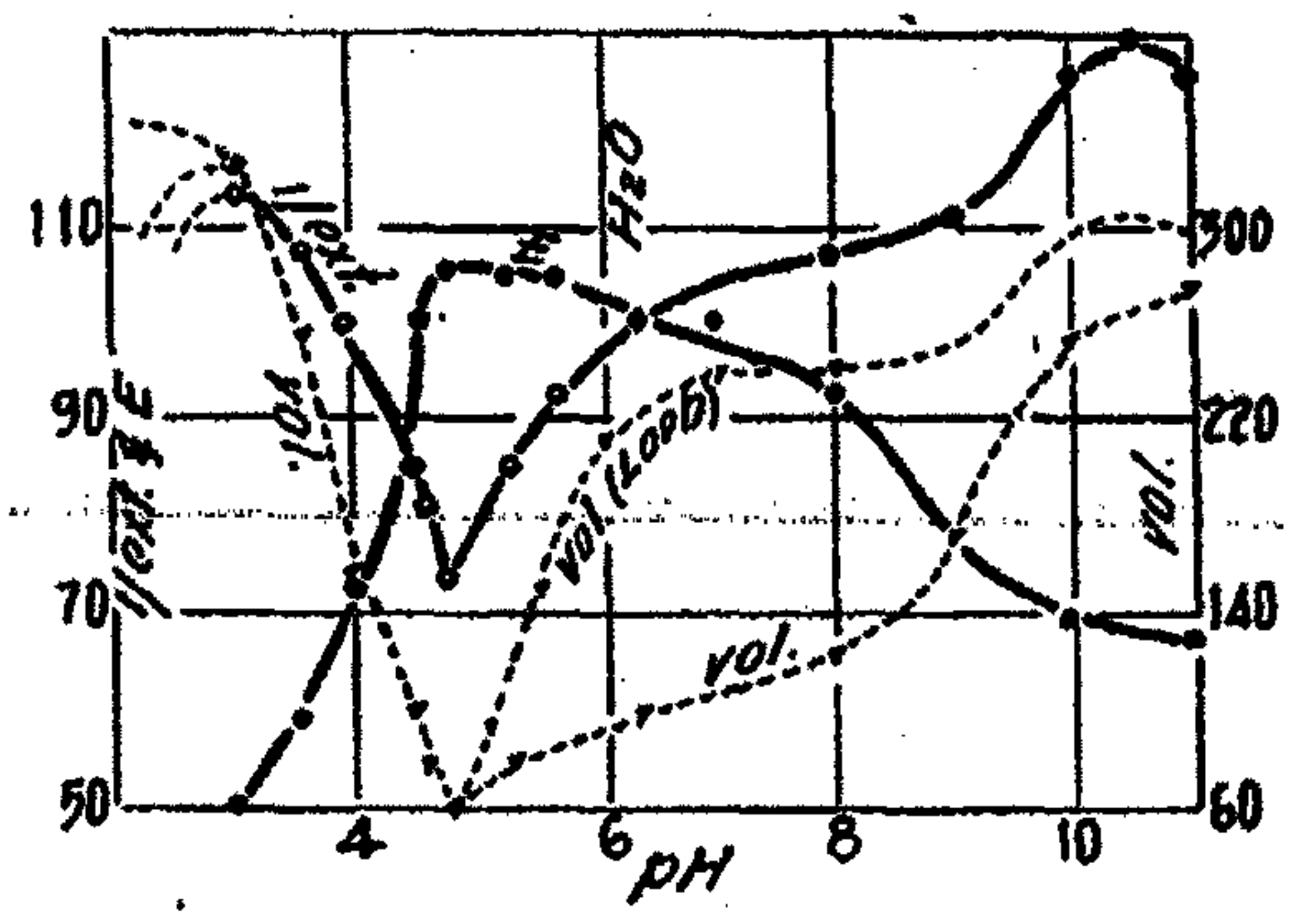

Fig. 2

Elasticity and Swelling of aeolotropic strips of gelatin in relation to pH of the medium.

Results: In Fig. 2 elasticity curves corresponding to those in Fig. 1 are given for aeolotropic commercial gelatin. Below is the approximate volume at the time of measurement of elasticity, and also a portion of the volume curve as given by Loeb for well washed gelatin. The variations in the curve of resistance to stretch are exaggerated as compared with those of Fig. 1, and demonstrate more strikingly the correlation with swelling.

The Young's Modulus curve falls away more rapidly in acid and alkali owing to the fact mentioned above that resistance to stretch in these aeolotropic strips does not increase *pari passu* with cross section area. The percentages are only approximate since thickness was measured not on the strips tested but on similar pieces kept in the same solution. The measurements were made by an adaptation of the apparatus used to measure extension.

In another set of experiments actual values of E were determined. Some averages are given below. That in distilled water is the same as for the isotropic gelatin of Fig. 1 which also had a similar amount of imbibed water.

TABLE I

Young's Modulus in grams per mm² for strips of commercial (aeolotropic) gelatin at varied pH.

Reagent	Lactic acid	Lactic acid	Lactic acid	Lactic acid	H_2O	NaOH	NaOH
Initial conc.	$\frac{M}{200}$	$\frac{M}{500}$		$\frac{M}{20000}$		$\frac{M}{2000}$	$\frac{M}{1000}$
Approx. final pH.	3.0	3.6	4.7	5.5	6.3	9.0	10.0
Gelatin conc. %	3	4	19	13	12	8	5
E. of av. strip.	3.5	3.6	6.4	6.0	6.0	4.8	4.1

Relationship of the Curves. Both in Figs. 1 and 2 the outstanding difference between the *resistance to stretch* and *volume* curves respectively is that in the case of the first the maximum is higher on the alkali side and in the case of the second on the acid side. Correspondingly Young's Modulus curve rises on the alkali side also.

Another asymmetry common to all the curves is a flattening between pH 4.7 and pH 8.0. In this connection it may be recalled that Wilson and Kearn (1922) obtained under certain conditions a second minimum of swelling at pH 7.7; Davis and Oakes (1922) found the minimum viscosity above 40°C. to be at the same point, while Sheppard and Sweet's elasticity curves are highest in this region also. To explain these and other (optical) phenomena the existence of two forms of gelatin has been postulated.* On this hypothesis if each form had its maximum cohesion at its "isoelectric point," viz. 4.7 and 7.7 respectively, the general shape of the compound curves could be explained. But while elasticity and volume are evidently correlated there can be no simple causal relation in one direction only, for the interaction is mutual. Before theorising on this subject, however, we must further investigate the separate factors which affect elasticity.

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*This view has however been criticised for example by Hitchcock (1924) and Kraemer (1925).

II. Relation to the Separate Factors in the pH Effect

Two methods were employed to distinguish the individual influence of the various factors involved in a change of pH, (1) separating them by critical time studies and (2) varying them independently.

(1) TIME STUDIES

I first quote an experiment on the progressive uptake of acid and loss of material into solution when acid is added to isoelectric gelatin.

Experiment: Five sheets of gelatin, each 1 gram, were kept at approximately the isoelectric point (ca. pH 4.7) for 24 hours (each in 250 c.c HCl 6×10^{-5} N (pH 4.2) at start, becoming pH 4.9 to 5.0 at end of period). Thereafter they were transferred to N/2000 HCl, (each 250 c.c.), the various pieces removed at intervals and the following determinations made:—

TABLE II

Pieces 1 to 5 of isoelectric gelatin put into N/2000 HCl, pH 3.31.

Piece No.	Time	pH of medium	Millimols acid taken up	Dry weight of gelatin. Original wt. 1 grm.	% of isoelectric wt.
1.	0 hrs.	3.31	——	.918 grms.	100.0
2.	1 "	3.51	.043	.901 "	98.3
3.	4 "	3.64	.064	.899 "	98.1
4.	26 "	3.81	.081	.886 "	96.8
5.	48 "	3.86	.082	.880 "	96.2

The amount of acid taken up would be equivalent to about one molecule to each molecule of gelatin—if its molecular weight were 12,000. As a maximum about 15 times that amount of acid can be absorbed.

Other time studies were made over several days of the corresponding variation in volume and resistance to stretch of aeolotropic gelatin. The results for a 22 hour period of both sets of studies are combined in Fig. 3. The curves start with the addition of N/2000 HCl after 24 hours at about pH 4.7. The time curve of resistance to stretch is seen to be compounded of three different curves, represented respectively by

1) A slight drop, corresponding to the period of maximum combination with reagent which is half completed in less than one hour. (If swelling is rapid this part of the curve is represented merely by a lag in rising).

2) A steep and large rise, corresponding to the period of maximum swelling which lags behind the absorption of acid and is half completed (taking three days swelling as the "total") only after about 8 hours.

3) A gradual fall thereafter, the cause for which is not apparent from the figure. It is not loss of material into solution, that factor being shown by the dry weight curve to be quite insignificant. This slow loss of elasticity explains perhaps the absence of a definite swelling limit.

The time curve of resistance to stretch in alkali differs from that in acid in showing no initial drop, as might have been anticipated from the corresponding values of Young's Modulus. A rapid rise followed by a gradual fall are exhibited just as in acid.

Of the 3 factors revealed in Figs. 3 the combination with reagent* and the imbibition of water are reversible when the pH is reversed. The third factor is only partially reversible as is shown by Fig. 4. After 12 hours exposure to N/2000 HCl the strip was transferred to a medium of pH 6 which it gradually changed to about 4.8. Volume falls rapidly, and with it, resistance to stretch for about 3 hours. As the volume curve flattens out elasticity begins to recover. This recovery, however, never restores elasticity to its former value; nor does volume revert entirely to the original. This is equally true of the result of swelling in alkali. The inference is that a persistent structural change is brought about by swelling even in dilute solutions of acid and alkali.

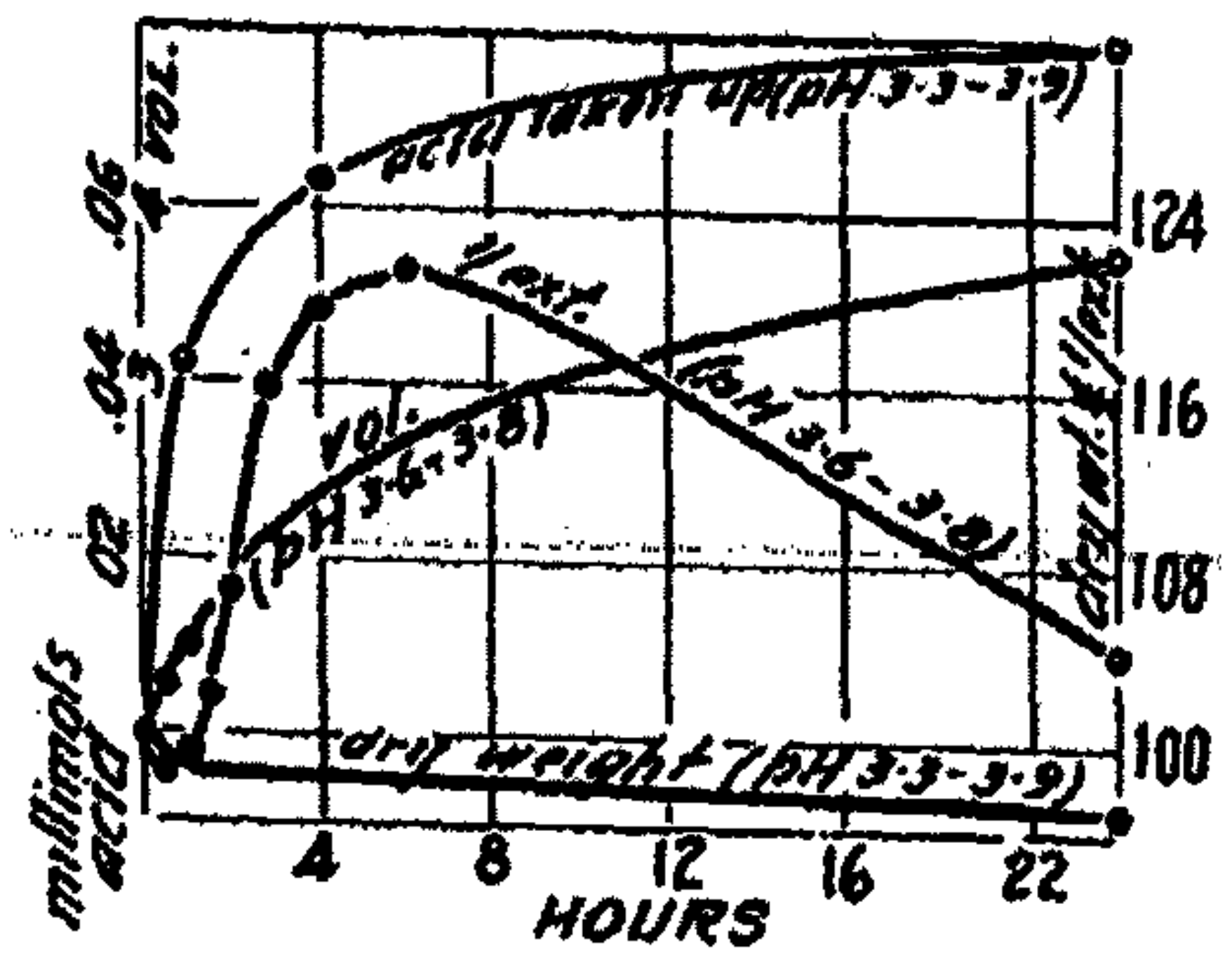

FIG. 3

Time study relating resistance to stretch to the separate factors involved in acidification of isoelectric gelatin. The experiment starts with the addition of N/2000 HCl after 24 hours at the isoelectric point.

Further indication of the persistence of a structural modification is indicated by the result of a repetition of the cycle under exactly the same conditions. Volume increases much more rapidly in the second or succeeding cycles than it does in the first, until the first swelling limit is approached, after which the rate is the same as before. The modulus of bulk elasticity must have suffered loss along with that of stretch to allow of the more rapid swelling.

As regards resistance to stretch the second rise is also much quicker and greater than the first—the result obviously of the more rapid imbibition. But the second maximum still falls short of the first because there has been a permanent loss of elasticity. The most instructive feature, however, of the second cycle is that if the swelling is not too prolonged there is little further loss of elasticity. The second minimum is little lower than the first. This points to an actual mechanical damage resulting from swelling, which, once done, does not require to be repeated by a similar distension.

(2). INDEPENDENT VARIATION OF FACTORS

(a) THE CHEMICAL FACTOR. Variation of pH with swelling partially suppressed.

By the addition of a neutral salt the swelling in acid or alkali can be largely inhibited, while the amount of acid or alkali taken up by the gelatin is changed but little.

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*The statement requires slight modification for reaction with strong alkali cf. Lloyd (1920), Wilson (1923), Fairbrother (1924).

The result in the case of acid and salt is seen in Curve B, Fig. 5. There is a considerable and protracted depression of the resistance to stretch indicating clearly that if swelling could be entirely suppressed, combination with acid would reduce elasticity.

In the case of alkali and salt, however (Curve B, Fig. 6) there is no fall in the resistance to stretch, but merely a diminished rise corresponding to the relatively diminished swelling.

(b) THE IMBIBITION FACTOR. Modification of swelling with H-ion concentration unchanged.

A comparison of the result when swelling is allowed free play as in Curves A, figs. 5 and 6, and when it is partially suppressed (Curves B) demonstrates the powerful effect of the imbibition factor in increasing the resistance to stretch.

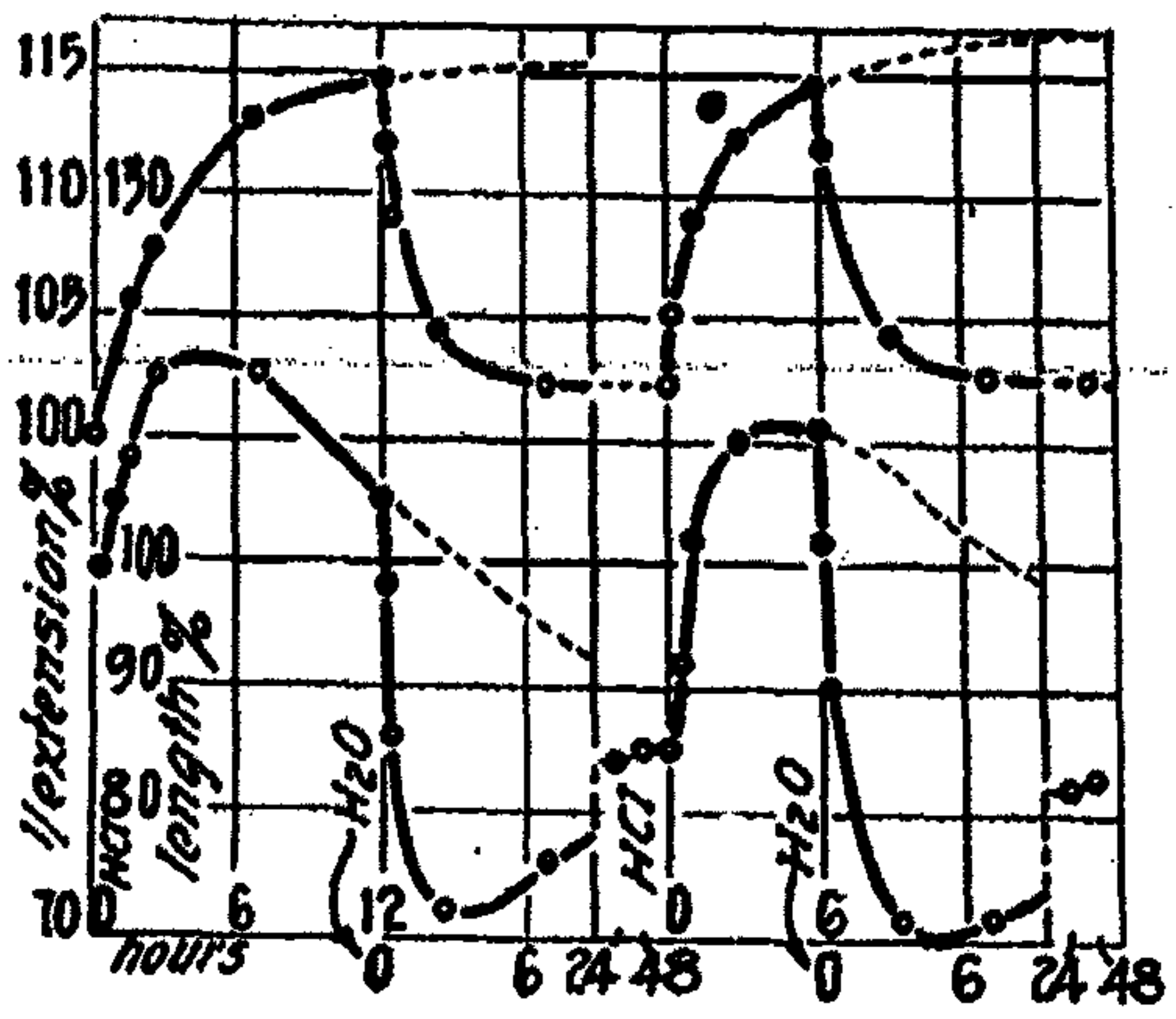


FIG. 4

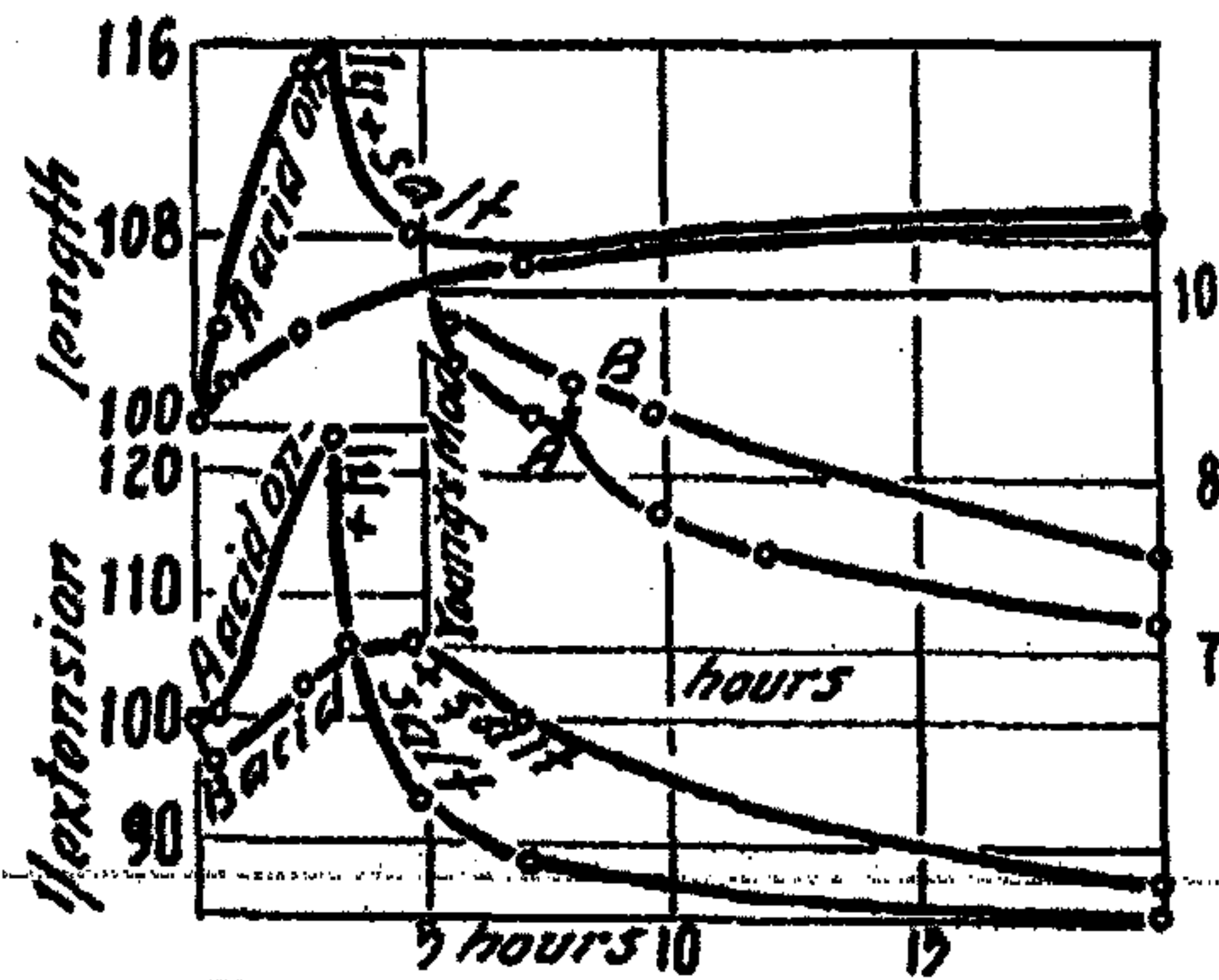
Time study. The effect of successively acidifying isoelectric gelatin with N/2000 HCl and restoring to the isoelectric state. The first swelling causes a permanent loss of elasticity, the second has little further effect.

The following experiments illustrate the same action of swelling when the pH is maintained at the isoelectric point.

Imbibition per se. It was noted that the cylinders of isoelectric and isotropic gelatin used in the first experiment, when imbibing water—as they did for some time in the pH 4.7 solution—became gradually less extensible, maintaining in fact, in spite of dilution, an almost constant modulus of elasticity.

Salt effect at the isoelectric point. The statement frequently made that neutral salts repress swelling at every pH is incorrect. In the pH zone of low swelling the effect of moderate concentrations of salt is to markedly increase the volume, higher concentrations bringing about a decrease. The maximum of course is much inferior to that induced by acid or alkali and in pH regions of high swelling only the depressing effect of salts remains conspicuous. But in the range including the isoelectric and neutral points the general effect of salts resembles that of acids or alkalis. Salts with a polyvalent ion are most active.

Experiment. To a cylinder of the above gelatin at constant equilibrium with a pure acid medium of pH 4.7 successively greater concentrations of $La(NO_3)_3$ were added at two day intervals keeping the same pH.



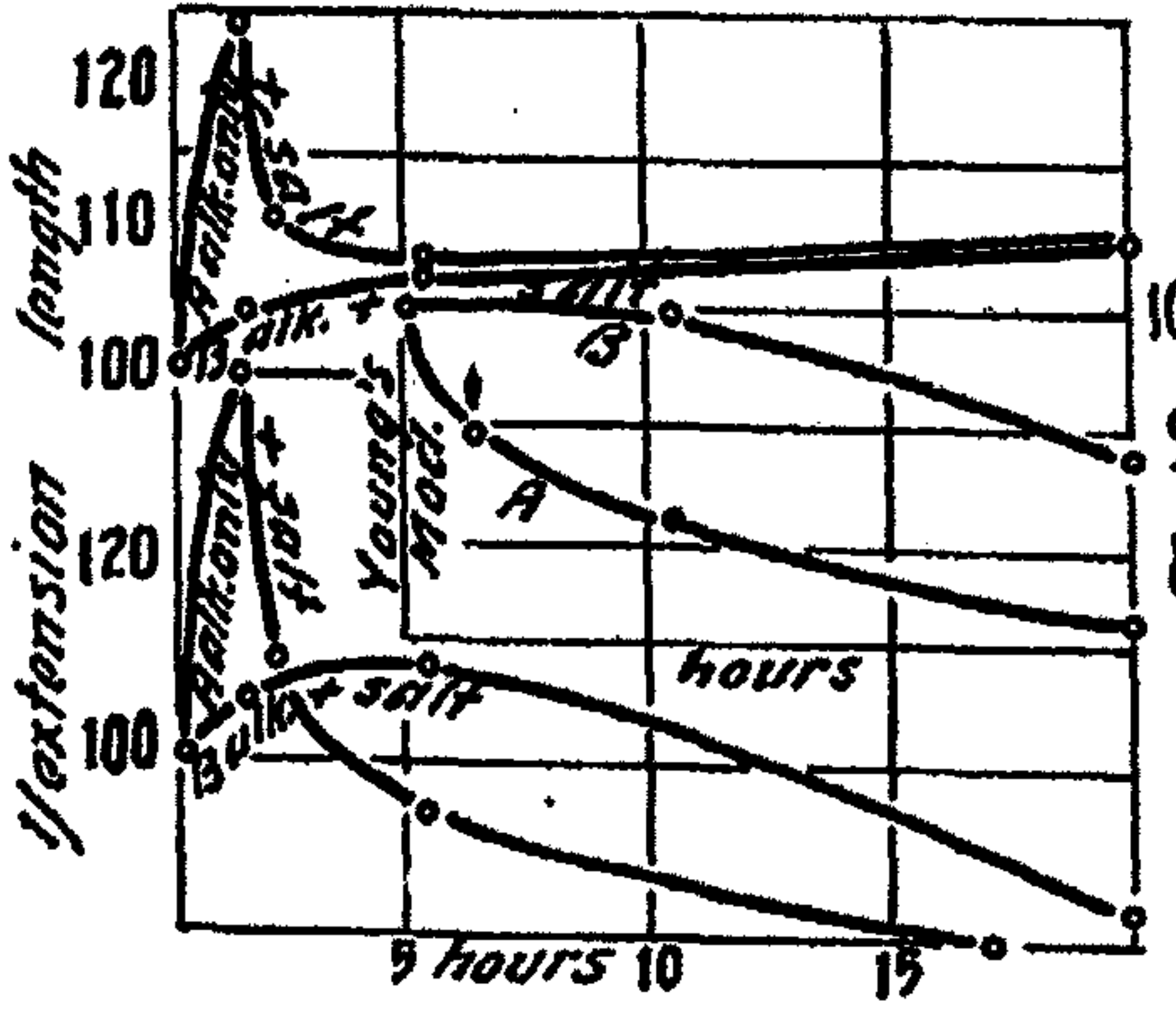


Fig. 5 (above)

Strip A (isoelectric gelatin) is treated with N/2000 HCl to which M/10 is later added; Strip B with mixture from the start. The greater swelling of A in pure acid causes greater loss of elasticity.

Fig. 6 (below)

Similar to Fig. 5, but using N/660 NaOH and M/20 $CaCl_2$. The swelling of Strip A is greater than in Fig. 5, consequently the loss of elasticity is greater.

TABLE III

Effect of $La(NO_3)_3$ at the isoelectric point.

Reagent	Temp. C	pH	Vol.	1/Ext.	E
After 4 days in HCl alone (ca. N/20,000)	15°	4.7	100	100	100
plus 2 days in HCl and M/1000 $La(NO_3)_3$	16°	4.7	130	106	98'
plus 2 days in HCl and M/200 La $(NO_3)_3$	14°	4.7	155	116	101
plus 2 days in HCl and M/10 $La(NO_3)_3$	14°	4.7	135	60	73

Volume and resistance to stretch increase to a point and fall thereafter. The concentration of $La(NO_3)_3$ at which the maxima lie is apparently of the same order of magnitude as the corresponding concentration of HCl, viz: between 10^{-2} and 10^{-3} molar. Young's Modulus remains perfectly constant until a high concentration of salt is reached.

(c) THE FACTOR OF STRUCTURAL CHANGE. *Its relation to the other two factors.*

Figs. 5 and 6 illustrate what happens when a strip (A) which has undergone high swelling in pure acid or alkali, is transferred to the same concentration of acid or alkali with neutral salt added. The volume falls and gradually approaches that of strip (B) which has remained for the same period in the mixed medium. But the point is that the resistance to stretch and the modulus of elasticity of A fall far below that of B. This relative loss of elasticity can only be ascribed to A's greater swelling. On the other hand, B with only moderate swelling loses elasticity also. It is not feasible entirely to suppress swelling in presence of acid or alkali in order that we may find out if any portion of the total loss of elasticity is directly due to the action of the reagents, but the indications are that it is; for cohesion is most rapidly weakened in high concentrations of acid and alkali beyond the points of maximum swelling.

Conclusions and Theoretical Considerations

Variation in pH of the surrounding medium affects the elasticity of a piece of gelatin in at least three different ways:—1) directly through chemical (or physical) combination or decombination; 2) indirectly through swelling or shrinkage, and 3) through slow, supposedly structural, changes induced by factors 1) and 2).

1) The direct effect of acid on isoelectric gelatin, apart from secondary swelling effects, is to cause a decrease in the resistance to stretch. Tensile strength is also markedly diminished though no quantitative measurements were made. It is probable therefore that molecular cohesiveness is decreased. This is what one might expect with an electrically charged as compared with a neutral state of the colloidal particles.

On the other hand there is no evidence that low concentration of alkali causes loss of cohesion. In this connection however the possibility that part of the gelatin is "isoelectric" at pH 7.7 must be kept in mind (see antea). On that assumption as the pH is shifted from 4.7 to 7.7 part of the gelatin is departing from and part approaching its isoelectric point. Hence loss of cohesion in the first case may be balanced by gain in the second.

2) Water of imbibition reinforces the elasticity of gelatin to such an extent as to compensate for diminished concentration of solid matter as long as structure is unimpaired. It was qualitatively evident in performing the experiments and has been proved by Sheppard and Sweet, that elasticity to torsional and bending stresses varies with that of stretch. Tensile strength however tends on the contrary to decrease with water of imbibition. That is to say, although, within the limits of elasticity, extensibility is decreased,

yet, if we increase the load, the breaking point is earlier attained in the more swollen gel.

As to the mechanism through which the water acts, fortified resistance—by increase of internal pressure—to a decrease of volume resulting from deformation is apparently ruled out since the volume of gelatin is unaffected by stress. Since the evidence points to a two-phase structure in the gel, it may be suggested that the more solid phase imbibes water at the expense of the more liquid, leaving less room for relative displacement of the strands of the mesh. By this hypothesis elasticity and rigidity in the gel become correlated with viscosity in the sol.

3) Structural changes may be induced by the above factors as is demonstrated by the persistent effect on elasticity and on subsequent swelling. It is recognized that properties of a gelatin jelly, which can only be ascribed to structure, date largely from the "last warming" as Bogue expresses it. Swelling capacity in relation to concentration at that moment has been most studied. But elasticity is equally influenced. A jelly set from a 14% sol has an elastic modulus greater by one half than that from an 11% sol. But if allowed to imbibe water till its concentration falls to 11%, its modulus, being scarcely diminished, is still one half greater than that of the jelly which was originally formed at that concentration.

The "last swelling" in acid or alkali must also be given a place in determining the structure of a formed jelly. The effect, and probably the mechanism, is the same as that of gentle warming. Presumably dispersion is increased, material passing from the gel to the sol phase and weakening the structure. On reversing the pH, as on cooling, re-aggregation occurs, but it begins in a more dilute gel and the reintegrated structure is thus less dense with a lower elastic coefficient than the original.

Application to Theories of Sewlling.

If gelatin were a homogeneous substance the modulus of bulk elasticity would be directly related to that of stretch. But in a diphasic system structural modification can influence rigidity without greatly affecting bulk elasticity when volume change is unaccompanied by change of shape. It is doubtful therefore if the resistance to swelling can be calculated directly from Young's Modulus of stretch. We have seen evidence however that they do in some degree vary together; consequently the rather surprising constancy of Young's Modulus (in the isotropic gelatin of which alone we need take account) justifies in large measure the assumption which J. A. and W. H. Wilson (1918) made for their hypothetical analogue of gelatin that the bulk modulus is a constant. The deviations from constancy, viz: a fall in acid and a slight rise in alkali up to a point are only such as to explain the asymmetry exhibited by the curve of swelling. It is clear at least that the larger undulations of this curve must be explained by variations in the force of imbibition, whatever its nature, rather than by variations in the opposing force.

Application to the Theory of Protoplasmic Contraction.

Muscle plasma is neutral or slightly alkaline, while the proteins of muscle have a decidedly acid isoelectric point. That of myosin is given as pH 3.9 (Granström), the average of the myoprotein granules as between pH 5 and 4.6 (Quagliariello). The first effect of lactic acid production must therefore be to render the alkaline proteins more nearly isoelectric. The contractile protoplasmic substance is aeolotropic. Now, in an aeolotropic gelatin jelly a corresponding change of pH produces more or less uniaxial shrinkage (i.e. contraction), and, as we have shown, an increased extensibility. Correspondingly increased extensibility, as is generally stated, is a feature of contracted muscle also. So, too, greater flexibility and flaccidity characterise a cilium at the end of its effective stroke, which, being the position of minimum potential energy, corresponds to the phase of maximum contraction in muscle (Gray).

Similarly a fall in viscosity toward the isoelectric point is shown by gelatin in the sol or sol-gel transition state (Bogue). Such a change is associated with a reversible contraction of the chloroplasts of Spirogyra (Scarth, 1922, 1924) while in Amoeba the contraction of the posterior portion of the ectoplasmic tube is accompanied by its liquefaction into endoplasm in the same region. Thus far the physical changes which we have noted in protoplasmic contraction agree with those occurring in gelatin when it is acidified to the isoelectric point.

Gelatin however is not completely representative of all protein gels in its physical behaviour when rendered isoelectric. The removal of electric charge from lyophobe colloidal particles tends to allow of their aggregation. The same tendency is imparted to lyophile particles with the additional tendency to lose some of the water which they hold. The two processes may have an opposite effect on physical properties, and the result will depend on which dominates. Only when dehydration predominates—as in gelatin—should viscosity and resistance to stretching fall. If the predominating result is the aggregation and linking up of particles, micellae or molecules—as in blood plasma—viscosity and elasticity must rise. Even in gelatin, it is at the isoelectric point that we find maximum turbidity and maximum syneresis and increase of viscosity on lapse of time—aggregation phenomena. The recent work of Gasser and Hill (1923), therefore, pointing to a decided increase both in viscosity and elastic modulus when a muscle is stimulated to contract is not opposed to the general theory of a shift to the isoelectric point, though the physical changes are not well typified by gelatin. A colloid more easily aggregated would form a better model. If, fundamentally, the process is the same in all cases, yet the difference in the effect on viscosity and elasticity in muscle, as compared with the more rudimentary structures mentioned, points to a corresponding difference in the nature of the colloidal substance on which the chemical factor acts.

Summary

The relation of the elasticity of gelatin to pH is determined by the method of transferring preformed gels from a medium of one pH to one of another and comparing the extensibility under a given stress after volume change is more or less completed.

The reciprocal of the extension (resistance to stretch) has a minimum value at pH 4.7 and maxima about pH 3 and pH 11, the alkali maximum being the higher.

Young's Modulus in the case of isotropic gelatin varies very little between pH 4.7 and pH 11; it falls slightly on the acid side of the isoelectric point.

A salt with a trivalent (i.e. colloidally active) cation has the same general effect on gelatin at a uniform pH of 4.7, as has the addition of acid or alkali to isoelectric gelatin. Volume and resistance to stretch increase up to a certain concentration of salt (between 10^{-3} and 10^{-2}M), and fall in higher concentration. The modulus of elasticity remains constant up to a certain limit.

Three separate factors affecting elasticity are involved in pH change:—

1) The direct action of the reagent in combining chemically or by adsorption with the gelatin. In the case of acid the effect is to reduce elasticity; in the case of alkali, in low concentration to increase it slightly, in high to decrease it. The change is reversible.

2) The modification of imbibition resulting from such combination. Swelling increases the total resistance to stretch and maintains the modulus of elasticity at a constant value in spite of dilution of the gel. The change is again reversible.

3) Structural change induced mainly by 2) by partly by 1). This entails a loss of elasticity, partly reversible and partly not.

Theoretical Conclusions.

Gelatin gels have a definite heterogeneous structure modifiable by swelling agents as well as by heat.

Variations in the degree of swelling with change of pH are not explicable as the result of contrary variations in bulk elasticity except as regards minor features such as the greater swelling in acid than in alkali. The major variations must be due to changes in a positive force attracting water.

The elasticity and viscosity changes attending protoplasmic contraction are analogous to those attending the shrinkage of protein gels when acidified from a neutral or alkali condition to the isoelectric point.

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THE FREE ENERGY OF DILUTION AND THE ACTIVITY OF THE IONS IN AQUEOUS SOLUTIONS OF BARIUM CHLORIDE

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The activities of the ions are connected with the electromotive forces of concentration cells and with the free energy of dilution, $(-\Delta F)$, by the thermodynamic relation:

$$-\Delta F = E.n.f = RT \ln \frac{a^{\cdot}_2 \cdot a'_2}{a^{\cdot}_1 \cdot a'_1}$$

where E is the electromotive force, n the valence, f the faraday (96494 coulombs), R the universal gas constant (8.316 joules), T the temperature on the absolute scale, and $a^{\cdot}_2 \cdot a'_2$ and $a^{\cdot}_1 \cdot a'_1$ are the products of the activities of the cation and anion in the concentrations c_2 and c_1, respectively. It is obvious that if we determine the electromotive force of a concentration cell, one solution of which has a concentration of c_1, (0.001 M), for which we assume that the activities of the ions are equal to their concentrations as determined by conductivity we may then substitute their product for $a^{\cdot}_1 \cdot a'_1$ and calculate the product of the activities of the ions, $a^{\cdot}_2 \cdot a'_2$, for any other concentration c_2.

Pearce and Hart[1] have determined the product of the activities of the potassium and bromide ions in aqueous solutions containing various concentrations of potassium bromide. Assuming with MacInnes[2] the hypothesis of the independent activity of the ions and further that the potassium ion has the same activity in a solution of potassium bromide as in the corresponding concentration of potassium chloride, they have calculated the activity of the bromide ion by means of the ratio, $(a_K . a'_{Br})/a^{\cdot}_K = a'_{Br}$. They have found that the activities of the chloride and bromide ions are practically identical in equivalent concentrations of their salts up to 0.5 M.

Ferguson and France[3] have measured the electromotive forces of concentration cells containing aqueous solutions of sulphuric acid both with and without ion-transference. Assuming that the degree of dissociation is calculated from freezing point data and that the sulphuric acid ionizes directly into hydrogen and sulphate ions, they found it possible to calculate accurately the voltage of concentration cells by means of the Nernst equation. It is a well known fact that in most cases ionic concentrations obtained from freezing point and electromotive force data may deviate widely. This would seem to indicate that at the concentrations at which they worked the number of the intermediate ions is negligible. They also calculated the transference numbers of the hydrogen and sulphate ions.

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[1] Pearce and Hart: J. Am. Chem. Soc., 43, 2483 (1921).

[2] MacInnes: J. Am. Chem. Soc., 41, 1086 (1919).

[3] Ferguson and France: J. Am. Chem. Soc., 43, 2150 (1921).

Of the other work which has been done on the ternary electrolytes we should mention that of Jahn[1], Goodwin[2], Wright and Thompson[3], Biron and Afanassjew[4], and Horsch[5]. These investigators have studied the electrode potentials and the electromotive forces of concentration cells containing cadmium and zinc electrodes in solutions of their chlorides. Their results need not be mentioned in the present work.

Lewis and Randall[6] have made an extensive study of the free energy of dilution and of the activities of the ions in aqueous solutions of electrolytes. They have derived equations by means of which it is possible to calculate activity coefficients from freezing point, vapor pressure. solubility, and electromotive force data. The results derived by the different methods are highly comparable.

The study of the activities of the ions, free energy, and electromotive force relations in aqueous solutions of electrolytes, hitherto, has been confined largely to the salts of the uni-univalent type. It is the purpose of this investigation to attempt to extend the study of these relations to the aqueous solutions of the salts of the alkaline earth metals. Barium chloride is the salt chosen for this purpose.

Materials and Apparatus

Barium Chloride.—Chemically pure barium chloride was thrice recrystallized from pure distilled water and finally from conductivity water. A sample of the pure salt was heated to constant weight at 150° in a previously tared flask. To this weighed portion conductivity water was added and the solution boiled to remove dissolved oxygen and carbon dioxide, then permitted to cool in an atmosphere of pure hydrogen. The solution was accurately weighed and the barium chloride content calculated. To a weighed quantity of this stock solution conductivity water, previously treated in a similar manner, was added to make the desired molal concentration. All processes involving the transference of water or of solutions were carried out in special devices which absolutely prevented any contact with air.

Mercury and Amalgams.—The mercury used for making the amalgams was repeatedly sprayed through dilute nitric acid and then distilled in a current of dry air. The amalgam was prepared by electrolyzing a saturated solution of pure barium chloride using the pure mercury as the cathode. The amalgam was quickly dried and filtered through a fine capillary tube into the storage chamber where it was kept under an atmosphere of dry hydrogen. Experience showed that the range of concentration of the amalgam suitable for electrode purposes is very limited. The most satisfactory concentration was approximately 0.05 percent.

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[1] Jahn: Wied. Ann., **28**, 21, 491 (1886).

[2] Goodwin: Z. physik. Chem. **13**, 577 (1894).

[3] Wright and Thompson: Phil. Mag., (5) **19**, 106 (1885).

[4] Biron and Afanassjew: J. Russ. Phys. Chem. Soc., **41**, 1175 (1909).

[5] Horsch: J. Am. Chem. Soc., **41**, 1787 (1919).

[6] Lewis and Randall: J. Am. Chem. Soc., **43**, 1112 (1921).

Electrodes.—The silver chloride electrodes were made in the usual way. The heavy pieces of platinum foil were first heavily coated with silver and then with silver chloride. During the electrolysis the solutions were rapidly stirred by means of a rotating platinum anode. The method was such that the maximum deviation of the potentials of a dozen electrodes prepared in parallel rarely exceeded 0.03 volt. The amalgam electrodes were of the dropping type used by Richards.[1]

All electromotive force measurements were made by means of a Wolff potentiometer, using a Leeds and Northrup, type R, galvanometer of very high sensitivity. The standard of reference was an Eppley cadmium cell having a certified potential of 1.01860 volts. All measurements were made in an electrically heated oil-bath, accurately regulated to ±0.01°. The temperatures were read on a standard thermometer, (B. S. No. 26688).

Precision and Duplication.—Three silver chloride electrodes having a maximum deviation of not more than 0.03 m.v. were placed in each half-cell and allowed to stand until equilibrium was established between the electrodes and the barium chloride solutions. Experience showed that a period of six to eight hours was usually necessary for this purpose. The electrodes reached a state of equilibrium more rapidly in the concentrated solutions than in the dilute, but deterioration was also more rapid, rendering the readings less reliable for this reason. Whenever the potential difference between the electrodes in any set-up exceeded 0.03 m.v. these electrodes were replaced by others freshly prepared.

Experimental

The cells studied in this work are of the following types:

(A) $Hg_xBa \mid BaCl_2(c_1), AgCl \mid Ag—Ag \mid AgCl, BaCl_2(c_2) \mid BaHg_x$,
(B) $Ag \mid AgCl, BaCl_1(c_1) \mid Hg_xBa—Hg_xBa \mid BaCl_2(c_2), AgCl \mid Ag$,
(C) $Hg_xBa \mid BaCl_2(c_1) \mid BaCl_2(c_2) \mid Hg_-Ba$, and
(D) $Ag \mid AgCl, BaCl_2(c_1) \mid BaCl_2(c)_2, AgCl \mid Ag$.

All of these combinations can be obtained from a single set-up of the apparatus. The cells with ion-transference, C and D, consisted of single half-cells connected by the flowing junction device recommended by Lamb and Larson[2]. It is obvious that since we are dealing with the same electrodes and solutions the electromotive forces in cells of types A and B should be identical and this was found to be true. Owing to the difference in the migration velocities of the barium and chloride ions we should, and did find, that the potentials of c cells C and D are different.

Measurement of Concentration Cells Without Ion-Transference

The cells used in these measurements were of the types A and B. Since both cells for the same concentration gave the same potentials to within 0.02 to 0.03 m.v., only one table of data is given. It was the intention to carry

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[1] Richards and Conant: J. Am. Chem. Soc., 44, 501 (1922).

[2] Lamb and Larson: J. Am. Chem. Soc., 42, 229 (1920).

out these determinations at the three temperatures, 25°, 30° and 35°, but owing to apparently unavoidable changes with temperature inherent in the barium amalgam itself only two concentration cells have been measured at all three temperatures. In each case the electromotive force values given in Table I are the mean values obtained for at least two set-ups of the apparatus. The difference between the duplicate values for any one cell did not exceed 0.05 m.v.

TABLE I

Electromotive Forces of Cells without Ion-Transference

c_1	c_2	E_{25} volts	E_{30} volts	E_{35} volts
0.003	0.030	0.07564	0.07639	0.07749
0.005	0.050	0.07530		
0.003	0.100	0.11420		
0.005	0.100	0.09646		
0.010	0.100	0.07442	0.07503	0.07608
0.030	0.300	0.07390		
0.100	1.000	0.07660		
0.300	1.256	0.06864		

The Free Energy Decrease and the Heat Content Decrease attending the Transfer of One Mol of Barium Chloride from Concentration c_2 to c_1

The free energy decrease, $(-\Delta F)$, attending the transfer of one mol of barium chloride from concentration c_2 to concentration c_1 is obtained by multiplying the electromotive force of the concentration cell by 2×96494. The decrease in heat content, $(-\Delta H)$, is derived from the Gibbs-Helmholtz equation and is related to the decrease in free energy by the expression: $(-\Delta H)_{25} = (-\Delta F)_{25}(1 - \alpha \cdot 298.09)$, where α is the temperature coefficient of the decrease in free energy. The temperature coefficients, α and β, are calculated from the values for the free energy decrease at the three temperatures by means of the equation: $(-\Delta F)_t = (-\Delta F)_{25}(1 + \alpha t + \beta t^2)$. The data obtained from these calculations is collected in Table II.

TABLE II

The Free Energy Decrease and the Heat Content Decrease attending the Transfer of One Mol of Barium Chloride from Concentration c_2 to c_1.

c_1	c_2	$-\Delta F_{25}$ joules	$\alpha \times 10^6$	$\beta \times 10^6$	$-\Delta H_{25}$ joules
0.003	0.030	+14598.	1520.	92.5	+7975.
0.005	0.050	+14532.			
0.003	0.100	+22039.			
0.005	0.100	+18615.			
0.010	0.100	+14362.	1209.	102.1	+9184.
0.030	0.300	+14262.			
0.100	1.000	+14783.			
0.300	1.256	+13427.			

By adding algebraically the values for the free energy decrease given in Table II it is possible to calculate the decrease in free energy attending the transfer of one mol of barium chloride from any concentration c to a concentration exactly 0.10 M. These values are given in Table III.

TABLE III

The Free Energy Decrease attending the Transfer of One Mol of Barium Chloride from Concentration (c) to 0.10 M.

c_1	$-\Delta F_{25}$ joules	c.	$-\Delta F_{25}$ joules
0.003	−22039.	0.100	00000
0.005	−18615.	0.300	+6821.
0.010	−14362.	1.000	+14783.
0.030	− 7441.	1.256	+20068.
0.050	− 4083.		

The electromotive forces of the cells with ion-transference were made immediately following the measurements without ion-transference. The results are easily reproducible to 0.05 m.v. They are given in Tables IV and V and are self explanatory.

TABLE IV

Electromotive Forces of Concentration Cells with Ion-Transference.

(C) $Hg_XBa \mid BaCl_2 (c_1) \mid BaCl_2 (c_2) \mid BaHg_X$.

(D) $Ag \mid AgCl, BaCl_2(c_1) \mid BaCl_2 (c_2), AgCl \mid Ag$.

c_1	c_2	E^C_{25} volts	E^D_{25} volts	$(N_{Cl})_{25}$	$(N_{Ba})_{25}$
0.003	0.030	0.04204	0.03444	0.556	0.455
0.005	0.050	0.04204	0.03373	0.558	0.449
0.010	0.100	0.04102	0.03212	0.551	0.431
0.030	0.300	0.04300	0.03097	0.582	0.419
0.100	1.000	0.04896	0.03119	0.639	0.407

Thermodynamically, the electromotive force of the concentration cell (C) is given by the relation,

$$E^C_t = N_a \frac{RT}{nF} \ln \frac{\alpha_2^+ \cdot \alpha_2^{-2}}{\alpha_1^+ \cdot \alpha_1^{-2}}$$

and that of the concentration cell (D) is given by $E^D_t = N_c \frac{RT}{nF} \ln \frac{\alpha_2^+ \cdot \alpha_2^{-2}}{\alpha_1^+ \cdot \alpha_1^{-2}}$

The electromotive force of the same cell (C) or (D) without ion-transference is given by the relation

$$E = \frac{RT}{nF} \ln \frac{\alpha_2^+ \cdot \alpha_2^{-2}}{\alpha_1^+ \cdot \alpha_1^{-2}}$$

Hence the ratios $E^C_t/E = N_a$, and $E^D_t/E = N_c$, give us directly the transference numbers of the chloride and barium ions, respectively. These values have been calculated and are inserted in the last two columns of Table IV. It should be noted in passing that as the concentration of the respective cells increase the transference number of the chloride ion increases while that of the barium ion decreases.

In considering the transference numbers of the ions of ternary electrolytes we must not lose sight of the possibility of the existence of complex ions, especially in the more concentrated solutions. When complex ions do occur the transference numbers calculated for the positive or negative ions may involve the transference numbers of more than one ion of the same sign. The sum of the transference numbers of the ions in any given concentration should be equal to unity, or $N_c + N_a = 1$. In spite of the difficulties encountered in manipulating with barium electrodes the sum of the transference numbers of the barium and chloride ions in any concentration cell are found to be practically equal to unity.

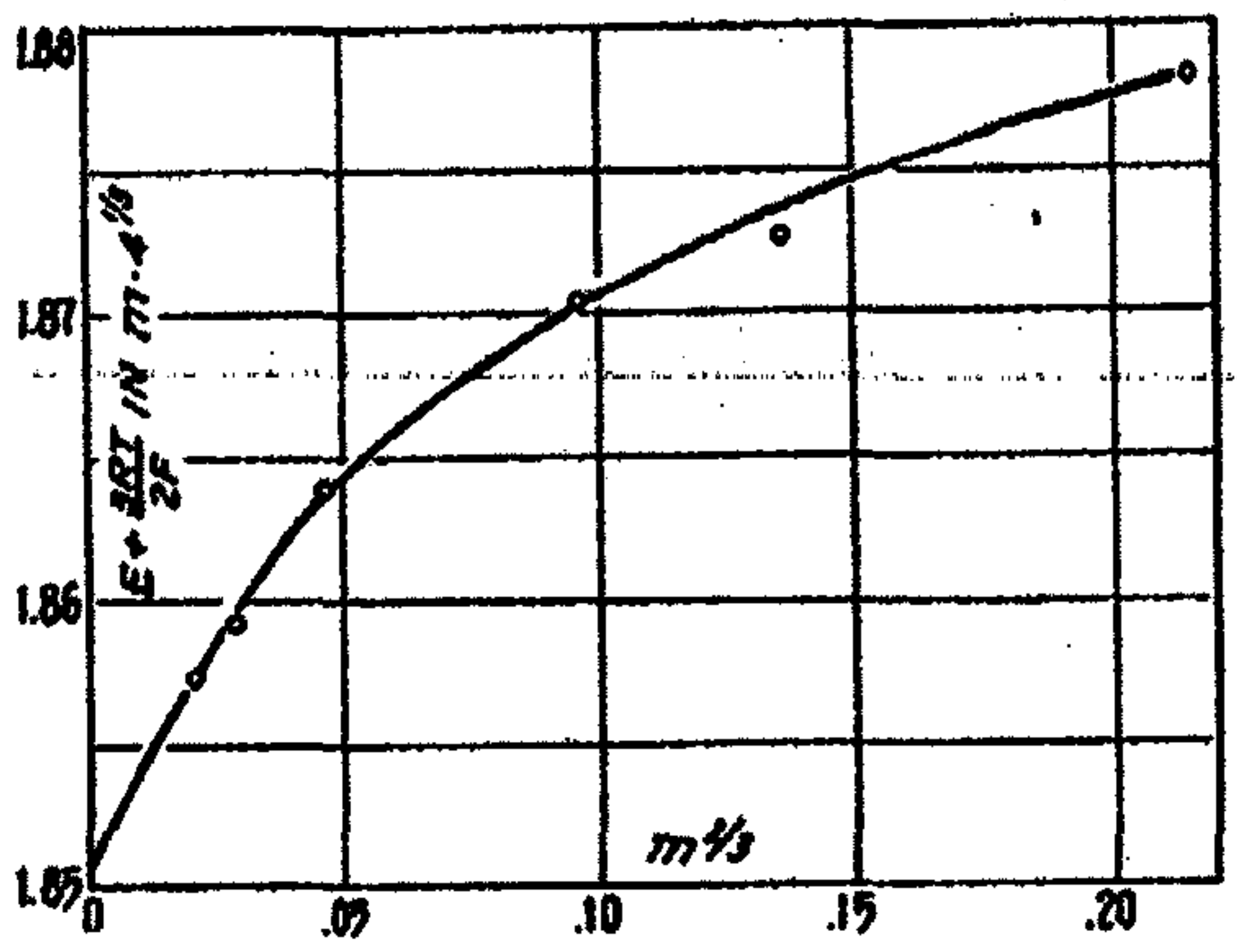

Fig. 1

The Activity of the Ions of Barium Chloride

In very dilute solutions of electrolytes the activities of the ions are equal to their molal concentrations. Thus, in very dilute solutions of barium chloride, say of molality m, the activity of the barium and chloride ions may be taken as equal to m and 2m, respectively. It is quite obvious then that the geometric mean activity of the ions, $\alpha\pm$, will be given by the relation, $\alpha\pm = [m(2m)^2] = 4^{1/3}m$. At finite concentrations, however, the activity of the ions cannot be taken as equal to their molality. For these concentrations we must use the relation, $\alpha\pm = (\alpha_+ \cdot \alpha_-^2)^{1/3} = 4^{1/3}\gamma m$, where γ is the well known activity coefficient.

A simple method for determining the values of γ has been devised by Lewis and Randall[1]. The decrease in free energy accompanying the transfer of one mol of barium chloride from concentration m to concentration m' is given by the expression, $\Delta F = \overline{F} - \overline{F}' = RT\ln \alpha/\alpha' = -2F(E-E')$, where E

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[1] Lewis and Randall: "Thermodynamics," p. 333 (1923).

and E' are the potentials of the electrodes, $\overline{F}$ and $\overline{F}'$ are the partial molal free energies, and α and α' are the activities of barium chloride in the concentrations m and m', respectively. If we so choose our cell that the barium chloride in one half is in its standard state, so that we may write $\overline{F} = \overline{F}'$, $E' = E^\circ$ and $\alpha' = 1$, then we may express the relation between the partial molal free energy and the activity of the barium chloride by the equation,

$$\overline{F}-F^\circ = RT\ln\alpha \doteq -2F(E-E^\circ).$$

But for barium chloride $\alpha^3_\pm = \alpha$, or $3\ln\alpha\pm = \ln\alpha' = 3\ln 4^{1/3}\gamma m$, hence on substituting the mean activity of the ions for the activity of the salt we obtain, $3RT\ln 4^{1/3}\gamma m = -2F(E-E^\circ)$. By substituting numerical values and rearranging terms this expression reduces to the final equation,

$$0.08873\log\gamma = E^\circ - (E + 0.08873\log 4^{1/3}m).$$

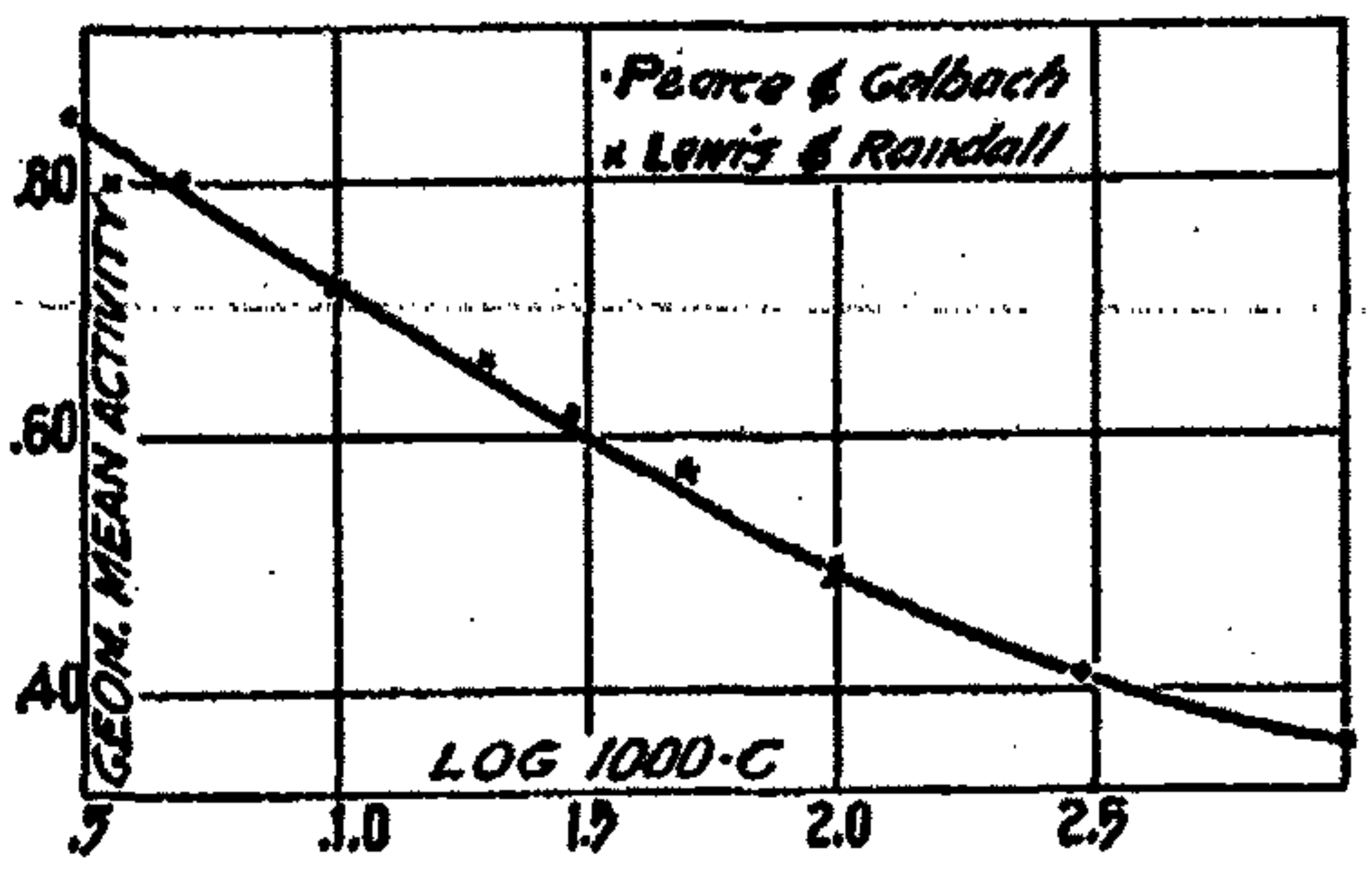

FIG. 2

The first member of our final equation vanishes at zero concentration. If now we plot the values of $(E = 0.08873\log 4^{1/3}m)$ for different values of m against some convenient function of m, the limit approached by the ordinate at infinite dilution is equal to E°. Knowing the value of E° and the value of E for any concentration m we are in a position to calculate the activity coefficient γ for that concentration.

The potential of the concentration cell, $BaHg_X$ | $BaCl_2$ (0.01M), AgCl | Ag—Ag | AgCl, $BaCl_2$(0.01M) | $BaHg_X$ at 25° was found to be 0.07442 volt. If we knew the potential of the cell containing 0.10 M barium chloride we could calculate the potential of the cell having an 0.01 M concentration. To this end we set up at different times four different cells containing the amalgam and silver chloride electrodes in 0.1 M barium chloride. The potentials obtained at 25° were, 1.9412, 1.94908, 1.94890 and 1.94928 volts, respectively. Mean = 1.94910 volts. Adding this mean value algebraically to the various potentials given in Table I, we obtained the electromotive forces of all of the single cells, $BaHg_X$ | $BaCl_2$(m), AgCl | Ag. These calculated values for E are given in Table V.

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[1] Lewis and Randall: "Thermodynamics," p. 333 (1923).

TABLE V

Electromotive Forces of Cells of Type:
$BaHg_{\times}$ | $BaCl_2$ (m), AgCl | Ag.

m	E_{25} volts	γ
0.003	2.06330	0.850
0.005	2.04556	0.808
0.010	2.02352	0.716
0.030	1.98766	0.619
0.050	1.97026	0.570
0.100	1.94910	0.493
0.300	1.91228	0.412
1.000	1.87250	0.360

Using these values of E, we plotted the values of $(E + 0.08873 \log 4^{1/3}m)$ as ordinates against the corresponding values of $m^{1/2}$ and obtained the smooth curve shown in Fig 1. The intercept of this curve with the ordinate gives the value of E° as 1.85100 volts. Substituting this value in the equation, $0.08873 \log \gamma = E^\circ - (E + 0.08873 \log 4^{1/3}m)$, we have calculated the values for the activity coefficients of barium chloride for the various concentrations. These are given in the third column of Table V. The close agreement between these activity coefficients and those calculated by Lewis and Randall[1] from freezing point data for the same concentrations[2] is shown by the curve of Fig. 2.

Summary

1. The electromotive forces of concentration cells containing barium chloride, both with and without ion-transference, have been measured. From these data the transference numbers of the barium and chloride ions have been calculated.

2. The free energy decrease and the heat content decrease attending the transfer one mol of barium chloride from concentration c_2 to concentration c_1 have been computed.

3. The free energy decrease attending the transfer of one mol of barium chloride from various concentrations (c) to a concentration exactly 0.10 M have been calculated.

4. The mean activity coefficients of barium chloride have been calculated and are found to be in close agreement with those calculated from freezing point data for the same range of concentration.

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[1] Lewis and Randall: "Thermodynamics," pp. 361-362 (1923).
[2] By interpolation.

HEATS OF ADSORPTION OF SULFUR DIOXIDE AND OF WATER VAPOR BY SILICA GEL AT 0°C*

BY W. A. PATRICK AND C. E. GREIDER

Heats of adsorption from the gas phase have been measured by a number of previous workers including Favre[1], Titoff[2], and Lamb and Coolidge[3]. In each case note is made of the fact that the heat of adsorption is greater per gram of vapor adsorbed than the corresponding heat of liquefaction at the temperature. Since it is assumed that the vapor is liquefied in the pores or on the surface of the adsorbent, various explanations have been advanced to account for the difference between the heat of adsorption and the heat of liquefaction. This difference should at saturation be equal to the heat of wetting, and is called by Lamb the net heat of adsorption. He assumes that this "net heat" is due to compression of the adsorbed liquid by the forces of molecular attraction, and from this he calculates that in the cases with which he worked the adsorbed liquid was under a pressure of about twenty thousand atmospheres.

Harkins and Ewing[4] have suggested that the heat of wetting, which they call the heat of spreading, is due to the change in surface energy involved, and derive equations to express their ideas, but do not attempt any quantitative calculations.

Recent work in this laboratory[5] has shown that, when silica gel is used as the adsorbent, it is possible to calculate quantitatively the heat of wetting from changes in surface energy. The most active samples of silica gel, activated by heating at 250°-300° in vacuo for a half hour or more, contain from three to six percent of water. It is therefore assumed that the gel before wetting exhibits a water surface. Wetting by water would therefore simply fill up the pores of the gel and reduce the water surface from its original very large value to practically zero. The heat of wetting of silica gel by water was measured at 25°, and the specific surface of the gel calculated on the assumption that the heat measured was due entirely to liberation of the total surface energy of the water. The specific surface obtained in this way agreed very well with that obtained from ultramicroscopic investigations.

The purpose of this work was to measure heats of adsorption at 0°, with silica gel as the adsorbent. In the adsorption of water vapor at 0°, the net heat of adsorption should be negative if it is due to compression of the adsorbed water. If, on the other hand, the net heat is due entirely to liberation of surface energy, it should at saturation be equal to the heat of wetting as

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* Contribution from the Chemical Laboratory of Johns Hopkins University.

[1] Ann. Chim. Phys. (5) 1, 209 (1874).

[2] Z. physik. Chem. 74, 641 (1910).

[3] J. Am. Chem. Soc. 42, 1146 (1920).

[4] Proc Nat. Acad. Sci. 6, 49 (1920).

[5] Patrick and Grimm: J. Am. Chem. Soc. 43, 2144 (1921).

measured at 25°, since the total surface energy of a liquid is, within the temperature limits under consideration (0° – 25°) independent of the temperature.

Apparatus

The system shown in Figs. 1 and 2 was used for all heat measurements at 0°. In Fig. 1, A leads from the first mercury trap to the vacuum line. Evacuation was produced by a Gaede mercury pump and a Hyvac oil pump in series. B is a McLeod gauge, C a second mercury trap, and D a three-way mercury sealed stopcock. G is a cooling coil surrounded with ice and water, and H a ground-glass joint connecting the adsorption bulb I with the remainder of the system.

If this system is evacuated to less than 0.001 mm. pressure for two successive days—the second evacuation to remove gas set free from the glass walls—it will hold the pressure below this point for at least a week.

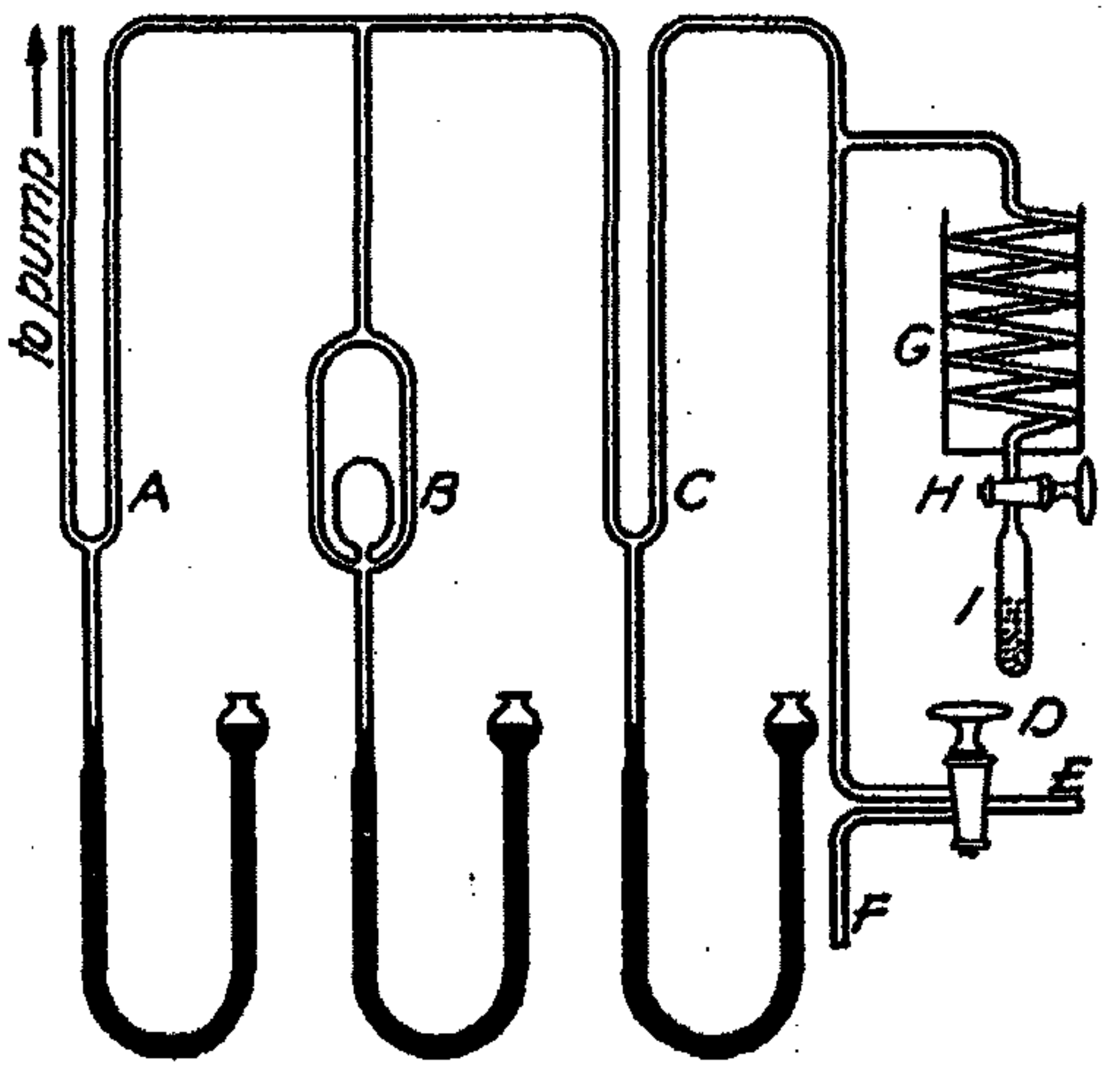

FIG. 1

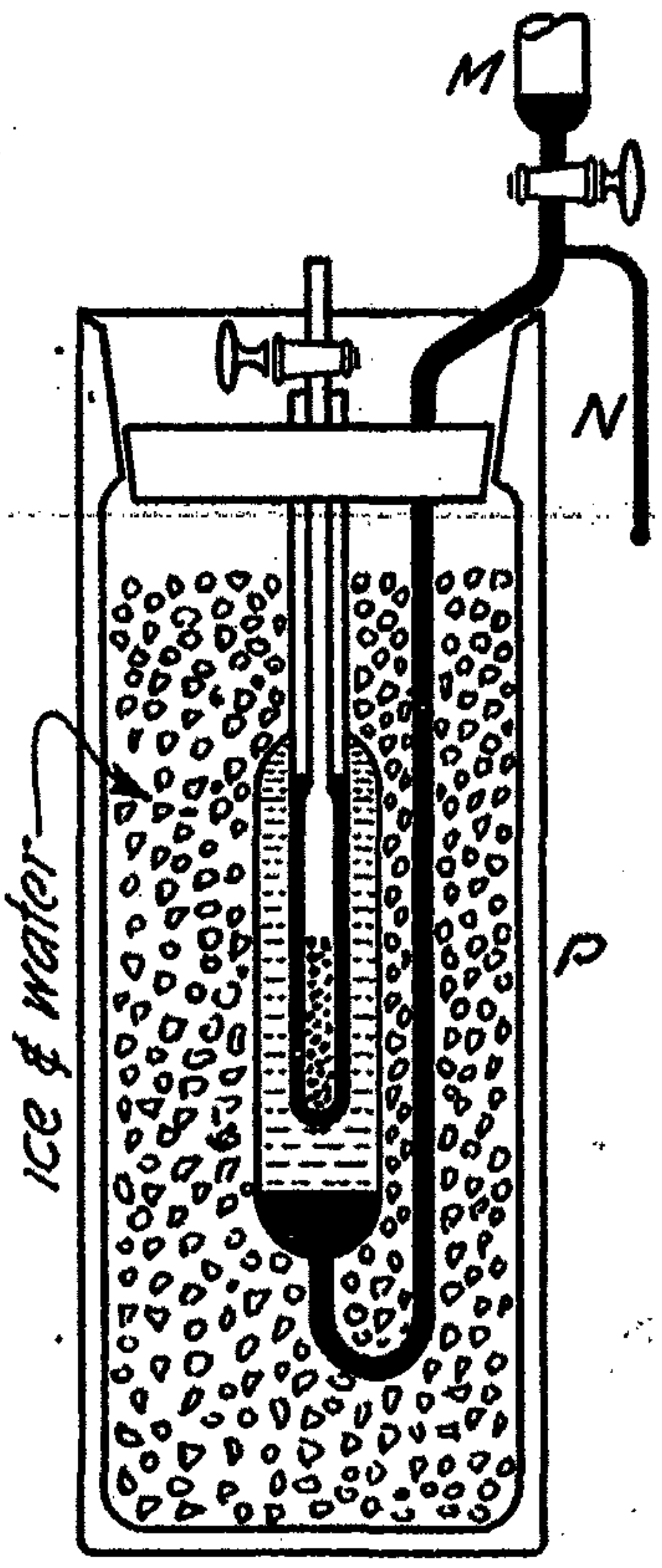

FIG. 2

The measurements of heat at this temperature were made with a modified Bunsen ice calorimeter, as shown in Fig. 2. M is a mercury reservoir, and N a capillary tube ending in a tip of the shape recommended by Ostwald and Luther.[1] The heat given off (or absorbed) is followed by the change in weight of small mercury cups placed under the tip of N. The inner tube of the calorimeter has in it sufficient mercury to stand to about the height shown in the figure, in order that thermal equilibrium between the adsorption bulb and the calorimeter might be more quickly attained.

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[1] "Physiko-chemische Messungen," 3d Ed. p. 332 (1910).

The calorimeter is placed in a two quart "Ferrostat" vacuum jar, filled with a mixture of ice and water. It was found that ordinary ice if well washed would keep the temperature at such a point that heat interchange between the calorimeter and its surroundings was negligible. This blank was, however, re-determined at each filling.

Materials

The mercury and the rubber connections were cleaned in the usual manner. The sulfur dioxide was taken from a tank of the commercial material, from which the first portions were allowed to escape. It was dried by passage through a U-tube filled with phosphorus pentoxide. The silica gel was prepared by the process used by Patrick and McGavack[1] and when dried for two hours at 300°, various preparations contained from 3.5 to 5.5 percent of water.

Procedure

In the adsorption of sulfur dioxide the following procedure was adopted. From 0.5 to 2 grams of the gel, previously heated for at least a half hour at 250°-300° in vacuo, was placed in a small bulb, which was then sealed to the stopcock and outer half of the ground-glass joint H, making the complete adsorption bulb I. The joint was lubricated with stopcock grease and fitted in place, and the system, including the bulb containing the gel, evacuated to a pressure of less than 0.001 mm. The stopcock of the bulb was then closed, and after equalizing pressure in the system, the bulb was detached, the lubricant on the joint removed with a clean cloth, and the bulb weighed.

Experiments were made to determine if the weight of the bulb, as determined in this way, was reproducible. The bulb was weighed, stopcock grease applied to the joint, then removed with a clean cloth, and the bulb re-weighed. A series of six such weighings agreed within 0.2 mg.

The bulb was placed in the calorimeter and again attached to the system, which was then evacuated, as before, to a pressure less than 0.001 mm. While the evacuation was in progress, sulfur dioxide was allowed to sweep out the drying train, connected to the system at E, the sulfur dioxide escaping at F. This drying train contained also an open manometer, in order better to regulate the admission of the gas. It was assumed that the air was completely displaced from the train between the tank and the stopcock D after sweeping the gas through at a moderate rate for half an hour. This was further checked by the time required for equilibrium to be established when the gas was adsorbed by the gel,—it having been shown by Patrick and McGavack that a pressure of air over the gel too small to materially affect the calculated pressure of sulfur dioxide would increase by several hours the time required for equilibrium to be attained.

Upon completion of the evacuation, the stopcock of the adsorption bulb was opened and the mercury reservoirs raised so as to close traps A and C. The calorimeter and adsorption bulb had come to thermal equilibrium at the end of the evacuation. The stopcock M, Fig. 2, was opened momentarily,

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[1] J. Am. Chem. Soc. 42, 946 (1920).

allowing the capillary N to become completely filled with mercury, and a small weighed cup of mercury so placed that the tip of N was immersed in it. The stopcock D, Fig. 1, was then opened to the system for a few seconds, admitting a small amount of sulfur dioxide. During a run, a moderate current of sulfur dioxide was continuously passing through the stopcock D and out of the opening F, except when it was being admitted to the adsorption bulb.

The mercury cups used to determine the heat were changed every fifteen minutes until the weight was constant (within 0.5 mg.). Attainment of equilibrium was also followed by observing the pressure of gas over the gel, measured as the difference between the mercury levels in the two arms of the trap C, and read with a cathetometer telescope. It was observed that at lower pressures equilibrium was reached in fifteen minutes or less, and that if evacuation was properly carried out, it required in no case more than half an hour to establish itself.

When equilibrium was reached, as shown by both pressure and heat measurements, the total loss in weight of the mercury cups, and the pressure were recorded. The stopcock to the bulb was then closed and pressure equalized, whereupon the bulb was removed, dried and weighed. The increase in weight, corrected for the amount of sulfur dioxide in the free space of the bulb at the pressure observed, gave the weight of the sulfur dioxide adsorbed.

The bulb was then replaced in the calorimeter and again attached to the system, which was evacuated as before, the stopcock to the bulb being kept closed during the evacuation. When evacuation was complete the mercury traps were again closed, the stopcock to the bulb opened, and a second portion of gas admitted in the same manner. For the new pressure the heat of adsorption was recorded as the sum of the two heats measured, and the amount adsorbed is also taken as the total (corrected) increase in weight of the bulb, rather than the difference between two successive weighings.

In this manner four successive portions of gas were admitted, and the equilibrium pressures, total heat, and weight of substance adsorbed recorded for each point. The final pressure was never much greater than 600 mm., since if this pressure exists in the bulb at 0°, the pressure therein becomes greater than the external pressure when the bulb is allowed to come to room temperature.

After its final weighing, the bulb was attached to the system and evacuated. In some cases it was first placed in the calorimeter and the heat of desorption measured. It was found that about 95 percent of the gas could be removed by evacuation at 0° for one hour. In any case, the evacuation was completed while heating the gel at 250°-300° for half an hour, after which the gel was ready for a second run. Several successive runs with the same sample of gel did not show any falling off in activity, the curves being practically coincident.

In the runs using water vapor, the method was, in general, the same. A bulb containing distilled water was sealed to the system at E. The water and the free space between the stopcock and the bulb containing the water were freed from air by repeated expansion into the remainder of the system, and were then kept air-free.

The time required for evacuation of the system was materially lowered by sweeping it out with water vapor by a suitable manipulation of the trap A and the stopcock D. Practically complete evacuation, except for water vapor, could be brought about in ten or fifteen minutes by this method. The stopcock to the adsorption bulb, which had been previously evacuated, was of course kept closed during this process.

A higher degree of evacuation was required for water vapor than for sulfur dioxide, in order that equilibrium might be established in the same time. The correction for water vapor in the free space of the bulb is negligible.

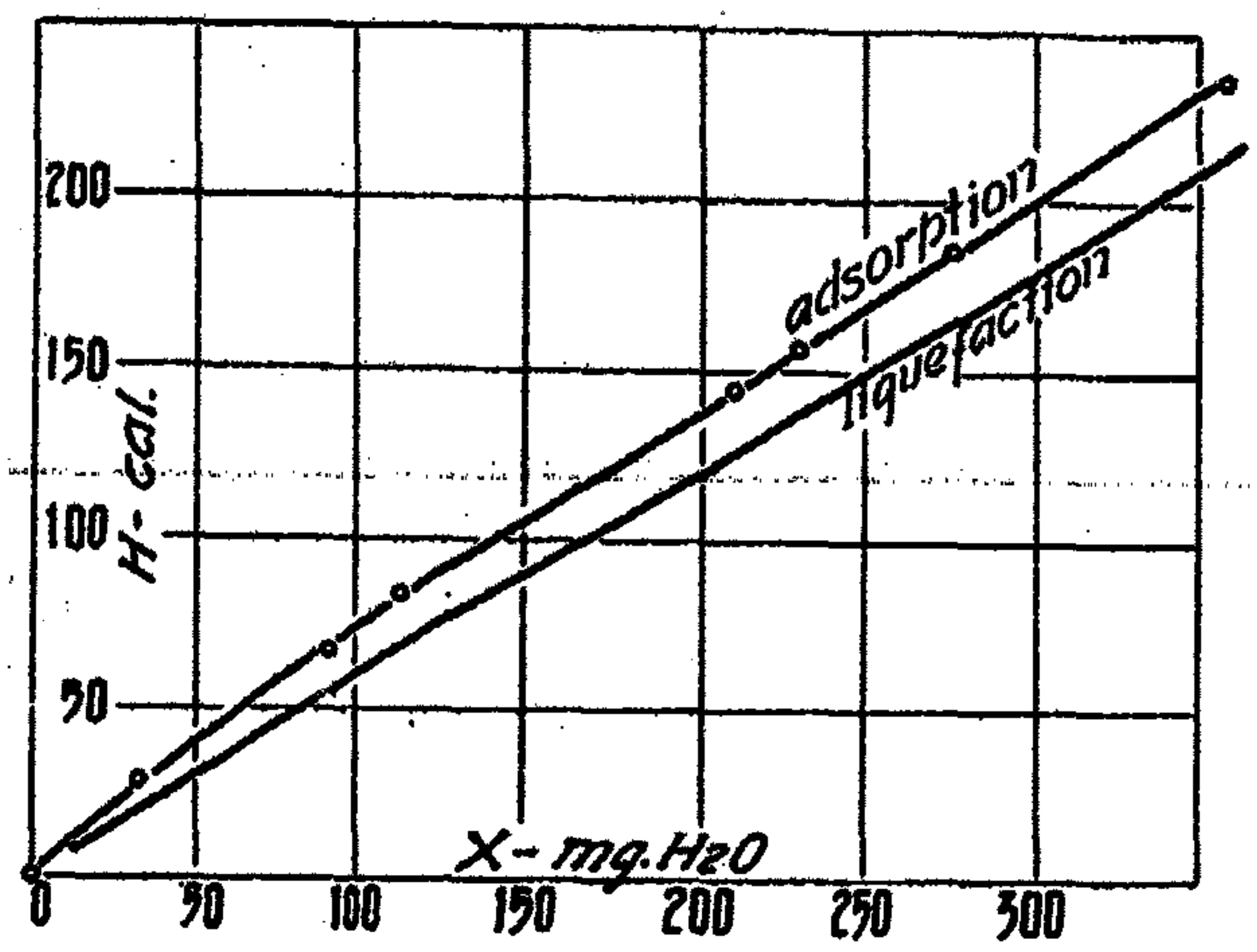

FIG. 3

Heat of Adsorption of Water Vapor at 0° C

Attempts to measure the heat of desorption were unsatisfactory, since only a small amount of water is removed from unit weight of gel on evacuation for one hour at 0°.

Discussion

The heat of adsorption of water vapor follows the upper curve of Fig. 3, which also shows the heat of liquefaction (vaporization) of water at 0°. The value of the latter is taken as 596.8 calories per gram, as measured by Dieterici[1]. The heat of adsorption is found to follow the equation $H = KX^{1/n}$ of Lamb and Coolidge, the values of K and 1/n being, respectively, 1.091 and 0.914. This is obtained from experiments 6 and 9 (Table I), which give partial heats of adsorption as well as the value at saturation. The other two runs give only the values at saturation of X and H. The mean weight of water adsorbed at saturation is 361.2 mg. per gram of gel, and the mean heat of adsorption at saturation is 236.2 calories per gram of gel. The heat of liquefaction at 0° of this weight for water is 215.6 calories, thus the net heat at saturation is 20.6 calories per gram of gel. The fact that this net heat is positive, while it

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[1] Wied. Ann. 37, 504 (1889).

does not preclude the possibility of compression of the adsorbed liquid by the forces of molecular attraction, makes it seem very improbable that this compression, if any, has any material effect on the heat of adsorption, since the compression of water at 0° would, according to the principle of LeChatelier, result in an absorption rather than an evolution of heat.

Table I

Heat of Adsorption—Water Vapor. 0°C.
Sample gel = 0.4568 gm.

Pressure (mm.)	Calories per gm. gel (H)	Milligrams adsorbed per gram gel (X)
	Run 4	
4.6	235	362
	Run 6	
0.8	66.4	90.8
1.6	143.9	210.1
3.4	184.4	276.5
4.6	233.0	359.2
	Run 9	
0.3	27.0	32.9
0.8	83.4	114.6
2.1	157.0	231.5
4.6	238.1	361.7
	Run 10	
4.6	237	362.0

The net heat may, however, be satisfactorily explained by a consideration of the changes in surface and in surface energy involved. As has been pointed out in a previous paper,[1] silica gel is assumed to have a water surface before wetting or adsorption, and the process of wetting or adsorption in the case of water simply consists in the filling of the pores of the gel, which reduces the original, very large surface to practically zero. The heat of wetting of silica gel by water as measured by Patrick and Grimm at 25° was 19.22 calories per gram of gel, while the net heat of adsorption of water vapor at 0° was shown by our measurements to be equal, at saturation, to 20.6 calories per gram of gel. The experimental error in the latter measurement is magnified considerably by the fact that the net heat, as is apparent from the curve, is less than one tenth of the total heat of adsorption as measured. It may be remarked in passing that in most of the cases observed by Lamb and Coolidge, the net heat was about one half of the total heat measured, and in our measurements of the heat of adsorption of sulfur dioxide on silica gel, shown below, the net heat also approaches this fraction of the total. That the heat of

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[1] Patrick and Grimm: J. Am. Chem. Soc. 43, 2144 (1921).

wetting at 25° should be equal to the net heat of adsorption at saturation at 0° is evident when one considers the equation

$$\frac{E}{\omega} = \sigma - T\frac{d\sigma}{dT}.$$

According to this equation, since $d\sigma/dT$ is a constant and negative in value, E, the total surface energy of the liquid, between the above temperature limits, is practically constant.

The above measurements, then, provide further justification for the statement, previously made, that heats of wetting, or net heats of adsorption, can be explained satisfactorily by a consideration of the changes in surface energy involved.

The heats of adsorption of sulfur dioxide by silica gel, tabulated in Table II, are shown graphically in Fig. 4. These heat measurements also follow approximately the equation $H = KX^{1/n}$, the values of K and $1/n$ being, respectively, 0.316 and 0.860.

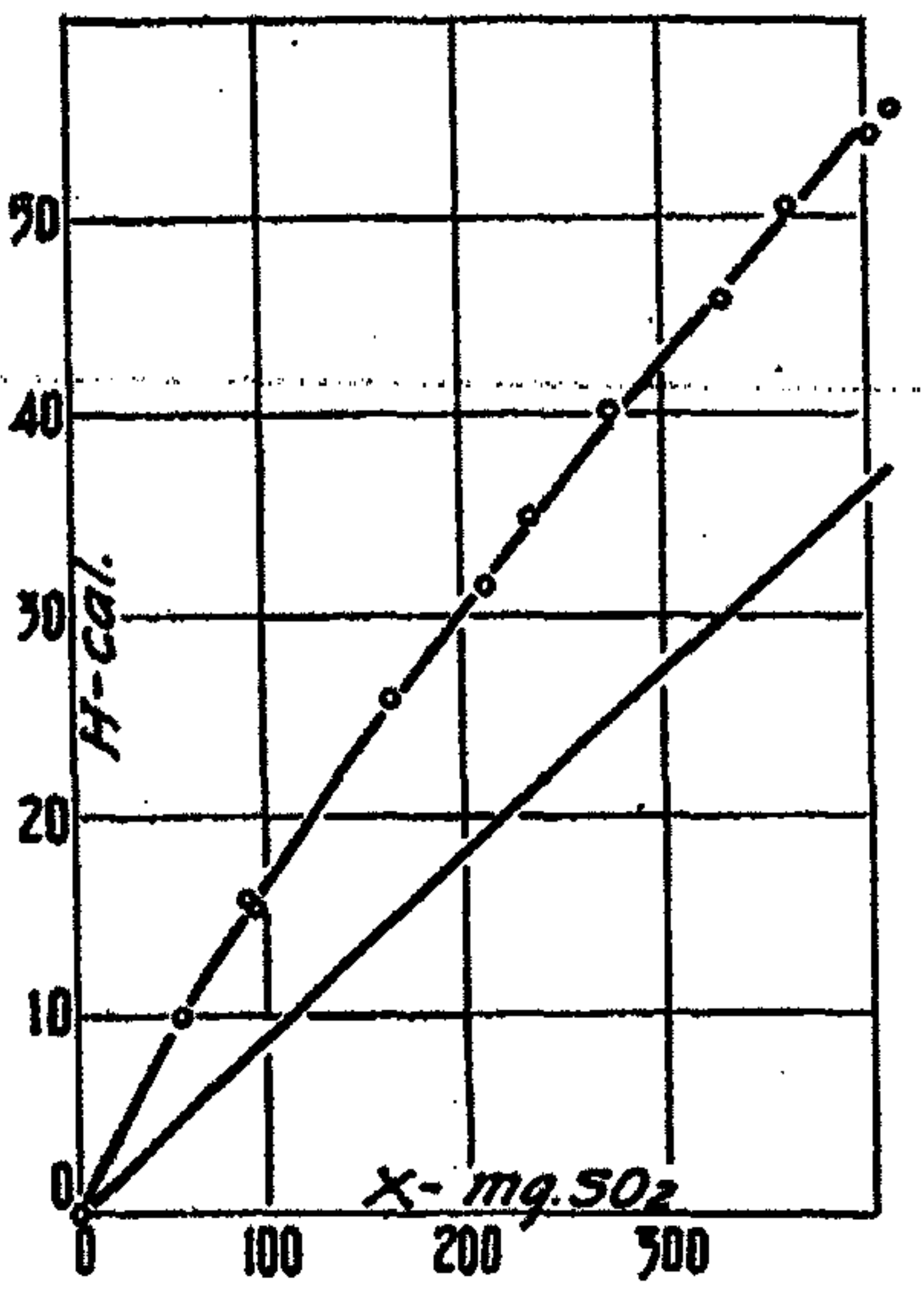

Fig. 4
Heat Adsorption of Sulfur Dioxide at 0°C

The adsorption of sulfur dioxide also follows the equation of Freundlich, $X = KP^{1/n}$, although the amount of sulfur dioxide adsorbed at any given pressure is slightly less than that observed at this temperature by Patrick and McGavack. This is undoubtedly due to slight differences in the structure of the different preparations of the gel. Inasmuch as the saturation pressure of sulfur dioxide in these experiments was in no case reached, our P – X curve (according to the Freundlich equation) was extended until P attained the saturation value at 0°. By this extrapolation, X attains the value 525 mg. per gm. gel. At saturation pressures, the volumes of all liquids held per gm. gel are, of course, equal. By substituting this value of X in the equation $H = KX^{1/n}$, one obtains a value of 69.1 calories per gm. gel for H,—which represents the heat of adsorption at saturation. Since the heat of vaporization at 0° of 525 mg. of sulfur dioxide is 47.9 cal., it follows that the net heat at saturation is 69.1 minus 47.9 or 21.2 cal. per gm.

The net heats of adsorption of sulfur dioxide were calculated also for the points measured, and it was found that they would follow approximately an equation of the form $H = KX^{1/n}$. The net heat of adsorption at saturation was extrapolated on this curve also, and a value was obtained of 21.4 calories per gram of gel, almost coincident with the value previously obtained.

TABLE II

Heat of Adsorption—Sulfur Dioxide at 0°.
Sample gel = 1.813 gm.

Pressure (mm.)	Calories per gm. gel (H)	Milligrams adsorbed per gram gel (X)
	Run 5	
11.8	15.5	94.8
78.7	31.4	213
290.0	45.8	330
577.5	54.2	405
	Run 7	
4.2	10.0	57.9
40.1	25.8	165
162.5	40.2	276
471.0	53.1	384
	Run 8	
10.7	16.0	90.8
102.5	34.8	236
388.8	50.6	360
611.2	55.8	416

Comparison Adsorption and Desorption Values (Run 5).

	Adsorption	Desorption
Cal. per gram	54.2	50.9
Mgms. per gram	405	369

The methods above used to obtain the net heat at saturation involve less chance of error than might at first be expected. The curve of the heat of adsorption, for instance, beyond the points measured, is approaching parallelism with the curve of the heat of liquefaction; so that the net heat,—the difference between these two values,—increases beyond the points measured rather slowly with increasing values of X. At the greatest measured value of X, the net heat is only 3 calories less than that calculated at saturation.

The saturation values for the net heat of adsorption of sulfur dioxide and of water vapor are thus seen to very nearly coincide,—the former exceeding the latter by less than one calorie. Since it is assumed that in the adsorption of water vapor the filling of the pores of the gel with water merely destroys the enormous water-air surface of the gel, reducing it to practically zero, it should follow in this case, that if the pores are filled with sulfur dioxide, the same water-air surface is destroyed, and the final liquid sulfur dioxide-air surface is as negligible as was the final water-air interface in the first instance. There is still the possibility, however, that the original water-air surface of the gel may now form a water-sulfur dioxide interface, with a certain positive or negative surface energy. This would be comparable to the wetting of silica gel by liquids not completely miscible with water, as observed by

Patrick and Grimm. In this case the net heat at saturation would vary from that observed in the case of water by the amount of total energy resident in this interface.

In most cases the total surface energy of an interface is positive, so that the heat of wetting of the gel by a liquid X would be less than that of pure water by the amount of energy resident in the interface water-X. However, cases have been observed in which a liquid-liquid interfacial tension has a positive temperature coefficient. In a case of this sort, although the free surface energy of the interface would of necessity be positive, it is conceivable that the total surface energy might be negative in sign, so that the heat of wetting, explained on this basis, would be greater in the case of a liquid exhibiting such a behavior with respect to water, than with water itself.

It is possible that the difference between the net heat of adsorption of water and of sulfur dioxide is to be explained upon this basis. There remains also, however, the possibility of reaction between the sulfur dioxide and the water already in the gel. It is stated in Gmelin-Kraut's "Anorganische Chemie" that water does not appreciably dissolve in liquid sulfur dioxide, except to form a hydrate. Most of the various possible hydrates of sulfur dioxide can exist at this temperature, but their heats of formation could not be obtained. It is possible, however, that the explanation of the slightly greater heat of adsorption at saturation in the case of sulfur dioxide than in the case of water is to be found in the formation of one of the various possible hydrates of sulfur dioxide by means of the water already in the gel.

Summary

1. The heats of adsorption of sulfur dioxide and of water vapor by silica gel have been measured at 0°.

2. Explanations, based upon surface energy considerations, have been advanced in both cases to account for the difference between the heat of adsorption and the heat of liquefaction; and possible causes of the difference between the net heats of adsorption of sulfur dioxide and of water have been discussed.

NEW BOOKS

Solubility. *By J. H. Hildebrand. 24 × 16 cm; pp. 206. New York: Chemical Catalog Company, 1924. Price: $3.00.* "The author has a twofold purpose, first to make available for the use of chemists confronted with practical difficulties the means so far available for their solution, and second, to present the subject as an inviting field for research." The chapters are entitled: introductory; methods of expressing solubility; the ideal solution—Raoult's law; solubility relations based upon Raoult's law; deviations from Raoult's law; Raoult's law and other properties of solutions; causes of deviations from Raoult's law; polarity; internal pressure; solvation; vapor pressures of liquid mixtures; solubilities of gases; solubilities of liquids in liquids; solubilities of non-electrolytes; solubilities of electrolytes; metallic solutions; partition of solutes between immiscible liquids; solubility and various related phenomena.

If the sole duty of a reviewer, as many people assume, is to decide whether an author has done well what he tried to do, one would say that this is a wonderfully good book. The subject is presented consistently and admirably from the author's view-point. It is only when one starts questioning the validity of the premises that one feels a bit worried.

On p. 19 is the statement that "the rôles of solvent and solute are interchangeable." This may be so; but this conception is less than forty years old and rests on the definition that the solute is the constituent which does not pass through the semipermeable membrane. Since two membranes may be imagined, one of which will stop one constituent and the other the other, it follows that either constituent may be the solute and that there is therefore no difference between solvent and solute. This is absolutely true so long as the only property assigned to the solute is the negative one of not passing through the semipermeable membrane; but it does not follow necessarily in regard to any other property.

On p. 25 the author states that "van't Hoff based his theoretical proof of his osmotic pressure law upon the assumed validity of Henry's law, so that the former rests upon a no more secure theoretical foundation than the latter." The reviewer cannot concede the accuracy of this statement. It seems probable that the author has not reread van't Hoff's paper recently.

The author means by Raoult's law the equation $(p-p')/p=n/(N+n)$ and he says, also on p. 25, that "while it is true that the laws of van't Hoff and Raoult become identical at infinite dilution, in concentrated solutions they yield very different results, and it is necessary to choose between them for the further pursuit of our topic. There are several reasons for preferring Raoult's law for our definition of the ideal solution. In the first place it rests upon a more satisfactory theoretical basis . . . A second advantage of Raoult's law is its agreement with the experimental data for a large number of solutions over the entire range of concentration, while the equation of van't Hoff not only lacks experimental confirmation at higher concentrations but actually leads to absurd figures, for, as the proportion of solvent in the solution approaches zero, the osmotic pressure actually approaches infinity, while according to the equation of van't Hoff it should never exceed a few hundred atmospheres."

The reviewer is still of the belief that the van't Hoff equation $PV=(N/n)RT\log(p/p')$ contains only the two assumptions, conceded by everybody, that the osmotic pressure is a function of the molecular weight of the solute and that the vapor of the solvent follows the gas law. Since the van't Hoff equation in this form is true for all concentrations, it is difficult to see how the Raoult law can be better since it only reduces to the van't Hoff formula for dilute solutions. The extraordinary statement that, according to van't Hoff, the osmotic pressure of a nearly pure solute cannot exceed a few hundred atmospheres must be due to the author's having fallen into the common error that the volume in the van't Hoff equation is the volume of the solution. Under these circumstances one wonders whether the calculation of activities is really worth while and especially in the case of the distribution coefficient, p. 188, when the effect of the third component in making the two solvents more miscible is ignored. The interesting thing about this is that Gibbs knew about and mentioned the solvent action of the third component; but Gibbs and his notation have apparently gone into the discard along with van't Hoff.

The reviewer supposed that it was generally admitted that liquid water was a mixture of substances having the generic formula $(H_2O)_n$; but he has not found any discussion of the way in which the solvent action of water does or might vary with a displacement of this equilibrium by the solute. For these reasons he feels that the author has builded his house upon sand and that it will fall.

Wilder D. Bancroft

SOLUBILITY RELATIONS OF ISOMERIC ORGANIC COMPOUNDS.
III. THE MUTUAL SOLUBILITY OF THE THREE DINITROBENZENES*

BY DONALD H. ANDREWS**

The measurements of mutual solubility of the three dinitrobenzenes presented in this paper were undertaken as part of the program outlined in a previous paper[1]. The results are of interest from two points of view: first in that they serve as a basis for a method of analysis of any mixture of the three isomers; second, in that these substances form essentially ideal solutions with one another.

The mode of experiment and the method of interpreting the observed time-temperature curves have been described in a previous paper[2], to which the reader is referred for details.

Materials. The *ortho*-dinitrobenzene was from Merck; the *meta*, taken from the laboratory stock, had been made in the usual way. The *para* was prepared by a method developed with the aid of Prof. A. J. Hill; a brief description of this method is appended because it proved successful whereas the procedures given in the literature did not.

Method for preparing para-dinitrobenzene: Dissolve about 30 g. *para*-nitroaniline in 45 cc. HNO_3 (sp. gr, 1.4) and diazotize with 16 g. $NaNO_2$; add this mixture to a solution of 90 g. $NaNO_2$ and 175 g. $CuSO_4$ dissolved in the least amount of H_2O. After a few hours warm on the steam bath until evolution of gas ceases. Filter off the brown earthy product. To purify from resins, etc., wash in turn with about 10 cc. alcohol, 10 cc ether and 10 cc ethyl acetate. Suspend the residue in a small amount of water and steam distill. This gives about 10 g. of a pale yellow crystalline product which is purified by recrystallization from alcohol. M. P. 173.5°C.

In each case the material was repeatedly crystallized from alcohol until its degree of purity, as indicated by the shape of its time-temperature curve, was satisfactory.

The melting points adopted, together with the standard and more recent data in the literature, follow:

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*Contribution from the Department of Chemistry of Yale University.

**From the dissertation presented by Donald H. Andrews to the Graduate School of Yale University, June, 1923, in candidacy for the degree of Doctor of Philosophy.

[1] J. Johnston: J. Phys. Chem., 29, 882 (1925).

[2] D. H. Andrews, G. T. Kohman, and J. Johnston: J. Phys. Chem., 29, 914 (1925).

ortho	*meta*	*para*	Observer
116.9	89.8*	173.5	Andrews
117.9	89.8	172	Körner[1]
——	89.8	——	Pushin[2]
——	91.0	——	Steinmetz[3]

An unstable form of the *meta*[4] has been reported, but no indications of it were observed in the present investigation.

Results. The results of the measurements in the three binary systems are brought together in Table I; each datum was derived by means of an extrapolation from at least two (and usually more than two) time-temperature curves, in which the amount of undercooling differed, as described in the previous paper.

TABLE I

Experimental data on solubility in the three binary systems of *ortho, meta* and *para* dinitrobenzene.

System *p-m*			System *p-o*			System *o-m*		
mol % *p* C_p	temp C t	solid phase	mol % *p* C_p	temp. C t	solid phase	mol % *o* C_o	temp. C t	solid phase
100.0	173.5	*p*	100.0	173.5	*p*	100.0	116.9	*o*
79.3	159.9	"	80.0	161.2	"	80.0	104.7	"
59.5	143.8	"	60.0	145.9	"	60.0	88.7	"
42.2	124.6	"	40.0	125.4	"	40.0	68.6	"
25.0	97.5	"	——	101.7	*p-o*	——	63.0	*o-m*
——	78.3	*p-m*	20.0	104.0	*o*	20.0	75.3	*m*
15.0	79.2	*m*	0.0	116.9	"	0.0	89.8	"
13.5	80.7	"						
9.2	83.9	"						
0.0	89.8	"						

When the several values of log C are plotted against the corresponding values of 1000/T(T being 273.1 + t), the resulting graph is a smooth curve which is very nearly a straight line; on a scale small enough to be reproduced here the ideal curve would appear to be a straight line and all of the experimental points would seem to lie on it. For this reason the concordance can be better shown by tabular comparison of observed and calculated values.

For an ideal solution the change of solubility with temperature is given by the equation $d \ln N_A/dT = \Delta H_A/RT^2$ (I) where N_A ($= C_A/100$) is the mol fraction in the liquid of the substance crystallizing at T, and ΔH_A is its heat of

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[1] Körner: Gazz. chim. ital. 4, 305 (1874).

[2] Pushin: J. Chem. Soc. 125, 2628 (1924).

[3] Steinmetz: Z. Kryst. 54, 467 (1915).

[4] Schaum and Schilling: Ann., 411, 161 (1916); Müller: Z. physik. Chem., 86, 177 (1913); Lehmann: Ber. 17, 1733 (1884); Z. Kryst. 6, 48 (1882); Padoa: Atti. Accad. Lincei (5) 13, 1, 329 (1904).

*Quite recently Mr. Lynn found this material, after being subjected to sixty fractional crystallizations, melts at 90.05°; but the value 89.8° is retained throughout the present paper since the work was done with material which melted at that temperature.

melting at that temperature. Now if we can represent the results of calorimetric experiments by the empirical expression

$$\Delta H_A = \alpha + \beta T + \gamma T^2 \qquad \text{(II)}$$

we can integrate equation I between T and T_A, the melting temperature of pure A (i.e. $N_A = 1$) and get

$$R \ln N_A = -\alpha(1/T - 1/T_A) + \beta \ln T/T_A + \gamma(T - T_A) \qquad \text{(III)}$$

When the values of ΔH are expressed in calories, this may be written

$$\log N_A = -{}^{\alpha}/4.579\,(1/T - 1/T_A) - (\beta \log T_A/T)/1.988 - \gamma\,(T_A - T)\,/4.579 \qquad \text{(IV)}$$

or

$$\log N_A = K_1\,(1/T - 1/T_A) + K_2 \log T_A/T + K_3(T_A - T) \qquad \text{(IVa)}$$

Direct calorimetric determinations[1] of the difference in heat content of the dinitrobenzenes at t° (solid or liquid, as t is below or above the melting temperature) and the solid at 22°C. are reproduced by the empirical formula $H_t - H_{22} = a + bt + ct^2$, the several values of a, b, and c being as follows:

	Solid at t			Liquid at t		
	a	b	c	a	b	c
ortho	−893.2	37.91	0.122	3031	63.66	—
meta	−927.3	40.85	0.059	1234	67.35	0.004
para	−904.5	39.73	0.063	1888	72.69	—

From these formulae we find by subtraction,[2] in terms of t (temperature centigrade) for *ortho* $\Delta H_o = 3924 + 25.75\,t - 0.122\,t^2$

meta $\Delta H_m = 2161 + 26.50\,t - 0.055\,t^2$

para $\Delta H_p = 2793 + 32.96\,t - 0.063\,t^2$

whence the several coefficients in equation IVa (in terms of T) are:

	Melting Temperature T_A	K_1	K_2	K_3
ortho	389.9	2668.8	−46.540	0.02671
meta	362.8	2003.3	−28.433	0.01201
para	446.5	2380.6	−33.880	0.01376

With these coefficients and data, values of log N were calculated by means of equation IVa for a series of temperatures; and the results, in terms of log C and C(= 100 N) are presented in Table II.

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[1] These measurements, by Messrs. Andrews and Lynn, will be described in a paper now in course of preparation. The accuracy of the data in a sense does not justify the use of all the places given in a, b, c, below, the uncertainty in Δ H seeming to be of the order to 50-100 calories; but these figures have been retained for purposes of computation to insure consistency.

[2] This of course involves the tacit assumption that the heat content of the liquid, at temperatures below the freezing temperature of the pure substance, is given by the formula above.

TABLE II

Values of log C and of C(= 100 N), along the ideal solubility curve of each of the three dinitrobenzenes as calculated (by equation IVa) from its heat of melting and melting temperature.

t°	1000/T	log C for *o*	log C for *m*	log C for *p*	C for *o*	C for *m*	C for *p*
173.5	2.239			2.00			100.0
160	2.309			1.900			79.5
140	2.421			1.746			55.7
120	2.544			1.584			38.4
116.9	2.564	2.00			100.0		
110	2.610	1.947		1.501	88.5		31.7
100.1	2.679	1.868		1.418	73.8		26.2
100	2.680	1.866		1.416	73.5		26.1
90	2.754	1.781		1.328	60.4		21.3
89.8	2.756		2.00			100.0	
80	2.832	1.691	1.933	1.241	49.1	85.7	17.4
77.8	2.850		1.920	1.225		83.2	16.8
70	2.915	1.598	1.863	1.152	39.6	73.0	14.3
62.8	2.977	1.535	1.818		34.3	65.7	
60	3.002	1.501	1.793	1.063	31.7	62.1	11.6
57.0	3.029	1.473	1.773	1.041	29.7	59.3	11.0

The table also includes the several eutectic temperatures and compositions derived from these curves. For, if C_p is the mol percent of *para* in the solution in equilibrium with solid *para* at each temperature, and likewise C_o with respect to *ortho*, then at the eutectic the solution is saturated with both, and therefore $C_o + C_p = 100$ in the binary system. Thus by plotting the ideal data for each isomer on a large scale, we can by trial find the eutectic temperature, which is that value of 1000/T at which the sum of the antilogarithms of log C_p and log C_o is 100. Similarly with the other two binary eutectics and also with the ternary, the condition for this case being $C_o + C_m + C_p = 100$. Comparing these ideal values, (in Table II) with those observed (in Table I) we find differences of only 1.6°, 0.5°, 0.2° and for the ternary 1°, the observed value being 58.1°. This constitutes an excellent test of the near approach to ideality of these solutions, of the accuracy of the experimental work involved and of the validity of the method of interpreting the time-temperature curves. The agreement is shown in another way in Table III in which, for a series of values of C, values of t, derived from 1000/T as interpolated from the ideal curve, are compared with those similarly interpolated from the experimental curve. The agreement is all that could be desired, except possibly in the $p-o$ system; this may be due to a lack of ideality or—more probably, we believe—to some slight impurity in the *ortho* used in the solubility measurements.

TABLE III

Comparison of ideal with observed values of t, for a series of values of the composition of the solution in terms of the mol percentage C of the substance crystallizing, for each of the three dinitrobenzenes.

C	*Ortho*			*Meta*			*Para*		
		observed in system			observed in system			observed in system	
	ideal	*o-m*	*o-p*	ideal	*m-o*	*m-p*	ideal	*p-m*	*p-o*
100	116.9			89.8			173.5		
90	110.0	111.0	110.6	83.2	83.2	83.2	167.1	167.1	167.7
80	104.5	104.8	104.0	75.5	75.5		160.4	160.4	161.2
70	97.2	97.2		67.6	67.6		152.3	152.3	154.5
60	89.6	88.7					144.3	144.3	146.1
50	80.7	79.5					134.3	134.3	136.6
40	70.4	68.7					122.1	122.0	125.2
30							107.1	107.0	111.7
20							87.1	87.5	93.7

It appears therefore as if the dinitrobenzenes form ideal solutions, in ternary as well as in binary systems. On this basis the data in Table II—or alternatively, interpolated values from the experimental results—enable one to plot the isothermal lines in, and so to construct, the complete ternary diagram. This matter will be discussed in a later paper, so that I shall merely point out that from the graphs of log C against 1000/T the eutectic valleys (loci of secondary freezing points) are easily located. Thus for instance at 70°, in the valley between the *meta* and *para* surface, the solution contains 73.0% *meta* and 14.3% *para*, since it is saturated with respect to both; therefore it contains 100−87.3 or 12.7% *ortho*. Likewise at 70° in the *o-p* valley, the solution contains 100−39.6−14.3 or 46.1% *meta*. Observations were made with a couple of ternary mixtures, and it was found that the secondary freezing temperature differed by only 0.1° from that predicted. Such a diagram can therefore be used with confidence as a criterion for the analysis of mixtures of the three pure isomers, provided that the methods followed are the same as those involved in the construction of the diagram.

A table is appended in which have been brought together the data in the literature dealing with the solubility of the dinitrobenzenes in various solvents. In some cases the melting temperature did not agree with the author's value, a difference which might be due either to impurity or to temperature error. An impurity with a molecular weight not differing much from that of dinitrobenzene would not alter the shape or the slope of the graph of log C against 1000/T, but would merely shift its position; and a constant thermometric error would have the same effect. Consequently, in order to secure a common basis of comparison, the graph was in such cases shifted parallel to itself until it passed through the melting point as given in Table I, and the values were then read from it. It is evident that the solubility, when expressed in terms of mol fraction (instead of the arbitrary grams per gram solvent), is much the same for the various solvents, and in some of them is quite close to the ideal solubility; consequently to a first approximation—which for many practical purposes would be sufficiently exact—the ideal solubility curve could be taken as a measure of the solubility of these substances in solvents not too dissimilar from themselves.

TABLE IV

Solubility of the dinitrobenzenes in various solvents. Values of C (mol percentage of solute) for regular values of 1000/T.

(*a*) *ortho*

1000/T	2.60	2.65	2.70	2.75	2.80	2.85	2.90	2.95
t	111.5	104.3	97.3	90.5	84.0	77.8	71.7	65.9
Solvent								
Ideal	91.2	79.7	69.8	61.2	53.6	47.0	41.2	36.3
aniline[8]	91.0	80.0	70.6	62.2	54.8	48.4	42.8	37.8
fluorene[7]	91.0	79.4	69.2	61.0				
naphthalene[8]	91.0	79.3	68.9	59.8	51.9	45.1	39.3	34.0
phenanthrene[2]	89.7	76.9	66.1	56.4	47.9	41.0		
p-toluidine[1]	93.8	85.9	78.5	71.8	65.5	60.0	54.6	49.9
benzene[2]			58.6	49.1	41.8			

(*b*) *meta*

1000/T	2.80	2.85	2.90	2.95	3.00	3.05
t	84.0	77.8	71.7	65.9	60.2	54.8
Solvent						
Ideal	91.6	83.0	75.3	68.5	62.5	57.2
benzene[8]	91.6	83.2	75.4	68.9	59.6	49.9
m-nitroaniline[4]	91.6	83.2	75.4	68.1	61.7	56.0
1.2.4 dinitrotoluene[5]	91.6	83.2	75.4	68.4	62.4	56.8
bromobenzene[8]	91.4	82.6	74.6	67.5	61.0	55.1
fluorene[7]	91.2	82.4	74.1	65.3	57.6	
p-toluidine[1]	94.6	89.2	83.6	78.5	74.1	70.2
phenanthrene[2]	88.5	80.2	73.0	66.8	61.8	57.0
acetanilide[4]	86.5	75.5	65.8			
*trinitrotoluene[5]	87.9	76.4	68.1	61.8	56.5	52.4
*aniline[6]	90.2	80.9	73.5	67.1	61.8	56.9
p-nitrotoluene[5]	93.3	86.0	79.3	73.0	67.3	61.8
*naphthalene[6]	91.0	84.5	79.1	74.6	71.1	67.9
chloroform[8]					56.1	49.7

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[1] Kremann and Petritschek: Monatshefte, 38, 385 (1917).
[2] Kremann: Ibid, 29, 863 (1903).
[3] Schröder: Z. physik. Chem. 11, 458 (1893).
[4] Crompton and Whitely: J. Chem. Soc. 67, 327 (1895).
[5] Guia: Gazz. chim. ital. 45, 557 (1915).
[6] Kremann: Monatshefte, 25, 1282, 1296 (1904).
[7] Kremann: Wien. Akad. 120, IIb, 329 (1911).
[8] Kremann and Rodinis: Monatshefte, 27, 125 (1906).
*There is evidence of compound formation in these systems.

(*c*) *para*

1000/T	2.30	2.35	2.40	2.45	2.50	2.55	2.60	2.65	2.70
t	161.7	152.4	143.6	135.1	126.9	119.1	111.5	104.3	97.3
Solvent									
Ideal	81.7	69.5	59.4	50.9	43.7	37.8	32.7	28.4	24.7
fluorene[7]	83.0	70.8	61.0	52.8	46.3	40.9	36.6	33.7	30.8
aniline[8]	83.2	71.5	61.7	53.7	47.4	42.6	38.9	35.9	32.1
p-toluidine[5]	89.5	80.7	72.9	65.5	58.6	52.5	47.5	43.1	39.4
*naphthalene[8]	85.3	74.6	65.3	57.1	49.9	43.6			
*phenanthrene[2]	80.5	71.0	62.4	55.6	50.0	45.3	41.7	38.5	35.6

(*d*) Solubility in some more volatile solvents, as given by the several authors.

Solvent	Temperature °C		Mol percentage of solute	
		ortho	*meta*	*para*
Ideal	20.0	12.0	32.8	5.09
	10.0	9.21	28.1	4.17
MeOH[9]	20.5	0.62	1.27	0.13
EtOH[9]	20.5	0.53	0.95	0.11
C_3H_7OH[9]	20.0	0.39	0.85	0.11
CS_2[9]	17.6	0.11	0.61	0.06
$CHCl_3$[9]	17.6	16.1	18.7	1.27
C_6H_6[9]	18.2	2.56	15.49	1.18
$C_6H_5CH_3$[9]	16.5	1.95	15.6	1.27
CCl_4[9]	16.5	0.13	1.07	0.11
H_2O[9]	room temperature	0.0015	0.0056	0.00085
EtOAc[9]	18.2	6.33	26.8	1.83
” [10]	30.0		17.72	
” [10]	20.0		14.29	
” [10]	10.0		11.52	

Summary

Complete data on the mutual solubility of the dinitrobenzenes, as derived from observations of freezing temperature, are presented and compared with results calculated from calorimetric data by means of the law of ideal solution. It appears that these solutions differ very slightly, if at all, from the ideal; this implies that the crystals of each isomer from mixtures with the other two are pure, and that the mixing of the liquids is not attended by an appreciable change in heat content or volume.

Data on the solubility of each isomer in several solvents, interpolated from the observations of various authors, are also tabulated for convenience of reference; they prove in general to depart comparatively little from the ideal curve, which could therefore be used as a criterion of the general accuracy of such determinations.

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[9] Lobry de Bruyn: Rec. Trav. chim. 13, 101 (1894).

[10] Cohen and Moesveld: Verslag Akad. Wetens. (Amsterdam) 26, 134 (1918).

SOLUBILITY RELATIONS OF ISOMERIC ORGANIC COMPOUNDS.
IV. THE MUTUAL SOLUBILITY OF *O, M, P* NITROANILINES AND OF *O, M, P* NITRO-CHLOROBENZENES*

BY G. T. KOHMAN**

The measurements of mutual solubility of the three nitroanilines and of the three nitro-chlorobenzenes presented in this paper were also undertaken as part of the general program outlined in previous papers of this series. In these systems again the isomers form ideal solutions with one another, a finding which leads one to believe that a large number of systems of this type will likewise behave ideally; in so far as this is so, the systems can be completely investigated with much less work than would otherwise be required.

The Nitroanilines

Although previous work on this system is reported in the literature[1], it seemed desirable to do it again in order to be sure as to whether the solutions are substantially ideal or not. For the previous measurements diverge from the ideal curve at the lower concentrations of solute, this being the region where a misinterpretation of the time-temperature curve leads to the greatest inaccuracy in the solubility curve.

The substances were crystallized repeatedly from alcohol and from water; the *ortho* compound was also sublimed. In each case time-temperature curves on the material used showed less than 0.02° lowering while half of the sample froze. For this reason it is believed that the melting temperature of each isomer is more reliable than the values recorded in the literature, which are as follows:

ortho	*meta*	*para*	Observer
68	111	147.5	Kremann and Rodinis[2]
71.1	112	146.8	Bogojavlensky et al[3].
—	113.5	146.2	Sudborough and Beard[4]
68.9	111.8	148	Valeton[1]
71	114	147	Kremann[1]
69.5	112.4	148.3	Holleman et al[1].
71.5	114	147.5	Swarts[5]
69.3	111.8	147.5	Kohman

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*Contribution from the Department of Chemistry of Yale University.

**From the dissertation presented by Girard T. Kohman to the Graduate School of Yale University, June, 1923, in candidacy for the Degree of Doctor of Philosophy.

[1] Valeton: Verslag Akad. Amsterdam, 18, 755 (1910); Kremann: Monatshefte, 31, 855 (1910): Holleman, Hartogs and van der Linden: Ber. 44, 704 (1911).

[2] Kremann and Rodinis: Monatshefte, 27, 149 (1906).

[3] Bogojavlensky, Bogoliubov and Vinogradov: through C. A. 1, 2875 (1907).

[4] Sudborough and Beard: J. Chem. Soc., 97, 784 (1910).

[5] Swarts: Rec. Trav. chim. 33, 281 (1914).

The results of the measurements are brought together in Table I; each datum again was derived by means of an extrapolation to zero undercooling from at least two (and usually more than two) time-temperature curves, in which the amount of undercooling differed. It may be mentioned that the melting behavior of *o*-nitroaniline in binary mixture gave indications of the existence of an unstable form of this isomer; though there is no record that this form has been observed hitherto.

TABLE I

Experimental data on solubility in the three binary systems of *ortho*, *meta* and *para* nitroaniline, and in the ternary system.

System *o-m*			System *o-p*			System *m-p*		
mol % *o* C_o	temp. C t	solid phase	mol % *o* C_o	temp. C t	solid phase	mol % *m* C_m	temp. C t	solid phase
100.0	69.3	*o*	100.0	69.3	*o*	100.0	111.8	*m*
84.2	57.0	"	86.6	60.7	"	80.1	101.7	"
—	50.6	*o*−*m*	—	55.9	*o*−*p*	—	89.1	*m*−*p*
67.4	60.0	*m*	76.2	64.5	*p*	50.4	102.1	*p*
49.9	79.3	"	53.3	99.3	"	21.8	130.8	"
20.4	101.0	"	21.7	132.4	"	19.9	131.6	"
0.0	111.8	"	0.0	147.5	"	0.0	147.5	"

System *o-m-p*

mol per cent			temp. C	
C_o	C_m	C_p	t	solid phases
71.5	12.2	16.3	47.1	*o*−*p*
75.8	5.9	18.3	52.4	*o*−*p*
36.8	37.8	25.4	67.0	*m*−*p*
9.9	55.0	35.1	83.7	"
4.6	58.2	37.2	87.0	"

In this case again the points lie so close to the ideal curve that the divergence could not be shown on any curve which would be of a reasonable size for publication.

Direct calorimetric determinations[1] of the difference in heat content of the nitroanilines at t° (solid or liquid) and the solid at 22° are reproduced by the empirical formula $H_t - H_{22} = a + bt + ct^2$, the several values of a, b, and c being:

	Solid at t			Liquid at t		
	a	b	c	a	b	c
ortho	−530	18.00	0.277	1782	54.67	0.0379
meta	−657	26.03	0.175	5526	26.36	0.1241
para	−810	35.00	0.084	2667	50.52	0.0532

Thus the heat of melting, in terms of t (temperature centigrade) is for

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[1] By Messrs. Andrews and Lynn, to be published shortly; *cf.* previous paper.

$$\begin{aligned} &\textit{ortho} \quad \Delta H_o = 2312 + 36.67\,t - 0.2391\,t^2 \\ &\textit{meta} \quad \Delta H_m = 6183 + 0.33\,t - 0.0509\,t^2 \\ &\textit{para} \quad \Delta H_p = 3477 + 15.52\,t - 0.0308\,t^2 \end{aligned}$$

Hence the several coefficients in the equation[1]

$$\log N = K_1(1/T - 1/T_A) + K_2 \log T_A/T + K_3(T_A - T) \qquad \text{(IVa)}$$

are:

	Melting temperature T_A	K_1	K_2	K_3
ortho	342.3	5573.4	−84.108	0.05222
meta	384.8	−502.3	−14.144	0.01112
para	420.5	−667.2	−16.261	0.00673

From the equation, with these coefficients, a series of values of log N were calculated; the results in terms of log C and C (= 100 N, where N is mol fraction) are presented in Table II.

TABLE II

Values of log C and of C(= 100N), along the ideal solubility curve of each of the three nitroanilines, as calculated (by equation IVa) from its heat of melting and melting temperature.

t°	1000/T	log C for *o*	log C for *m*	log C for *p*	C for *o*	C for *m*	C for *p*
147.5	2.377			2.00			100.0
140	2.421			1.952			89.5
120	2.544			1.818			65.8
111.8	2.598		2.00			100.0	
110	2.610			1.748			56.0
100	2.680		1.898	1.675		79.1	47.3
90	2.754		1.806	1.600		64.0	39.8
88.0	2.769		1.789	1.586		61.5	38.5
80	2.832		1.706	1.522		50.8	33.3
70	2.915		1.599	1.441		39.7	27.6
69.3	2.921	2.00			100.0		
60	3.002	1.934	1.484	1.358	85.9	30.5	22.8
55.2	3.046	1.899		1.316	79.3		20.7
52.2	3.074	1.878	1.390		75.5	24.5	
50	3.096	1.860	1.362	1.270	72.5	23.0	18.6
43.5	3.159	1.810	1.280	1.212	64.6	19.1	16.3

The foregoing table also includes the several eutectic temperatures and concentrations derived from the ideal curves by finding by trial the temperatures at which the sum of the antilogarithms of log C is 100. The comparison of the eutectic temperature calculated entirely from thermal data with those observed follows:

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[1] For the development of this equation, etc., see previous paper.

m—p	*o—p*	*o—m*	*o—m—p*	
88.0	55.2	52.2	43.5	ideal
89.1	55.9	50.6	43.4	observed Kohman
89.7	55.6	51.1	43.5	" Valeton[1]
86	52	47	—	" Kremann[2]
89.9	52.2	56.6	—	" Holleman, etc.[3]

The agreement between the ideal and the observed curve, derived from Table I, is evident from Table III which contains values graphically interpolated from each for a series of values of C; the divergences are unimportant until C is less than 40%. It may be noted however that for the *meta* the divergences are regular and indicate that there may be some error in the calorimetric measurements, especially since the form of the ideal curve in this case differs slightly from that in all other cases investigated. The data of earlier authors agree with those of Table III within about 1° at the higher concentrations, but at the lower concentrations their temperatures are frequently as much as 3° too low.

TABLE III

Comparison of ideal with observed values of t, for a series of values of the composition of the solution in terms of the mol percentage C of the substance crystallizing, for each of the three nitroanilines.

C	*ortho*		*meta*		*para*	
	ideal	obs.	ideal	obs.	ideal	obs.
100	69.3		111.8		147.5	
90	62.8	62.8	106.3	106.6	140.5	140.5
80	55.6	55.6	100.5	101.2	132.8	132.8
70	48.1	48.1	94.1	94.9	124.0	124.0
60			87.1	87.7	114.2	114.2
50			79.2	79.2	103.2	103.2
40			70.1	69.2	90.2	90.2
30			59.4	56.8	74.4	75.4
20			45.2	40.6	53.4	56.7

A number of observations were also made of primary and secondary freezing temperatures in the tenary system; and the results are in harmony with the ternary diagram deduced from the data of table II, which therefore can be used as the basis of a method of analyzing mixtures of the three pure isomers.

The available data on the solubility of the nitroanilines in other solvents will be discussed, together with several series of new measurements, in a later paper.

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[1] Valeton: Verslag Akad. Amsterdam, **18**, 755 (1910).

[2] Kremann: Monatshefte, **31**, 855 (1910).

[3] Holleman, Hartogs and van der Linden: Ber. **44**, 704 (1911).

The Chloronitrobenzenes

The *ortho* and *para* isomers were recrystallized from 95% alcohol and carried through a series of fractional crystallizations; the samples so obtained still showed some impurity, as indicated by the time-temperature curve; this was eliminated by further recrystallization from a fraction of ligroin boiling at 50-51°.

The *meta* isomer could not be bought, and so a method was developed, with the aid of Prof. A. J. Hill, which gives a yield of 80-90%, considerably better than was found in trying any of the methods heretofore described. The method is as follows:

Dissolve 50 g. *meta*-nitroaniline in 75 g. hydrochloric acid (sp. gr. 1.19) and dilute with 225 g. water. Cool the solution to 0° C and add slowly, with vigorous stirring, a solution of 25 g. sodium nitrite in 70 g. water, keeping the solution of nitroaniline at 0°. Add the diazotized solution slowly to a boiling solution of 20 g. cuprous chloride in 150 g. water and 25 g. concentrated hydrochloric acid, keeping the diazotized solution as near zero as possible. The cuprous chloride solution is contained in a flask connected to a reflux condenser and dropping funnel. As the diazotized material hits the cuprous chloride solution it loses nitrogen and changes to an oil. The chloronitrobenzene can be isolated by steam distillation in a very pure state. It comes from the condenser as an oil in an unstable form but if the oil is chilled or inoculated it solidifies to a white solid.

The cuprous chloride must be freshly prepared and this is done conveniently as follows: Heat 25 parts of copper sulfate, 12 parts of sodium chloride and 50 parts of water in a flask connected to a reflux condenser until the reaction is completed as indicated by the precipitation of sodium sulfate. Then add 100 parts concentrated hydrochloric acid, 15 parts copper borings and boil the solution until it becomes colorless. Now add enough concentrated hydrochloric acid to make the whole up to 210 parts by weight. About 20 g. of cuprous chloride are obtained by pouring the solution into cold water and filtering.

The purity of the samples was controlled through the form of the time-temperature curve; the melting temperatures, so derived, are compared with the more recent recorded values in the subjoined table:

ortho	*meta*	*para*	Observer
32.1	—	82.1	Holleman[1]
31.5	43.7	82.3	Bogojavlensky et al[2].
32	43	82.5	Kremann[3]
32.5	44.4	83	Jona[4]
32.0	—	83.5	Cauwood and Turner[5]
32.0	43.4	82.5	Kohman

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[1] Holleman: Rec. Trav. chim. 19, 191 (1900).

[2] Bogojavlensky, Bogoliubov and Vinogradov; through C. A., 1, 2875 (1907).

[3] Kremann: Monatshefte, 28, 7 (1907).

[4] Jona: Gazz. chim. ital. 39 II, 289 (1909).

[5] Cauwood and Turner: J. Chem. Soc., 107, 276 (1915).

The *meta* isomer appears also in an unstable form, stated to melt at 23.7°, which tends to come out if the melt is cooled rapidly, but readily goes over into the stable form[1]. This form gave no trouble in the binary $m-o$ system or in the ternary mixtures investigated, but did cause difficulties along the *meta* branch of the $m-p$ system. For instance, the temperature rise after the cooled melt was inoculated was very slow, even with 1° undercooling; and the maximum temperature reached was higher when the melt had been undercooled 2-3° than with 1° undercooling. This behavior which, for lack of time, was not studied further, suggests that the unstable form resembles the *para* isomer in crystal structure and that these two can appear as mix-crystals.

The experimental data in the binary systems are brought together in Table IV; each datum is the result of from three to five cooling curves upon the same mixture, and the uncertainty in the extrapolation to zero undercooling is not greater than 0.2°, except along the *meta* branch of the $m-p$ system. The observations, made in the same way, of the primary freezing temperatures in ternary mixtures, are given in Table V.

TABLE IV

Experimental data on solubility in the three binary systems of *ortho*, *meta*, and *para* chloronitrobenzene.

System $o-m$			System $o-p$[2]			System $m-p$		
mol % o C_o	temp. C t	solid phase	mol % o C_o	temp. C t	solid phase	mol % m C_m	temp. C t	solid phase
100.0	32.0	*o*	100.0	32.0	*o*	100.0	43.4	*m*
89.8	26.5	"	91.9	27.5	"	87.3	35.6	"
87.7	25.8	"	86.0	24.2	"	76.9	29.3	"
79.7	21.1	"	85.3	24.0	"	70.7	26.5	"
78.9	20.5	"	78.9	20.3	"	67.4	23.9	"
70.0	15.4	"	76.9	19.5	"	—	21.1	$m-p$
59.7	8.5	"	71.3	16.1	"	58.6	26.8	*p*
—	7.8	$o-m$	70.0	14.9	"	48.0	40.1	"
50.1	13.3	*m*	—	13.4	$o-p$	39.7	49.6	"
40.0	20.8	"	65.2	15.5	*p*	30.2	59.0	"
28.8	28.1	"	62.8	19.4	"	20.5	67.1	"
24.8	30.8	"	62.4	19.8	"	11.4	74.3	"
0.0	43.4	"	50.3	37.3	"	0.0	82.5	"
			50.1	37.6	"			
			40.5	48.1	"			
			35.0	53.2	"			
			28.2	59.4	"			
			20.0	67.7	"			
			10.0	75.3	"			
			0.0	82.5	"			

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[1] Laubenheimer: Ber. 9, 766 (1876); Schenck: Z. physik. Chem., 33, 445 (1900).

[2] Holleman (Rec. Trav. chim. 19, 191 (1900)) had previously investigated this system; his temperatures are slightly higher—but by no more than 1°—than those given here.

TABLE V

Experimental data on solubility in the ternary system $o-m-p-$chloronitrobenzene.

Ortho surface			*Meta* surface			*Para* surface		
mol % o C_o	mol % p C_p	temp. t	mol % m C_m	mol % p C_p	temp. t	mol % p C_p	mol % o C_o	temp. t
100.0	0.0	32.0	100.0	0.0	43.4	100.0	0.0	82.5
87.7	4.2	25.6	80.0	6.1	33.4	85.0	5.8	71.8
82.9	6.3	23.0	70.0	9.0	27.5	70.2	14.4	58.8
71.3	10.0	15.6	66.0	30.1	25.0	59.5	19.6	48.8
61.5	13.3	9.6	60.0	3.1	20.7	47.4	25.1	34.4
54.2	15.8	3.9	55.0	14.0	16.9	40.1	11.9	24.4
						40.1	28.9	24.2

In this case the calorimetric measurements requisite to the calculation of the ideal curve have not been made; but it is evident nevertheless that the actual curves are substantially ideal. For if, as before, we plot log C_A, as observed either in the binary or ternary systems, (where C_A is the mol percentage in the solution of the substance A which crystallizes) against $1/T$, we find that all the points for any one solid phase fall on a single curve; and that these three curves are very nearly straight lines and altogether similar to those for the two systems already discussed. The distances of individual points from the curve are—apart from the *meta* branch of the $m-p$ system, where it goes up to 1.5°—too small to be apparent on a diagram of publishable size. By seeking on the curves those values of $1/T$ at which the sum of the antilogarithms of log C is 100, we derive the following values of eutectic composition and temperature and compare with the observed values of the latter:

System	composition mol per cent	eutectic temperature calc.	obs.	diff.
$o-m$	57.5 *ortho*	6.7	7.8	1.1
$o-p$	66.6 "	13.1	13.4	0.3
$m-p$	61.2 *meta*	21.7	21.1	−0.6
$o-m-p$	47.2 o, 34.2 m	− 5.0	− 3.4	1.6

It is clear therefore that the solutions in this system also may be regarded as ideal. On this basis the heat of melting of each isomer, was calculated from the initial slope of the curve; the values are compared below with those observed or calculated by others.

Heat of fusion of the chloronitrobenzenes.

ortho		*meta*		*para*		Author
obs.	calc.	obs.	calc.	obs.	calc.	
		4610		3360		Bruner[1]
					3670	Bruni[2]
		5100				Bogojavlensky et al[3].
	3870		5180			Jona[4]
	3780		4280		3580	Kohman

A table is appended which brings together the solubility of each isomer in a few solvents, as interpolated from a log C vs. 1/T plot, for regular values of 1/T, based on data in the literature. Each of these again was adjusted, by being moved parallel to itself, so that its end-point is the melting temperature of the solute here adopted;[5] and in these cases again it is clear that the several solubility curves, when the solubility is expressed in mol percentage, are very similar.

TABLE VI

Solubility of the chloronitrobenzenes in various solvents. Values of C (mol percentage of solute) for regular values of 1000/T.

(a) *ortho*

1000/T	3.30	3.35	3.40	3.45	3.50	3.55	3.60
t	29.9	25.4	21.0	16.8	12.6	8.6	4.7
Solvent							
m or *p* chloronitrobenzene	96.4	87.5	79.4	72.4	66.1	60.3	55.1
aniline[3]	96.4	85.5	76.6	68.4	61.1	54.8	49.0
benzene[2]	95.1	83.8	74.0	65.3	57.5	50.6	44.4

(b) *meta*

1000/T	3.20	3.25	3.30	3.35	3.40	3.45	3.50	3.60	3.70
t	39.4	34.6	29.9	25.4	21.0	16.8	12.6	4.7	2.8
o-chloronitrobenzene	91.6	82.2	74.1	66.8	60.3	54.3	49.2	40.4	
napthalene[1]	90.6	80.9	73.8	67.6	63.1				
benzene[2]	91.0	78.9	68.7	59.4	51.3	44.1	37.8	27.8	20.8
aniline[1]	88.5	77.6	67.9	59.7	52.0	45.4	39.7	29.7	20.9

(*Table VI continued on page 1056*)

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[1] Bruner: Ber., 27, 2102 (1894).

[2] Bruni: Gazz. chim. ital., 34, II, 350 (1904).

[3] Bogojavelnsky, Bogoliubov and Vinogradov: Z. physik. Chem. 64, 251 (1908).

[4] Jona: Gazz. chim. ital. 39 II, 284 (1909).

[5] *Cf.* preceding paper.

(c) *para*

1000/T	2.9	3.0	3.1	3.2	3.3	3.4	3.5
t	71.7	60.2	49.5	39.4	29.9	21.0	12.6
o-chloronitrobenzene	85.1	71.6	60.5	51.6	44.4	38.3	33.1
napthalene[1]	82.2	66.4	54.7	47.8			
benzene[2]	83.4	67.6	54.8	44.5	36.1	29.1	23.9
aniline[1]	80.7	65.3	53.6	44.4	37.2	31.9	27.9

Summary

This paper presents complete data on the mutual solubility of the three nitroanilines, likewise of the nitrochlorobenzenes. The results for the former, compared with the ideal as calculated from calorimetric data, show that these solutions are very nearly, if not quite, ideal; and the same is doubtless true for the nitrochlorobenzenes, for which calorimetric data are not available. This indicates that a large number of systems made up of the *ortho*, *meta* and *para* isomers of a substance will prove to be ideal; hence that the complete solubility diagram requisite for the analysis of such isomeric mixtures, is determinable from a small number of observations.

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[1] Kremann and Rodinis: Monatshefte, **27**, 125 (1906).

[2] Bogojavlensky, Bogoliubov and Vinogradov: *C. A.* 1, 2875 (1907).

[3] Kremann: Monatshefte, **28**, 7 (1907).

OXIDATION AND REDUCTION[1]

BY HAMILTON PERKINS CADY AND ROBERT TAFT

I. Statement of the Problem

Apparently the first introduction into chemical literature of the conception of oxidation and reduction as a change of valence was made by the American chemist Johnson,[2] in 1880. According to his definition an oxidizing agent "is one that can increase the number of bonds of some other substance; hence oxidation of one substance must involve the reduction of some other."

It is this definition which is virtually adopted in all American text books of general or inorganic chemistry. The term "bond," since the introduction of the ionic theory, is now used with the idea of unit charge. Oxidation thus being a gain in positive charge (or charges) or a loss in negative charge (or charges); reduction would be the reverse of the above operation. Some of the most modern chemists define oxidation as a loss of electrons by an element, while reduction is the gain of electrons. In the past few years, this conception of change of valence has been applied with more or less success in the interpretation of organic reactions.[3]

As to the actual mechanism of oxidation-reduction processes, whether of chemical or electrochemical origin, no general theory has been satisfactorily established. Nevertheless, a more or less well-defined concept of the process is now almost universally taught in this country. The general form of this concept may be stated as follows: In oxidation, the primary action is the liberation of oxygen, either from the oxidizing agent itself or from water; the liberated oxygen then reacts with the substance which is oxidized. In reduction, the primary action is the liberation of hydrogen, either from the reducing agent or from water, which then causes the reduction of the remaining substance.

To make the point more specific, we quote from several of the most widely used texts:

1. Smith[4]: "Inorganic Chemistry," third edition (1918).

A. "The permanganic acid, with excess of sulfuric acid, tends to undergo . . . . the following changes, provided a substance is present which can take possession of the oxygen that would remain as a balance," page 320.

$2HMnO_4+2H_2SO_4=2MnSO_4+3H_2O(+5O)$

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[1] The work included in this paper has been taken from the thesis presented in January of 1925 by Robert Taft in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the University of Kansas.

[2] Chemical News, 42, 51 (1880).

[3] Falk and Nelson: J. Am. Chem. Soc., 32, 1637 (1910); Fry: "Electronic Conception of Valence and the Constitution of Benzene."

[4] Smith's ideas on the nascent state should be reviewed in this connection. See page 543.

B. In the preparation of NO from ferrous sulfate, sulfuric acid, and nitric acid, the following equation is used:
$2FeSO_4 + H_2SO_4 = Fe_2(SO_4)_3 + (2H)$ page 529.

C. In the action of nitric acid upon non-metals the following equation is given, page 536.
$2HNO_3 = (H_2O.N_2O_5) = 2NO + H_2O + (3O)$

D. The oxidation of HCl by potassium dichromate is represented by two equations, the first of which is
$K_2Cr_2O_6 + 8HCl = 2KCl + CrCl_3 + 4H_2O\ (+3O)$, page 858.

2. Holmes: "General Chemistry" (1921).

"In the presence of a reducing agent, dilute nitric acid breaks up, yielding three oxygen atoms for every two molecules of the acid," page 242. In speaking of the reduction of nitric acid by zinc, "all of the oxygen is torn away from the nitrogen by the nascent hydrogen and then hydrogen begins to add on," page 244.

3. McPherson and Henderson: "General Chemistry," 2nd edition, (1921).

A. In speaking of the final equation representing the action of zinc on nitric acid, "It is unsatisfactory in that it does not . . . . suggest that hydrogen is first formed, and subsequently transformed into water," page 267.

B. "$Fe_2(SO_4)_3 + 2H$ (nascent) $= 2FeSO_4 + H_2SO_4$," page 628.

C. "$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$. This action is not very noticeable unless some reducing agent is present to take up the oxygen," page 687.

4. Norris: "Inorganic Chemistry," (1921).

A. "All processes of oxidation may be considered as taking place in two steps—first, the breaking down of the oxidizing agent to furnish oxygen, and, second, the oxidation of the element or compound present." page 258.

Bancroft[1] also cites a number of illustrations from various texts of this idea in connection with the action of nitric acid upon metals.

That these views are not confined to elementary text books alone is shown by the following reference, although many others could be cited:

1. Nernst: "Theoretical Chemistry" 5th English edition, page 867.

"Chemically an oxidizing material is characterized by its power of giving off oxygen, a reducing material by its power of given off hydrogen."

The original literature, of course, is replete with similar suggestions. To cite again only a few of the many:—

Kempf[2] in an article on the "Electrolytic Oxidation of p-benzoquinone"

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[1] J. Phys. Chem. 28, 475 (1924).

[2] J. prakt. Chem., (2) Folge, 83, 329 (1911).

inclines to the view that in all cases of electrolytic oxidation the actual oxidizing agent is a metallic peroxide formed by the action of nascent oxygen on the anode.

Armstrong and Colgate[1] state that "there is no immediate direct combination between the oxidizing agent and the oxidizedsubstance . . . the oxygen of the former acts merely as a depolarizer"[2].

Dunstan, Jowett, and Goulding[3] in studying the oxidation of iron in the absence of free oxygen, but in the presence of an oxidizing agent and water summarize their theory of the process as follows:

$$Fe + H_2O = FeO + H_2$$
$$H_2 + O_2 \text{ (source not stated) } = H_2O_2$$
$$2FeO + H_2O_2 = Fe_2O_2(OH)_2$$

Munn[4] believes like Armstrong that H_2O_2 is formed (necessarily) before oxidation can take place.

Orlov has determined what he thinks are the rates of the following two reactions:[5]

$$Mn_2O_5 = 2MnO + 5O$$
$$3Mn_2O_7 = 6MnO_3 + 3O$$

which take place when an acid solution of permanganate oxidizes potassium iodide.

Denis[6] in discussing the action of permanganate on alcohol uses the following equation to explain the reduction of the permanganate; the hydrogen, which is "atomic" comes from the action of ethylidene on water:

$$KMnO_4 + 3H = KOH + MnO_2 + H_2O$$

These are but a few of the many illustrations, picked more or less at random over a considerable number of years, which could be cited as proof of our assertion. The number of cases where the writer or investigator assumes such an oxidation—reduction process without actually stating in so many words that oxygen and hydrogen are liberated, is much greater—so great that no attempt has been made to cite references. An examination of the literature would soon convince the most sceptical of this fact.

The introduction of this explanation is not hard to trace. It originally started from the fact that many metals in contact with acids gave hydrogen, which gave rise to the supposition that *all* metals in contact with *all* acids gave hydrogen[7]. Later, the development of the theory of electrolytic dissociation with the explanation which it offered for the appearance of oxygen and hydrogen at the electrodes during electrolysis of certain aqueous solutions, together with the subsequent development of the theory of auto-

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[1] J. Soc. Chem. Ind. 32, 391 (1913).

[2] Compare also Armstrong and Acworth: J. Chem. Soc. 32, 56 (1877).

[3] J. Chem. Soc. 87, 1564 (1905).

[4] Z. physik. Chem. 59, 459 (1907).

[5] J. Russ. Phys. Chem. Soc. 43, 1524—abstracted in Chem. Abs. 6, 1247 (1912).

[6] Am. Chem. J. 38, 564 (1907)

[7] Compare Armstrong and Acworth: J. Chem. Soc. 32, 56 (1877).

oxidation[1] which was used to account for the fact that during certain types of reactions hydrogen peroxide was actually obtained during an oxidation, were considered as good grounds for explaining all oxidation and reduction phenomena as involving a primary liberation of oxygen and hydrogen and the subsequent action of these substances, either directly in the so-called nascent state or indirectly (formation of peroxide).

It is strange that this concept with practically no experimental proof should have been so long in use. Presumably on account of the difficult nature of the experimental disproof it has been continued in use for want of any better.

Objections have, of course, been made to the theory. These in the last few years have grown to considerable volume. We shall attempt to marshal the facts and arguments against the theory in the following summary:

1. It is not necessary to assume the intermediate formation of hydrogen and oxygen. Oxidation and reduction phenomena can be satisfactorily explained from both a qualitative and a quantitative standpoint without the assumption of the intermediate stage suggested above. Thus, from a qualitative standpoint, the process may be regarded as a direct transfer of charges, or, if one prefers, of electron transfer. Both of these methods are in use in several standard texts[2].

Clark[3] has developed the quantitative side of the case with considerable care and at considerable length. In this connection, it is worth while quoting him:

"As suggested . . . . we can regard the reversible transformation of ferric to ferrous ion to proceed through say one of a number of possible courses such as the following:

$$2Fe^{\cdot\cdot\cdot} + H_2 = 2Fe^{\cdot\cdot} + 2H^{\cdot}$$
$$2Fe^{\cdot\cdot\cdot} + 2O' = 2Fe^{\cdot\cdot} + O_2$$
$$Fe^{\cdot\cdot\cdot} + e = Fe^{\cdot\cdot}$$

"If we express the concentrations by means of brackets, the equations expressing the equilibrium condition for the cases mentioned are as follows:

$$\frac{(Fe^{\cdot\cdot\cdot})^2(H_2)}{(Fe^{\cdot\cdot})^2(H^{\cdot})^2} = K_1 \text{ or } \frac{(Fe^{\cdot\cdot\cdot})}{(Fe^{\cdot\cdot})} = \sqrt{\frac{K_1(H^{\cdot})^2}{(H_2)}}$$

$$\frac{(Fe^{\cdot\cdot\cdot})^2(O')^2}{(Fe^{\cdot\cdot})^2(O_2)} = K_2 \text{ or } \frac{(Fe^{\cdot\cdot\cdot})}{(Fe^{\cdot\cdot})} = \sqrt{\frac{K_2(O_2)}{(O')^2}}$$

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[1] Mellor: "Treatise" Vol. 1, 925, for explanation and references.

[2] Bailey and Cady: "Qualitative Analysis," 8th edition, p. 64 and Stieglitz: "Qualitative Chemical Analysis," Vol. I, pp. 262 and 282. Stieglitz (loc. cit.) also gives a very thorough and careful development of the quantitative side of the theory. His complete development is well worth study. See Chaps. 14 and 15.

[3] Studies on Oxidation and Reduction, Parts one and two. Reprints No. 823 and 826, Public Health Reports. Quotation is from Part I, page 5.

$$\frac{(Fe^{\cdot\cdot\cdot})(e)}{(Fe^{\cdot\cdot})} = K_3 \text{ or } \frac{(Fe^{\cdot\cdot\cdot})}{(Fe^{\cdot\cdot})} = \frac{K_3}{(e)}$$

"For any given ratio of $\frac{(Fe^{\cdot\cdot\cdot})}{(Fe^{\cdot\cdot})}$

$$\sqrt{\frac{K_1(H^{\cdot})^2}{(H_2)}} = \sqrt{\frac{K_2(O_2)}{(O')^2}} = \frac{K_3}{(e)}$$

"This procedure is capable of indefinite expansion and shows that from the schematic point of view we are at liberty to choose any hypothetical scheme with which to express the equilibrium state."

It should be noted in passing that although any hypothetical scheme may be used to express these equilibrium conditions, "e" (one faraday per mole) is the only one of the quantities experimentally determinable. Clark goes on to show that, no matter which scheme we prefer to use, all lead to the same result in calculating the electrode potentials of any given oxidation-reduction system, and further that "it is possible to express relative oxidation—reduction intensities in terms of electrode potential."

2. In most cases, the liberation of hydrogen and oxygen is purely hypothetical. That is, it is not experimentally possible to determine the actual presence of either substance during the course of the reaction.[1] In those cases where gases are actually detectable, it remains to be proved whether they are produced during consecutive reactions or as the result of concurrent reactions.

3. If the formation of oxygen and hydrogen is presupposed in electrolytic oxidation and reduction, then the decomposition voltages of oxidation and reduction systems should be not greater than that of an oxygen—hydrogen system, which is 1.79 volts with polished platinum electrodes.[2] Bancroft[3] has found that certain oxidation-reduction cells have voltages considerably in excess of this value. Thus, the cell

$$Pt — (SnCl_2.KOH) — NaCl — (KMnO_4.H_2SO_4) — Pt$$

gave an E. M. F. of 2.061 volts. If hydrogen and oxygen were the actual reducing and oxidizing agents and had been formed at the electrodes, this should not have exceeded 1.79 volts.

4. There is considerable experimental evidence that does not support this oxygen-hydrogen theory, some of which may be cited:

A. Sugden[4] has shown that the reduction of ferric sulfate by zinc in the presence of sulfuric acid passes through a minimum by varying the concentra-

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[1] Compare B, Objection No. 4 of this paper.

[2] Lehfeldt: "Electrochemistry," page 177 (1904).

[3] Z. physik. Chem. **10**, 394 (1892).

[4] J. Chem. Soc. **119**, 236 (1921).

tion of the acid and the salt, a fact which is in direct disagreement with the view that "nascent" hydrogen is the reducing agent.

B. Milligan and Gillette[1] found no experimental evidence of the liberation of either of these gases in the reduction of nitric acid by certain salts. According to Milligan and Gillette, the reduction of nitric acid by ferrous sulfate proceeds according to the equations:

$$2FeSO_4 + HNO_3 + H_2SO_4 = Fe_2(SO_4)_3 + HNO_2 + H_2O$$
$$3HNO_2 = HNO_3 + 2NO + H_2O$$

C. Benson[2], in studying the rate of reaction of ferrous sulfate, potassium iodide and chromic acid, found that the speed of the reaction could not be accounted for on the basis of the peroxide theory. "The 'peroxide theory' was set up before the rate measurements were made and in attempting to explain them, it falls down."

D. Oxidation can take place in the absence of oxygen and reduction can take place in the absence of hydrogen. A few typical cases will suffice:

1. Anhydrous ferrous chloride can be oxidized to ferric chloride by dry chlorine, the chlorine being reduced to chloride.

2. Manganous compounds can be oxidized in the dry state to manganates by potassium nitrate, the nitrate being reduced to nitrite.

This, of course, may be a case of thermal decomposition of the nitrate, but nevertheless, the nitrogen has been reduced in the absence of hydrogen.

3. Some compounds are capable of being reduced by other reducing agents than hydrogen; carbon and potassium cyanide for example[3].

4. Sulfur is reduced as indicated in the following equation, all substances being dry solids[4]:
$2SnO_2 + 2Na_2CO_3 + 9S = 3SO_2 + 2Na_2SnS_3 + 2CO_2$.
In this case, sulfur acts both as an oxidizing agent and a reducing agent; being oxidized to +4 in sulfur dioxide and being reduced to —2 in the thiostannate.

E. Oxidation and reduction are simultaneous processes—one necessarily accompanies the other. If the advocates of the gas theory are consistent, then *both* hydrogen and oxygen must be assumed to be formed during oxidation and reduction. Very few of the proponents of the theory apparently are willing to go this far. Very considerable trouble would be experienced in explaining the differences in oxidizing and reducing reactions in acid and alkaline solutions if this theory were carried out to its logical conclusion[5]. If both gases are formed, these reactions would of necessity be slow as will be shown by a consideration of the next paragraph.

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[1] J. Phys. Chem. **28**, 744 (1924).

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

[3] Caven and Lander: "Systematic Inorganic Chemistry" page 88, for many other examples.

[4] Treadwell-Hall: "Analytical Chemistry" 4th English edition, Vol. I, page 260.

[5] See explanation offered by Stieglitz: "Qualitative Analysis," Vol. I, p. 284, et seq.

F. As has been pointed out by Dhar[1], gases react rather slowly with liquids, so that either there should be a sufficient lapse of time such that the free gases would be produced or these oxidation-reduction reactions would proceed slowly. Both of these possibilities are contrary to fact.

These are the main arguments against the theory of actual formation of hydrogen and oxygen in oxidation and reduction processes. While some are debatable, we believe that, in the absence of any proof to the contrary, the most convenient and the most generally correct view, is to regard the process as a direct transfer of charges according to the original definition of Johnson, a conception which is also in accord with the present electronic theory of valence. It must be understood that we are advancing no arguments against the formation of intermediate *compounds* in oxidation and reduction reactions as there is experimental evidence on record in so large a number of cases that this is not a question for argument. Ostwald's law of successive reactions is aptly applied to these oxidation-reduction reactions. *We are arguing against the actual formation of hydrogen and oxygen during this type of reaction.*

It will be noted in the cases cited above under objection "D" that they are for the most part reactions which take place at high temperatures, i.e. reactions which might be possible on account of thermal decomposition. The proof would be much more convincing if the reactions took place at normal temperatures or under. It was with this view that the present investigation was begun. Our plan, in brief, was to carry out the electrolytic reduction of a substance containing no hydrogen in a solvent free from that element, and to carry out the electrolytic oxidation of a substance containing no oxygen in a solvent containing no oxygen[2]. It is generally understood that any chemical reaction which involves oxidation and reduction is separable by electrolysis into two reactions, a cathodic process (reduction) and an anodic one (oxidation)[3].

Choice of Solvents

After having stated the problem, the question of choice of solvents naturally arises. A solvent which will conform to the above restriction and still be a good conductor upon the addition of oxidizable or reducible salts is a "rara avis." Ammonia suggests itself upon the work of Cady[4] and of Franklin and Kraus[5] as being a suitable medium in which to carry out oxidations.

In carrying out reductions, liquid sulfur dioxide was chosen for trial but on account of the complex character of the cathodic processes was abandoned

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[1] J. Phys. Chem. 29, 142 (1925)

[2] It should be understood that even if it could be shown that the discharged ions of these solvents are the actual reducing and oxidizing agents, our argument would still hold good, as oxidation would take place in the absence of oxygen and reduction in the absence of hydrogen.

[3] Compare Bancroft: Trans. Am. Electrochem. Soc. 8, 33 (1905); 9, 13 (1906).

[4] J. Phys. Chem. 1, 707 (1897).

[5] Am. Chem. J. 20, 820 (1898): 23, 277 (1900).

TABLE I

Property	$POCl_3$.		NH_3.	
Freezing Point	1.25°	Walden Z. anorg. Chem. **68**, 309 (1910)	−77.7°	Elliott J. Phys. Chem. **28**, 620 (1924)
Boiling Point	105.8° 75.3 cm.	Walden Z. anorg. Chem. **25**, 212 (1900)	−33.4°	Bergstrom J. Phys. Chem. **26**, 876 (1922)
Critical Temperature	329° (calc.)	Ramsay and Shields J. Chem. Soc. **63**, 1108 (1893)	130.°	Dewar Phil. Mag. **18**, 214 (1884)
Pressure			115.	Dewar Phil. Mag. **18**, 212 (1884)
Specific Gravity.	$1.66^{19.5^{\circ}}$	Mendelejeff Compt. rend. **51**, 97 (1860)	$.6825^{-33.5^{\circ}}$	Fitzgerald J. Phys. Chem. **16**, 654 (1912)
Ebullioscopic Constant	54.7 (calc.)	Walden Z. physik. Chem. **65**, 271 (1909)	3.4	Franklin and Kraus Am. Chem. J. **20**, 851 (1898)
Cryoscopic Constant	76.8	Walden Z. anorg. Chem. **68**, 310 (1910)	9.7	Elliott J. Phys. Chem. **28**, 628 (1924)
Heat of Fusion.	19.8 (calc.)	Walden Z. anorg. Chem. **68**, 311 (1910)	78.7 (calc.)	Elliott J. Phys. Chem. **28**, 628 (1924)
Heat of Vaporization at B. P.	52.6 (calc.)	Walden Z. physik. Chem. **65**, 271 (1909)	$327.9^{-33.4^{\circ}}$	Osborne and Van Dusen. Bull. B. S. **14**, 470 (1918)
Association Factor.	1	Ramsay and Shields. J. Chem. Soc. **63**, 1099 (1893)	1	Grunmach. Akad. Berlin **38**, 839 (1900)
Dielectric Constant.	$13.9^{22^{\circ}}$	Schlundt. J. Phys. Chem. **5**, 515 (1901)	$\overset{-34^{\circ}}{22}$	Goodwin-Thomson Phys. Rev. **8**, 38 (1899)
Specific Conductivity	$.17 \times 10^{-5}$	Walden Z. physik. Chem. **43**, 445 (1903)	$.5 \times 10^{-8}$ -33°	Franklin and Kraus J. Am. Chem. Soc. **27**, 193 (1905)
Viscosity*			$.002543^{-33.5^{\circ}}$	Elsey J. Am. Chem. Soc. **42**, 2474 (1920)

*Water = .01006 at 25°

in favor of phosphoric oxychloride[1]. Our results of these electrolytic experiments in SO_2 have been recorded and published separately[2].

During the course of the investigation, a knowledge of the physical properties of the above solvents was required. It is needless to say that a knowledge of these physical constants is not only useful in the choice of a solvent for a given purpose but also helpful in interpreting results. As much time was spent in the search of the literature for some of these constants, it was thought worth while to include as complete as list as possible of these values together with the authority from which they were compiled. The constants are given in Table I.

Experimental Part

Phosphoric Oxychloride as a Solvent.

This liquid was chosen on account of the fact that not only is its dielectric constant somewhat higher than is that of sulfur dioxide and that its boiling point is much higher (thus increasing the ease of manipulation), but chiefly because neither the liquid itself or its hydrolytic products are reducing agents. The chief objection to its use for our purposes lay in the fact that it readily takes up water and undergoes hydrolysis—the hydrolytic products, where the oxychloride is in excess, being metaphosphoric acid and hydrogen chloride; the presence of these substances vitiating the results of electrolysis.

There is an erroneous idea that phosphoric oxychloride hydrolyzes slowly[3], If a small amount of water is poured over $POCl_3$, two liquid layers are formed. hydrolysis takes place slowly at first and then more rapidly until the reaction takes place with semi-explosive violence, the entire reaction not taking more than several minutes. If the water is agitated with the liquid, hydrolysis takes place immediately. It should be noted that the temperature was not kept constant in carrying out the experiment described above; it should also be remembered that under working conditions reactions are not carried out under constant temperature unless for the specific purpose of determining the rate of reaction.

In general, this liquid is a better solvent than is sulfur dioxide; a more varied number of inorganic solids are appreciably soluble than is the case with the first solvent. Walden[4] was the first to call attention to the solvent properties of this substance. In his paper, he lists as soluble in phosphoric oxychloride the following substances: alkali, and many of the heavier metallic, iodides; ferric chloride, hydrocarbons, esters and tertiary amines. Walden determined the conductances of some four solutions and concluded that $POCl_3$ was a good ionizing agent for binary salts.

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[1] This substance is called "phosphorus" or "phosphoryl" oxychloride in text books and in the literature but the name "phosphoric" is preferable to avoid confusion (which is frequent) with "phosphorous" oxychloride, POCl.

[2] J. Phys. Chem. 29, page 1075, (1925).

[3] Roscoe and Schorlemmer: "Treatise on Chemistry," Vol. 1, p. 677, 5th ed.

[4] Z. anorg. Chem. 26, 212 (1900).

As no reference to the solubilities of oxy-salts was found, some qualitative determinations were carried out. Our method was similar to that in the case of sulfur dioxide[1] save that smaller amounts of solvent were used. The results of these determinations together with the solubilities of a few other substances are given in Table II.

TABLE II

Appreciably Soluble		Insoluble
[2]I_2	$AsBr_3$	KNO_3
[3]$KClO_3$	$KClO_4$(slight)	HgCl
[3]$KBrO_3$	KIO_4(slight)	$K_3Fe(CN)_6$
[3]KIO_3	$FeCl_2$	$K_2C_2O_4$
$K_2Cr_2O_7$	CuBr	$CuCl_2$
K_2CrO_4	$Hg(CN)_2$(slight)	$MnCl_2$

In addition to these cases, mention should be made of several others. Potassium permanganate dissolves giving a faint pink color; if this solution be allowed to stand for a day or so out of contact with air, the color is discharged. This is probably due to the action of the permanganate on hydrogen chloride, as even freshly-distilled phosphoric oxychloride contains some dissolved HCl. After standing some months in a sealed tube, the solution precipitates a white gelatinous substance. Whether this is due to hydrolytic action of the solvent or was simply the reduced manganous salt is at present undetermined. The formation of gelatinous precipitates seems to be quite common in solutions of this solvent. Copper chromate behaves similarly, a reddish-colored solution is first formed which, on standing, changes to a semi-solid, greenish mass. Similar changes were noted in the case of solutions of ferric chloride and of potassium iodate which had been sealed up for some months.

Nearly all inorganic salts which dissolve in phosphoric oxychloride form colored solutions. In the case of the alkali iodides, it is stated in the literature that free iodine is liberated upon solution in this solvent. It is doubtful in our judgment if such would be the case if the solvent were entirely free from traces of hydrogen compounds. A sample of potassium iodide which has been sealed up for some six months with the solvent is brown in color, whereas, a similar tube containing free iodine is red. The absorption spectra of the two solutions are quite different—that of potassium iodide showing absorption of all but the red and a small portion of the green whereas that of iodine absorbs only in the violet.

As is to be expected, colored solutions of other salts in phosphoric oxychloride give absorption spectra; none of those so far examined have been banded spectra but consist in a more or less complete extinction of the violet end of the spectrum, the absorption rarely extending into the blue.

Upon obtaining some knowledge of solubilities in phosphoric oxychloride, preliminary electrolyses were run upon several substances, potassium iodate

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[1] loc. cit.

[2] More so than in SO_2; [3] Increasing solubility in the order named.

and ferric chloride being finally chosen as the most suitable for our purposes. It was noted, however, in one of our preliminary trials when electrolyzing potassium iodate that a gas was liberated at both electrodes. The solvent which we used was freshly distilled and we were at a loss to account for the rather unexpected result. The idea occurred to us that the formation of the gas might be due to traces of dissolved hydrogen chloride which would be present as the result of partial hydrolysis of the solvent. Metaphosphoric acid, the other hydrolytic product, would be completely removed by the distillation. To test out the correctness of our assumption, a quantity of the freshly distilled liquid was placed in a eudiometer tube and pieces of metallic potassium introduced—after standing for a day, sufficient gas was collected for analysis. Upon analyzing this gas, it was found to consist very largely of hydrogen[1]. We considered this as proof of our assumption and undertook to remove hydrogen chloride from the liquid. We finally succeeded by distilling the oxy-chloride with metallic potassium. It seems remarkable that such an experienced chemist as Walden[2] should have used phosphorus pentoxide in an attempt to "dry" phosphoric oxychloride. Any moisture present would be converted to metaphosphoric acid and hydrogen chloride, the first of which would be removed by distillation, whereas the pentoxide would be without effect on the hydrogen chloride either physically or chemically.

In our first attempts to remove the hydrogen chloride with metallic potassium, we added the potassium to the distilling flask containing the commercial oxychloride. After distilling off about half of the original mixture, the material in the flask would explode, completely shattering the apparatus. The explosions were finally attributed to the increasing concentration of the glacial phosphoric acid, which, upon reaching a certain value, would react with explosive violence with the potassium at the somewhat elevated temperature (105-107°). A first distillation without the metallic potassium to remove the glacial phosphoric acid and then a subsequent distillation with potassium in an atmosphere of dry natural gas enabled us to distill the liquid with safety.

The same electrolysis tube as was used in our experiments with sulfur dioxide[3] was used in our trials with solutions in phosphoric oxychloride. The purified solvent was distilled into a separatory funnel protected with a drying tower of calcium chloride. The liquid was transferred to the electrolysis tube by inserting the stem of the funnel into one of the necks of the tube, closing all openings save the neck and passing a current of dry natural gas through the apparatus during the operation; the solute having first been introduced in the same manner as described under sulfur dioxide. A solution of potassium iodate obtained by purifying and transferring the solvent as just described gave no gas at either electrode upon electrolysis.

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[1] Thanks are due to Mr. I. G. Malm for the analysis of the gas.

[2] Z. anorg. Chem. **26**, 212 (1900).

[3] J. Phys. Chem. **29**, 1075 (1925).

A. Electrolysis of Chromates.

It was hoped upon finding that the chromates (or dichromates) were soluble in phosphoric oxychloride that electrolysis of their solutions would result in the reduction of the chromium from the hexavalent condition to some lower state of oxidation. Such a change could be followed by the eye as the chromates (or dichromates) form dark red solutions with this solvent. Electrolysis of potassium dichromate did not yield the desired result nor were any of the forms of chromium in the lower states of oxidation detectable in the residue. Furthermore, there was no deposit upon either electrode—very probably gas was produced but the solutions were too dark colored to observe any electrode phenomena. Similar results took place with copper chromate although one would expect that at least copper would be deposited upon the cathode. None was observed.

It should be stated, however, that these results were obtained before our method of purifying phosphoric oxychloride was worked out, freshly distilled solvent being used. Electrolysis was continued for several hours in most cases, which should have been sufficient time to remove any hydrogen chloride present.

B. Electrolysis of Potassium Iodate.

Potassium iodate dissolves sparingly in phosphoric oxychloride. The saturated solution is light reddish-brown in color, darkening on long contact with the solvent (several months), and is a poor conductor of the current when compared to aqueous solutions, but at least a ten times better conductor than is a similar solution in sulfur dioxide. The solvent is without action upon the solute, for upon distilling the substance with a quantity of the solvent, the residue gave no test for iodide or free iodine, nor was any free iodine found in the distillate.

Our first trials gave results showing that iodine was set free during the course of the electrolysis, either as a result of the direct reduction from iodate to iodine, or from iodate to iodide with a subsequent reaction between the two to produce free iodine. The iodide and iodate will react in freshly distilled solvent to give iodine but there is the possibility that the reaction is caused by the presence of traces of hydrogen chloride. Several electrolyses were carried out after we had devised our method for purifying the solvent, in which case most of the cathodic current is used in the deposition of metallic potassium, no iodides being found in the residue but in each case free iodine was present. Our last trial is reported below:

Grams of KIO_3 used	1.166
Time of electrolysis	12 days
Current	0.01 amp.
Voltage	110

The current varied somewhat from the value given above but the fluctuations were not marked. The cathode became coated with a white crystalline deposit, which proved, upon examination to be metallic potassium. The anode (wire) was covered with a thin yellowish cast which did not grow perceptibly during the electrolysis. The solution was stirred by dried gas from time to time to increase the concentration of potassium iodate, an excess of the solid being always present. The stirring also prevented the potassium from bridging across to the anode. At the completion of the electrolysis, the liquid was transferred to a distilling flask and after distillation, the residue was extracted with ether. The residue left after extraction with ether contained no iodide. The iodine obtained by the ether extraction was titrated against a standard thiosulfate solution and found to contain 0.0563 grams of iodine. The formation of this iodine was taken to prove our point that reduction had taken place in the absence of hydrogen. We feel especially confident of this fact due to the formation and continued presence of the metallic potassium, which would certainly insure the complete absence of any hydrogen. It should be stated further, that the solution deepened in color during the course of the electrolysis, giving additional proof that iodine was accumulating in the solution.

Examination was made of the anode deposit, the quantity of which was exceedingly small. Upon immersing the anode in water, the deposit was freed from the wire and dissolved slowly. The aqueous solution gave tests for chlorides and phosphates, which, of course, might be due to adhering solvent. A qualitative test for iodides was made on this aqueous solution but it gave negative results.

C. *Electrolysis of Ferric Chloride.*

Ferric chloride dissolves to a somewhat greater extent in phosphoric oxychloride than it does in sulfur dioxide, the resulting solution is accordingly a better conductor than a solution of the same compound in sulfur dioxide. The chief difficulty in the use of anhydrous ferric chloride lies in its great affinity for water—especial care was therefore exercised in introducing this substance into the electrolysis tube; the method has already been described in connection with our work upon sulfur dioxide.

The electrolysis of this compound produced a black, thin, adhering deposit upon the cathode. After the electrolysis had continued several hours, the solution was removed, most of it being subjected to distillation. A portion of the solution was cautiously added to water; potassium ferricyanide was then added to the cold solution, whereupon a dark blue precipitate was formed. Similar results were obtained with the residue left from the distillation—the residue was extracted with water and then treated with potassium ferricyanide, the dark blue precipitate again appearing. This was taken to be proof that the change $Fe^{\cdot\cdot\cdot} + (-) = Fe^{\cdot\cdot}$ had taken place.

The nature of the deposit upon the cathode was determined as far as the scantness of the material would allow. An acid solution of this substance had strong reducing properties; producing with silver nitrate a precipitate of various colors, finally becoming black. It also decolorized permanganate solution. These properties resemble to some extent those of the hypophosphites. There is the possibility that the positive ion of the solvent itself has been reduced and combined with a part of the $Fe^{\cdot\cdot}$ to form an insoluble substance. According to Walden, phosphoric oxychloride ionizes

$$POCl_3 = PO^{\cdot\cdot\cdot} + 3Cl'$$

If the reaction

$$PO^{\cdot\cdot\cdot} + 4(-) = PO'$$

be assumed to take place, the formal resemblance to the hypophosphites becomes apparent, for

$$H_3PO_2 - H_2O = HPO = H^{\cdot} + PO'$$

While there is no meta hypophosphorous acid recorded in the literature, it requires no great stretch of the imagination to see that, if it were formed in a solution entirely free from water, it would probably have the composition given above.

If this is the correct analysis of the situation, it might be possible that it was PO' which reduced $Fe^{\cdot\cdot\cdot}$ to $Fe^{\cdot\cdot}$; it is immaterial from our point of view, as in either case, reduction has taken place in the absence of hydrogen.

II. Liquid Ammonia as a Solvent

The amount of work which has been done upon the various solvent properties of liquid ammonia is very large as compared to the amount of work which has been done upon the solvent already described.

As it was in this solvent that we hoped to carry out the oxidation of substances in the complete absence of oxygen, a knowledge of the solubilities of substances capable of being oxidized was required. A study of the papers of Cady[1] and of Franklin and Kraus[2] together with some preliminary trials led us to confine our work to the electrolysis of solutions of the following substances: thallous iodide, cuprous iodide, hydrazobenzene, methyl and ethylamine hydrochlorides.

Our experimental procedure was much the same as that described in the electrolysis of solutions in sulfur dioxide[3]. The apparatus was dried at 110° over night, dry natural gas freed from CO_2 was passed thru the tube while cooling, and the substance to be electrolyzed, carefully dried, was then introduced. The exit tube "C" was closed with a tube about a meter in length which dipped into mercury at its farther extremity. This change was made to secure some pressure within the tube as an aid in the condensation of the ammonia and, also, to give some indication of the direction of the pressure.

The solvent was drawn from a cylinder which had been charged some years previously with metallic sodium to dry it, and was then passed through a drying tower filled with ignited asbestos to remove any mechanical impurities which previous investigators had found were carried by the moving gas. Commercial ammonia, vaporized rapidly below its boiling point by bubbling natural gas through the liquid, was used as a refrigerant to condense the dried ammonia.

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[1] J. Phys. Chem. 1, 707 (1897).

[2] Am. Chem. J. 20, 820 (1899), 23, 277 (1900).

[3] J. Phys. Chem. 29, 1075 (1925).

Upon completion of the electrolysis, the Dewar flask containing the refrigerant was removed and the solvent allowed to vaporize through "C," the adjustment of the height of the mercury being used to regulate the pressure in the tube. Pressure was at all times kept greater within the electrolysis tube than out, so that any flow by diffusion would be outwards, this serving as an additional precaution in keeping the solution entirely free from moisture.

The electrode "D" served in these experiments as the anode.

A. *Electrolysis of Thallous Iodide.*

This salt was prepared by adding the requisite amount of potassium iodide to a hot solution of chemically pure thallous sulfate. The filtrate from the insoluble thallous iodide continued to give tests for sulfates after many washings. The residual sulfate was finally removed by suspending the thallous iodide in several liters of distilled water, shaking for sometime, allowing the iodide to settle out, and then pouring off the supernatant liquid. After several such treatments, no sulfate could be detected. The salt, which is a bright yellow solid, was then dried at 110° over night, powdered and then redried over another night. The yellow solid dissolves quite freely in liquid ammonia giving a colorless solution.

Upon electrolyzing this solution, black amorphous thallium was deposited with exceeding rapidity upon the cathode—the wire cathode "growing" to at least ten times its original size in the course of a few minutes. This necessitated breaking the current and stirring with dry natural gas to prevent bridging between the electrodes. At best, the electrolysis could be continued only a short time.

A trial using .544 grams of thallous iodide gave a current of 0.6 amperes, the voltage being 110. A gas was given off at the cathode. After fifteen minutes, the electrolysis was stopped and the solvent distilled off. The cathode was removed and the residue extracted with ammonia water and filtered. This would leave as a residue thallic hydroxide if any of the thallous ion had been oxidized to thallic, thallous hydroxide being quite soluble in water. A considerable residue was formed; this was dissolved in a small quantity of hydrochloric acid and the solution then neutralized with ammonium hydroxide. A voluminous white precipitate resembling aluminum hydroxide was formed. This was filtered, washed and dissolved again in a small quantity of acid. Sufficient ammonium sulfide reagent was then added to neutralize the acid and precipitate the thallic ion as thallous sulfide, as thallic ion is reduced by this reagent to the thallous state. An abundant black precipitate was formed, as thallous sulfide is black. This was considered as proof that the reaction $Tl^{\cdot} + 2(+) = Tl^{\cdot\cdot\cdot}$ had taken place.

Liquid ammonia itself is without oxidizing action upon thallous iodide, as was shown by the fact that a small quantity of thallous iodide, when dissolved in liquid ammonia, gave no test for $Tl^{\cdot\cdot\cdot}$ after removing the solvent.

B. *Electrolysis of Cuprous Iodide*

Some cuprous salts are soluble in liquid ammonia, the chief difficulty from our point of view being the fact that it is difficult to free them from traces of cupric ion in liquid ammonia solution. Sloan[1] prepared an ammonate of cuprous nitrate but was unable to obtain a colorless solution. Franklin[2] cites a number of instances of cuprous compounds, all of which give colored solutions in liquid ammonia, thus showing the presence of the cupric ion. He was able to prepare a colorless solution of cuprous amide from solutions of considerable age.

Cuprous iodide appeared to be the best choice among the copper compounds, as it is soluble in liquid ammonia and contains no oxygen. It was prepared by adding together the calculated amounts of blue vitriol and potassium iodide, the excess iodine being removed by passing sulfur dioxide through the solution. It was washed and dried in the absence of air, ground and redried. The dry salt had a grayish appearance. Upon dissolving this salt in liquid ammonia, a blue solution resulted. Another trial in which metallic copper was allowed to stand in contact with the solution of cuprous iodide, gave similar results—although the solution was not as dark colored as before. This solution upon electrolysis apparently became darker blue in color, although it was difficult to judge by the eye the extent of the color change. It was hoped that the cuprous solution might be obtained colorless, for any color change which occured could be easily followed. There is a possibility then, that the change $Cu^{\cdot} + (+) = Cu^{\cdot\cdot}$ has taken place.

C. *Electrolysis of Hydrazobenzene*

White and Knight[3] have called attention to the solubility of this compound in liquid ammonia. As the change from hydrazobenzene to azobenzene is a typical oxidation, the electrolytic oxidation of the substance would offer considerable evidence in favor of our concept.

The sample of hydrazobenzene[4] used was clear white, melting at 131°. It dissolved in liquid ammonia, giving a pale yellow solution, the solution, however, was an exceedingly poor conductor and other solutes were added to carry the current. In aqueous solution, hydrazobenzene can be electrolytically oxidized in the presence of alkali. By analogy, since amides give alkaline solutions in liquid ammonia, it appeared possible to electrolytically oxidize hydrazobenzene in the presence of an amide in liquid ammonia. However, the simple addition of sodamide to a solution of hydrazobenzene produced a red coloration, which, after studying the paper of White and Knight[5], was ascribed to the presence of metallic sodium in the sodamide (sodium and hydrazobenzene give according to these investigators a red solution in liquid ammonia.) Another explanation of the red color thus produced might be found in the possible presence of the ammonia analogue of sodium peroxide in the sodamide. Additional evidence on this last explanation is furnished by the fact that sodium peroxide and hydrazobenzene in liquid ammonia give a red solution.

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[1] J. Am. Chem. Soc. 32, 972 (1910).

[2] Private communication.

[3] J. Am. Chem. Soc. 45, 1780 (1923)

[4] Thanks are due to Mr. Edwin C. Wise for the preparation of this compound.

[5] J. Am. Chem. Soc. 45, 1780 (1923).

Electrolysis in neutral solution was then tried, sodium chloride being used as the carrier of the current. This gave a red solution at the cathode which was without doubt due to the reaction between the hydrazobenzene and the sodium formed at the cathode, as suggested by White and Knight.

Finally, electrolysis in acid solution was carried out, dried ammonium chloride being added to produce the acidity. As this attempt gave positive results, the following trial was made:

Weight of NH_4Cl used...............0.68 grams
Weight of $C_6H_5NHHNC_6H_5$..........0.2344 "

During the electrolysis, the color of the solution deepened and after passing the current through the liquid for an hour the current was shut off, the solvent evaporated and the residue extracted with toluene. From the toluene solution, long blade-like crystals, dark red in color, were obtained. This amounted to 0.1878 grams and had a melting point of 65°. A second crystallization gave a product melting sharply at 67°. The recorded melting point of azobenzene is 68°. The agreement was considered satisfactory, taking into consideration the difference between the melting points of the azo and hydrazo compounds. We have shown, therefore, that eighty per cent. of the hydrazobenzene had been oxidized to azobenzene.

A blank trial, (i.e., a similar solution without electrolysis) gave no evidence of the formation of any azo benzene.

The cathode, after the completion of the electrolysis, was found to be covered with a black substance, insoluble in toluene, alcohol, or water.

D. *Electrolysis of the Amine Hydrochlorides*

In alkaline aqueous solutions, ethyl alcohol can be oxidized in the presence of iodine to iodoform. A somewhat analogous process in liquid ammonia, would be the oxidation of the amines in the presence of iodine to iodoform. On paper, for example, the following reaction appears possible:

$$CH_3NH_2 + 2I_2 = CHI_3 + NH_4I$$

the oxidation consisting in replacing the positive hydrogen by the negative iodine, i.e., the valence of carbon changes from -2 to $+2$.

No iodoform could be detected when the electrolysis was carried out in the presence of potassium iodide and sodamide[1], but upon electrolyzing a solution of methyl ammonium chloride and ammonium iodide, i.e., an acid solution, a trace of iodoform was detectable[2] by its odor in the residue left after the water extraction of the contents of the cell. Several trials did not give a greater yield.

Since the oxidation of ethyl amine to iodoform would be more strictly analogous to the oxidation of ethyl alcohol in aqueous solution, attempts were made to oxidize this compound in the form of the hydrochloride, but neither in alkaline or acid solutions were any traces of iodoform observable.

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[1] Rather than use the free amine, the hydrochloride from Eastman's purified base was used.

[2] Identified by three independent observers.

The main product of the reaction appeared to be an iodine substituted amine, probably $C_2H_5NI_2$.

III. Discussion of Results

The number of cases where positive evidence of our main thesis has been experimentally shown is not large. It must be remembered, however, that limitations were placed upon our problem by the nature of the problem itself and by our method of attack. A review of our work would show that these limitations were:

A. The number of substances available for experimental purposes was limited. That is, we restricted ourselves to those compounds which contained no oxygen in a non-oxygen solvent and vice-versa.

B. The number of compounds available with the restriction placed in (A) was still further reduced by the fact that they were required to be appreciably soluble in the solvent under consideration.

C. The very marked difference in the electrolytic behavior of aqueous and non-aqueous solutions.

In the light of these limitations, we believe that we have succeeded in proving our contention that oxidation can take place in the absence of oxygen and that reduction can take place in the absence of hydrogen. These results are summarized in Table III.

In addition, some evidence has been produced showing that the following reactions take place:

$$Cu^{\cdot} + (+) = Cu^{\cdot\cdot}$$

and

$$CH_3NH_2 + 2I_2 = CHI_3 + NH_4I$$

TABLE III

Substance	Solvent	Product	Analysis
KIO_3	$POCl_3$	I_2	0.0563 grams
$FeCl_3$	$POCl_3$	$Fe^{\cdot\cdot}$	Qualitative
TlI	NH_3	$Tl^{\cdot\cdot\cdot}$	Qualitative
$C_6H_5NHHNC_6H_5$	NH_3	$(C_6H_5N)_2$	80% yield.

Summary

1. Objections to the conception that oxygen and hydrogen are actually formed during oxidation-reduction actions have been pointed out.

2. It has been shown experimentally that oxidation can take place in the absence of oxygen and that reduction can take place in the absence of hydrogen.

3. The qualitative solubilities of a number of substances in phosphoric oxychloride have been examined.

4. Some experimental facts have been added to our knowledge of the electrochemistry of solutions in phosphoric oxychloride and liquid ammonia.

Chemical Laboratory,
University of Kansas,
Lawrence, Kansas,
March, 1926.

ELECTROLYSIS IN LIQUID SULFUR DIOXIDE[1]

BY HAMILTON PERKINS CADY AND ROBERT TAFT

In carrying out an investigation upon electrolytic oxidation and reduction in non-aqueous solvents[2], a number of trials were made using liquid sulfur dioxide as a solvent. As the cathodic process in general consisted of decomposition of the solvent rather than the solute, it was thought best to include the results of our observations of electrolytic phenomena in this solvent as a separate paper. The results given are not complete as, in general, only secondary consideration was paid to electrolytic phenomena at the anode. Nevertheless, we feel that the results obtained add somewhat to our limited knowledge in the field of electrochemistry in non-aqueous solutions.

While considerable work has been done on the electrolytic conductances of solutions[3] in SO_2, comparatively little work has been done on the actual separation of the products of electrolysis. Bruner and Bekier[4] examined the products of the electrolysis of the halogen halides with a view to determining the validity of Faraday's laws in this solvent. Bagster and Steele[5] and later Centnerzwer and Drucker[6] reported on investigations of these electrolytic products, but their observations do not agree upon a very fundamental point. Bagster and Steele claimed to have obtained free sulfur at the cathode in amounts approximately called for by Faraday's law. Centnerzwer and Drucker found no sulfur but a deposit of strongly reducing properties rich in combined sulfur. The present investigation confirms the work of Centnerzwer.

Other discrepancies have been reported in connection with this solvent. For example, Franklin's work[7] on conductivity does not agree with that of Dutoit and Gyr[8]. In most of these cases, the disturbing factor is probably due to the presence of traces of dissolved water. The work of Bagster and Steele and of Bagster and Cooling[9] on the effect of dissolved water upon the conductivity of certain solutions in sulfur dioxide show this. Our own work also confirms this (see Table III). Zerner, Weiss, and Opalski[10] reported that toluene was not completely miscible with liquid sulfur dioxide at −10°. Fontein[11] later showed that the dry hydrocarbon and dry solvent were homogeneous at temperatures as low as −21° and accounted for Zerner's error as due to the presence of water in his solvent, a result which was afterwards accepted by Zerner[12]. It is possible that the anomolous results of Franklin

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[1] The work included in this paper has been taken from the thesis presented in January of 1925 by Robert Taft in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the University of Kansas.

[2] J. Phys. Chem. 29, 1057 (1925).

[3] Walden: "Elektrochemie nichtwässriger Lösungen," pp. 85, 327 (1924).

[4] Z. physik. Chem. 84, 570 (1913).

[5] Trans. Faraday Soc. 8, 51 (1912).

[6] Z. Elektrochem. 29, 210 (1923).

[7] J. Phys. Chem. 15, 675 (1911)

[8] J. chim. phys. 7, 189 (1909)

[9] J. Chem. Soc. 117, 693 (1920)

[10] Z. angew. Chem. 35, 253 (1922).

[11] Z. angew. Chem. 36, 4 (1923).

[12] Z. angew. Chem. 36, 6 (1923).

and of Dutoit and Gyr may be traced to the same origin, namely the presence of traces of water in the sulfur dioxide of the latter as their results in general are high as compared to those of Franklin.

In the course of the investigation, a knowledge of some of the physical properties of this solvent was required. This necessitated a considerable search of the literature on account of which we have thought it advisable to include a rather complete list of the properties as found. These will be found in Table I.

TABLE I

Property		Value	Authority
Freezing Point		−72.7°	Walden and Centnerzwer Z. physik. Chem. **42**, 449 (1903)
Boiling Point		−10.2°	Bergström J. Phys. Chem. **26**, 876 (1922)
Critical	Temperature	157.26°	Centnerzwer Z. physik. Chem. **46**, 474 (1903)
	Pressure	77.65	Cardoso and Bell J. Chim. phys. **10**, 497 (1912)
Specific Gravity		1.43 at 0° 1.46 at −10°	Cailletet and Mathias Compt. rend **104**, 1565 (1887)
Ebullioscopic Constant		15	Walden and Centnerzwer Z. physik. Chem. **39**, 568 (1901)
Vapor Pressure at 0°		1163 m. m.	Cardoso, Coppola and Fiorentino Atti Congresso Naz. Chim. pura applicata 404 (1923)
Heat of Vaporization		$91.7^{-10°}$	Chappuis Am. Chim. Phys. (6) **15**, 517 (1888)
Association Factor		1	Grunmach Berlin Akad. **38**, 839 (1900).
Dielectric Constant		$12.35^{22°}$	Schlundt J. Phys. Chem. **5**, 515 (1901)
Specific Conductivity		$.4 \times 10^{-7}$ −10°	Franklin J. Phys. Chem. **15**, 678 (1911)
Viscosity*		.004285 −10°	Fitzgerald J. Phys. Chem. **16**, 644 (1912)

*Water = .01778 at 0°

Experimental Results

A. *Solubility.*

Walden[1], and Walden and Centnerzwer[2] record the solubilities of a number of substances in liquid sulfur dioxide. We have extended the list to a number of other substances, examining especially the oxygen salts. Our method was to suspend the dried, powdered, salt in some 30 c.c. of the liquid contained in a small Dewar flask, agitate the solution for some minutes, allow the excess salt to settle, and then filter the liquid through paper. If, on evaporating a portion of the solution, any residue remained, the substance was called "appreciably soluble," otherwise "insoluble." None of the compounds, at best are largely soluble in this solvent[3]. The qualitative results thus obtained are listed in Table II.

B. *Method of Electrolysis.*

After many preliminary trials with various forms of apparatus, an electrolytic cell as illustrated in Figures 1a and 1b was used for the greater number of our experiments[4].

TABLE II

Soluble Appreciably	Insoluble
KIO_3	$KClO_4$
*$Na_2S_2O_3$	$Ca(NO_3)_2$
$Ce(NO_3)_3$	$(NH_4)_2MoO_4$
BaO_2	Cr_2O_2
K_2S	Ca_3P_2
$KBrO_3$	$KMnO_4$
*$NaCN$	$KC_2H_3O_2$
$Ca(ClO_3)_2$	K_2CrO_2
$KClO_3$	Na
$AgNO_3$	H_3BO_3
*$K_2Cr_2O_7$	
$K_3Fe(CN)_6$	

*very slight.

"G," the cell, was a pyrex tube having an external diameter of 4.5 cms., and an approximate length of 28 centimeters. The cell was made of considerable length so that it could be immersed for the greater part of its length in liquid ammonia, which was used as the refrigerant for the condensation of the sulfur dioxide. "B" is a two way stopcock connected to the glass tube "E" which reaches to the bottom of the cell. Commercial liquid sulfur dioxide contained in an iron cylinder was distilled into the cell through the lower

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[1] Ber. 32, 2862 (1899)

[2] Z. physik. Chem. 39, 513 (1901); Z. anorg. Chem. 30, 145 (1902).

[3] I. W. Cox: Master's Thesis, Univ. of Kansas, 1922.

[4] Thanks are due to Dr. H. M. Elsey for the construction of this tube.

arm of "B," after passing through a drying column consisting of some 75 centimeters of phosphorus pentoxide. The upper arm of "B" was used to draw off liquid under its own pressure when occasion arose. "C" is the exit tube which was protected by a phosphorus pentoxide tube. The glass cap "A" was fitted to the cell by means of a ground joint. Passing through this cap was a piece of glass tubing bearing at its lower end the electrode "D." "D" was constructed of platinum foil and was approximately 6 by 2.4 centimeters in size. A similar cap to the rear of "A" (see Figure 1a) held the other electrode which consisted of some six centimeters of No. 28 (B and S) platinum wire. Connection was made to the source of current by filling the glass tubes bearing the electrodes with mercury and immersing in the mercury the wire terminals from the source of potential. Unless otherwise stated, the electrode "D" served as the cathode. The source of current for most of the experiments was a 110 D. C. line. Voltage was measured by means of a Koehler 50,000 ohm voltmeter and current by means of a small three-range Weston ammeter.

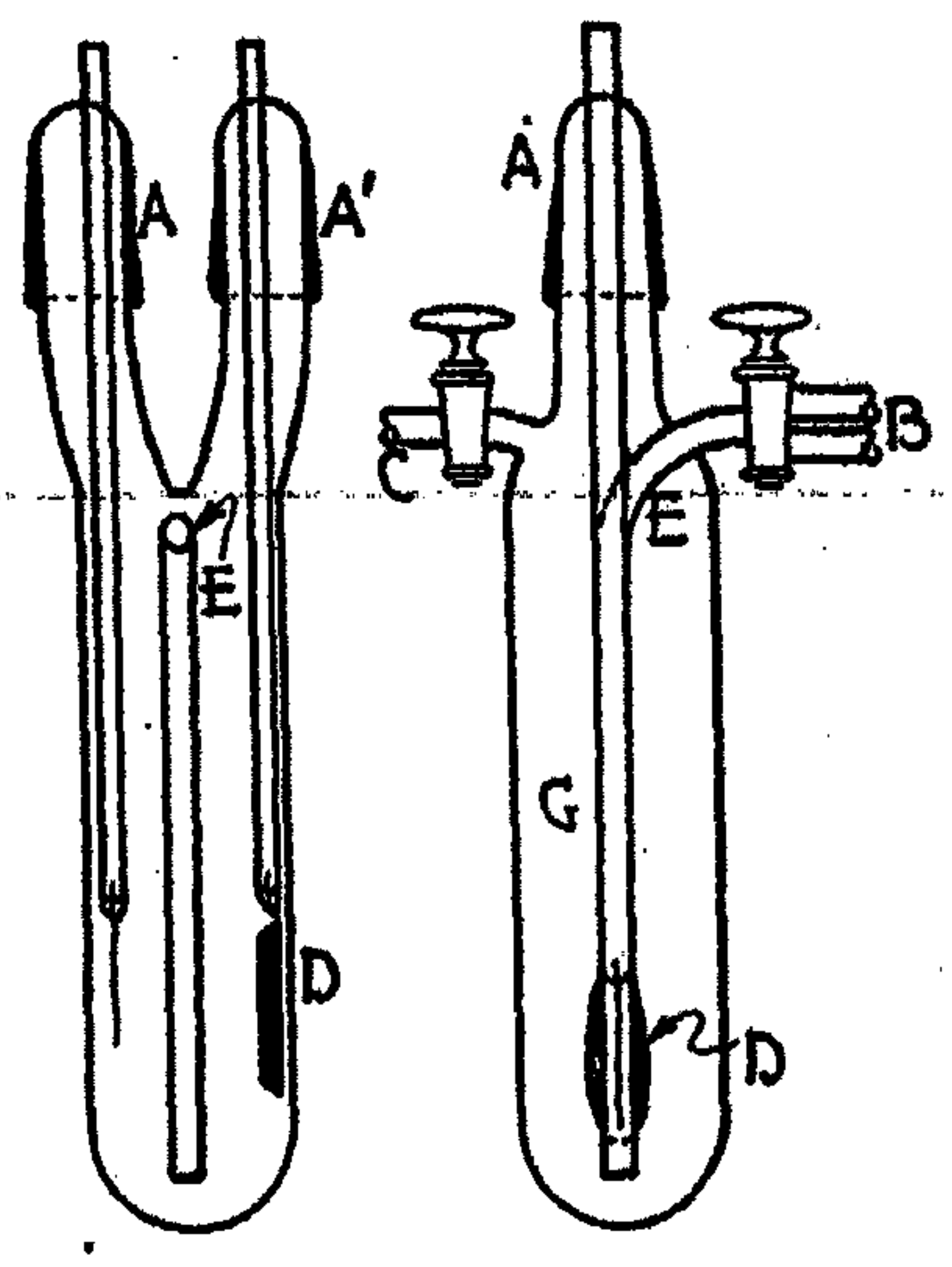

Fig. 1a Fig. 1b
Electrolysis Tube

The method of procedure in general was to dry the tube "G" in an oven at 110° overnight. The phosphorus pentoxide was then adjusted to the hot tube, all openings, except "C," being closed. The tube was then allowed to cool to room temperature. The salt, which had been previously dried either by heating or by desiccation for considerable periods of time, was rapidly introduced through "A." If the salt was hygroscopic, the tube was filled with dry natural gas and the openings all closed. "A" was then partially opened while the gas was allowed to flow. The stoppered weighing bottle containing the salt was then brought into the escaping gas and opened and a small portion of the salt introduced through "A." After the introduction of the salt, the sulfur dioxide was distilled in, until the electrodes were covered and electrolysis was then commenced. At the conclusion of the electrolysis, the refrigerant was removed and the sulfur dioxide was allowed to boil off, escaping through "C." The tube was then heated, usually by bringing hot water around the electrolysis tube and at the same time passing dry natural gas through the interior of the tube. The residue in the tube was then subjected to analysis, as was the deposit upon the cathode.

C. *Electrodes.*

The electrolysis of solutions in sulfur dioxide produces at the cathode, a deposit, whose formation cuts the current, which at best is not large, to very small values. Bagster and Steele used cathodes of various materials in an effort to find one which would eliminate the effect described above. Upon the basis of their work, they recommend silver and copper as the most suitable cathode material. They ascribe the advantage of these materials as due to the formation of the respective sulfides of these metals, these substances being conducting materials. After numerous trials with various cathode materials, we were unable to find any great advantage in the use of the metals recommended by Bagster and Steele. While the original current which passes when silver is used as a cathode is larger than any of the other metals tried, the current soon falls to values approaching that of other metals; any advantage which silver possessed was lost on account of the time that would have been required to silver plate the electrode before each trial. The explanation offered by these investigators for the conducting properties of the silver cathode is certainly in error, for trials with a cathode coated with a layer of silver sulfide gave smaller values of current than did silver itself. Table III gives some of our results in this connection. The electrolyte was a saturated solution of potassium iodate, the cathodes with the exception of mercury, were of the same size, and the anode in each case was the same platinum wire. In each case, the original current fell to values one-tenth or less of the initial value, although somewhat more slowly with the silver electrode; the value recorded in Table III for silver remained constant for nearly an hour before it started to fall.

TABLE III

Cathode	Original Current	Voltage
Platinum	.02 amp.	19
Mercury	.01 "	20
Aluminum	.005 "	18
Silver	.04 "	18
Silver sulfide	.02 "	17
Silver oxide	.02 "	40
Silver oxide*	.20 "	40

*One drop of water was added to the solution.

D. *Electrolysis of KCNS.*

This is one of the few salts which is quite soluble in this liquid, and will conduct a current of considerable magnitude. A light-colored deposit is formed at the cathode which darkens when removed from the solvent, a phenomenon which is general in the electrolysis of all salts studied. The deposit which was carefully dried out of contact of air was dissolved in water, the major portion being soluble. The clear aqueous solution had the following properties:

Acid in reaction, smelled of SO_2.

Reagent	Color of Precipitate
$HgCl_2$	white
$HgNO_3$	black
$AgNO_3$	yellow, white, brown, red, black
$KMnO_4$	brown
$BaCl_2$	white

The water-insoluble residue was extracted with carbon disulfide but was found to contain no free sulfur. When ignited on platinum foil with a small quantity of potassium nitrate it gave a test for sulfates and was therefore a sulfur compound. The reactions indicated above were taken to prove the presence of a sulfite, thiosulfate, and probably one or more of the salts of the thionic acids. Centnerzwer on the basis of a quantitative examination of the cathode deposit from the electrolysis of potassium iodide regards the deposit as a mixture of potassium thiosulfate and potassium pyrosulfite, $K_2S_2O_5$. Whatever may be the true composition of the deposit, it seems well established that it contains no free sulfur as had been suggested by Bagster and Steele. In none of our trials[1] with various cathode materials was free sulfur found; the cathode deposit in general having the properties as described in this case. The anodic products were usually not determined with as great care as were those at the cathode, for, it will be recalled, our purpose was to determine if possible the formation of any reduction products of the electrolyte. However, our observations are recorded as confirming and extending the observations of Bagster and Steele that the anodic products are similar to those produced in the electrolysis of the substance in question in aqueous solution.

In the case of potassium thiocyanate, an amorphous, light-yellow product was formed around the anode. This corresponded in qualitative properties and approximately in quantitative proportions to that obtained when this substance is electrolyzed in aqueous solution[2] namely (CNS)n.

E. Electrolysis of Potassium Iodate.

Potassium iodate is not readily soluble in this solvent and its solutions are therefore not good conductors of the electric current. However, due to the marked chemical differences of the various states of oxidation of iodine, several careful attempts were made to determine if iodine was reduced during the electrolysis of this substance. In a few cases, iodine was produced but this, in the light of more extended experiments, was ascribed to either improperly dried apparatus or solvent, or through failure to remove all traces of sulfur dioxide before subjecting the residue to analysis. It may be stated at this point that this was the most difficult feature encountered in the work with sulfur dioxide as a solvent. A portion of the solvent is retained by the solids present, from which it is extremely difficult to separate. As sulfur dioxide

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[1] Between 50 and 60 in number.

[2] Beilstein: 3, p. 143, 4th ed.

in aqueous solution is itself a reducing substance, results of analyses were frequently misleading. In some cases, this difficulty was obviated by extracting the residue with anhydrous ether.

As has been stated, various cathode materials were tried in connection with this solute—the cathode products in all cases with the exception of mercury were the same—namely the deposit described in paragraph five of this part. The anode deposit appeared to be a gas, although it was not collected or were attempts made to analyze it—at least no solid deposit remained on the anode.

A description of one of the more elaborate experiments with this solute will serve to summarize our results:

Weight of KIO_3	1.3 grams.
Electrodes	Platinum.
Original current	.04 amps.[1]
Voltage	21
Duration of electrolysis	52 hours
Calculated quantity[2]	31.2 coulombs.
Quantity necessary to reduce	1.3 gms.
KIO_3 to KI	362. coulombs.

If reduction to either iodine or iodide had taken place approximately .05 grams of iodine or its equivalent should be present—a quantity much larger than could easily escape detection. On extracting with dry ether, none was obtained. After the ether extraction was completed, the residue, unchanged iodate, was dissolved in water and acidified. No iodine formed showing the absence of iodides.

F. Electrolysis of Ferric Chlorate.

Ferric chloride is moderately soluble in SO_2. On this account, attempts were made to reduce $Fe^{\cdot\cdot\cdot}$ to $Fe^{\cdot\cdot}$ by electrolyzing a solution of this substance in sulfur dioxide. The first attempt resulted in an apparent reduction of some 18% of the $Fe^{\cdot\cdot\cdot}$ originally present. We were not satisfied, however, that reduction came from the action of the current on the salt. The following experiment showed that we were correct in this respect.

Approximately .25 of a gram of ferric chloride was allowed to stand in the liquid for an hour. The solvent was distilled off and then dried gas (carbon dioxide and natural gas) was passed through the tube for two nights and a day. During the day, it was heated by boiling water at one or two hour intervals. At the end of this time, the escaping gas was passed through one cubic centimeter of dilute potassium permanganate solution (about one-fifteenth normal) and in the course of an hour was almost completely decolorized. The dried gas had no effect on the permanganate in the same interval of time. The residue in the tube upon solution in water gave a very good test for $Fe^{\cdot\cdot}$.

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[1] Soon fell to .01 amps.

[2] On basis of constant current of .01 amperes.

The cathode deposit was the typical dark-colored substance already described; the anode was covered with a small amount of a reddish deposit but a gas was also evolved.

G. Electrolysis of Potassium Chlorate.

Potassium chlorate is even less soluble than is potassium iodate. It was hoped that by adding other solutes to carry the current that some of the chlorine would be reduced. Potassium iodide and sulfur trioxide were added in different attempts but in no case was a chloride or free chlorine found. Addition of sulfur trioxide to the potassium chlorate solution caused the solution to become dark red in color. The characteristic deposit was formed at the cathode and a gas at the anode (iodine when potassium iodide was used). The gas was not free chlorine as the platinum anode was not attacked.

H. Electrolysis of Potassium Ferricyanide.

A saturated solution of this salt is but feebly conducting; with platinum electrodes, the current never rose above two milliamperes in a saturated solution. Due to the very low solubility of the salt and the corresponding low current the electrode changes were slight—the cathode had a very thin coat of deposit apparently similar to that already described; no anodic changes were observed. The residue showed the presence of $Fe(CN)_6''''$, but a subsequent experiment without electrolysis gave similar results, reduction being due evidently to occluded solvent.

I. Electrolysis of Potassium Iodide.

It was at this stage of our work that we became acquainted with the work of Bagster and Steele[1] and as our results in some particulars did not agree with theirs, it was thought best to repeat some of their work, potassium iodide being selected for the trial. In addition, it was thought that in a previous case (potassium iodide and potassium chlorate) iodine had been liberated at the cathode. This proved to be a faulty observation which we were able to observe correctly by constructing a cell in which the anode and cathode compartments were separated.

The substance obtained at the cathode was that already described as characteristic; no free sulfur was observed. At the anode, iodine was liberated. This was collected and estimated by extracting the residue after the removal of the solvent with dry ether and titrating the ether solution against standard thiosulfate solution. In several of our trials, an iodine coulometer was placed in series with the electrolytic cell. The highest ratio of $\frac{\text{iodine from KI in } SO_2}{\text{iodine in coulometer}}$ which we obtained was .74. This would indicate either a departure from Faraday's laws[2] or the formation of an anion containing iodine and some

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[1] Trans. Faraday Soc, 8, 51 (1912).

[2] According to Bruner and Bekier, Faraday's laws do hold in SO_2 solutions.

other substance. The following equation[1] might account for such a case as the last suggested:

$$6I' + (SO_3)'' = (SO_3I_6)''''''''$$

We do not claim absolute accuracy for the above ratio; in the three experiments where this was determined the value of this ratio increased each time. It is possible that with improved technique, we could have obtained more consistent results or even a ratio of one, but the time required we felt would take us too far afield from our topic of investigation.

Discussion of Results

An examination of the experimental results just given shows that in none of the electrolyses attempted were cathodic reduction products of the electrolyte found. In each case where sufficient material for analysis was produced, the products possessed similar qualitative properties. These substances are evidently produced by the discharge of the ions of the solvent. All investigators in this field agree that from the standpoint of quantity the chief products are thiosulfates.

Cathodic reduction of the sulfur of the solvent has occurred as the valence of sulfur has changed from +4 to an average valence of +2 in the thiosulfate.

This brings up the interesting question of current density in connection with electrolytic oxidation and reduction.

In the discussion of electrolytic oxidation and reduction, it is generally stated that low current density at the anode or cathode favors oxidation or reduction as the case may be. However, this is far from being universally true as the following argument will show:

Let us consider oxidation first. In addition to the substance to be oxidized, which we may designate as "A," there will always be present the anion of the solvent so that the current at the anode has the choice of at least two paths. It may oxidize the anion of the solvent or it may oxidize the substance "A." Now, since nature always takes the easiest way under the existing conditions, what will happen will depend largely upon the relative ease of oxidation of the anion of the solvent and of "A." If "A" is the more easily oxidized, the solvent will be untouched providing the concentration of "A," the rate of stirring of the solution and the area of the anode is such as to bring in contact with the electrode in unit time a sufficient amount of "A" to take care of all the coulombs passing in that time. If this is not the case, then "A" will be oxidized up to the limit and the necessary coulombs not taken care of by "A," will act upon the anion of the solvent.

From this, it can be readily seen that when "A" is more easily oxidized than the anion of the solvent the oxidation of "A" will be favored by low cur-

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[1] SO_2 probably dissociates in one (or more) of several ways, some of which may be cited:

1. $SO_2 = SO^{\cdot\cdot} + O''$
2. $2SO_2 = SO^{\cdot\cdot} + SO_3''$
3. $SO_2 = S^{\cdot\cdot\cdot\cdot} + 2O''$

See Walden: "Elektrochemie nichtwässriger Lösungen," p. 207; Walden and Centnerszwer: Z. physik. Chem. 39, 513; Puffett: Master's Thesis, University of Kansas, 1923, page 3.

rent density. But when "A" is less easily oxidized than the anion of the solvent, the case is very different. Now, nature by preference would confine her attention to the oxidation of the anions of the solvent with the liberation of oxygen in the case of water and if the current density at the anode is low enough to provide a sufficient quantity of these anions to come in contact with the electrode to take care of the current flowing "A" will be untouched. To get "A" to be oxidized, therefore, it will be necessary to raise the current density by decreasing the size of the anode and advisably, if possible, to decrease the concentration of the anion of the solvent by increasing that of its cation. As an example of this, we may cite a solution of a manganous salt which cannot be oxidized to permanganate by a low current density but may be so oxidized by a high current density especially in acid solution.

Therefore, we must modify the rule to read high current density at the anode is favorable to the oxidation of substances more difficulty oxidized than the anion of the solvent while low current density favors those more easily oxidized than this anion. The same argument and rule holds for reduction at the cathode with the obvious change in terms.

Here, we are dealing with a case where the solvent ions are more easily reduced than the electrolyte and hence their *reduction will be favored by low current densities.* It will be recalled that, at best, solutions in liquid sulfur dioxide transport but small currents; .02 ampere may be taken as a maximum for our experiments. This would give a maximum current density at the cathode approximating .001 ampere per square centimeter which should certainly favor the reduction of the most easily reduced substance.

Summary and Results

1. The qualitative solubilities of a number of substances in liquid sulfur dioxide have been examined. Sulfur dioxide in general is a poor solvent as compared to water or liquid ammonia.

2. Electrolyses of a variety of salts have been carried out in this solvent. Anodic processes are in general similar to those of the same substances in aqueous solutions; cathodic processes involve the discharge of the ions of the solvent.

3. An explanation of the effect of varying current density on electrolytic oxidation and reduction has been advanced.

Chemical Laboratory,
University of Kansas,
Lawrence, Kansas,
March, 1925.

ACID CATALYSIS IN LACTONE FORMATION*

BY HUGH STOTT TAYLOR AND HAROLD WILBERFORCE CLOSE**

The catalytic activity of acids in a variety of reactions, the velocities of which are sufficiently slow to be measurable, has been the object of continued study since the formulation of the dissociation theory. The results of such study have been used to check conclusions regarding the nature of solutions, obtained by other methods of investigation. Arrhenius showed the parallelism between conductivity and catalytic activity in weak acids. He illustrated the principle of isohydry by reaction velocity studies with acetic acid solutions containing sodium acetate. He showed the abnormality of strong electrolytes by showing that, with strong acids, the proportionality between hydrogen ion concentration and reaction velocity effect was not exact, and by the neutral salt effect with such strong acids.

These abnormal catalytic effects with strong acids have at various times been utilised to support (a) the Arrhenius theory of 'active' and 'inactive' molecules and its modern successor the 'radiation' theory of catalytic action (b) the solvate theory of electrolytes, in which the abnormalities were attributed either to the solvation of the ions or of the undissociated salt or acid (c) the dual theory of catalytic activity in which, to both hydrogen ion and undissociated acid molecule, a catalytic activity was ascribed (d) the theory that only the non-hydrated hydrogen ion had any catalytic activity (c) the theory that only alcoholated hydrogen ions had catalytic activity in esterification and (f) the activity theory, which attempts to correlate reaction velocity with the thermodynamic concentrations or activities of the reacting species without specifying the actual molecular nature of those species[1].

There were two main objects in mind in undertaking the present experimental investigations. We desired to ascertain whether the catalytic conversion of hydroxy-acids to lactones exhibits the same characteristics which are shown by various hydrolytic reactions catalysed by acids. We also desired, by study of this reaction in detail, especially in various solvents, to learn, if possible, what is the active agent in acid catalysis.

Henry[2] investigated this reaction under the influence of acids, and came to the conclusion that the reaction velocity is proportional to the hydrogen ion concentration. An examination of his results indicates that the proportionality is not exact, but that, as the concentration of catalysing acid is raised, the reaction velocity increases faster than the hydrogen ion concentration. It was decided to undertake a systematic study of the reaction by vary-

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*Contribution from the Laboratory of Physical Chemistry, Princeton University.

**Abstracted from the thesis of Harold Wilberforce Close presented in partial fulfillment of the requirements for the Ph. D. degree, Princeton University, April 1922. Presented at the Pittsburgh meeting of the A. C. S., September 1922.

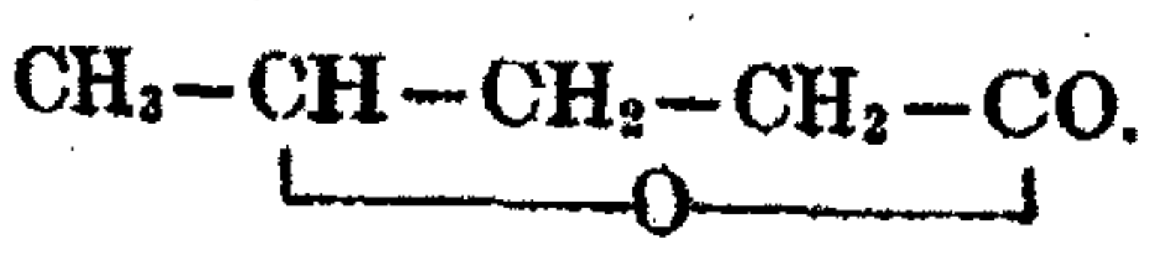
[1] A useful summary of these various points of view is to be found in "A Treatise of Physical Chemistry," Vol. II, Chapter XII, p. 779; Chapter XIV, p. 914 (1924).

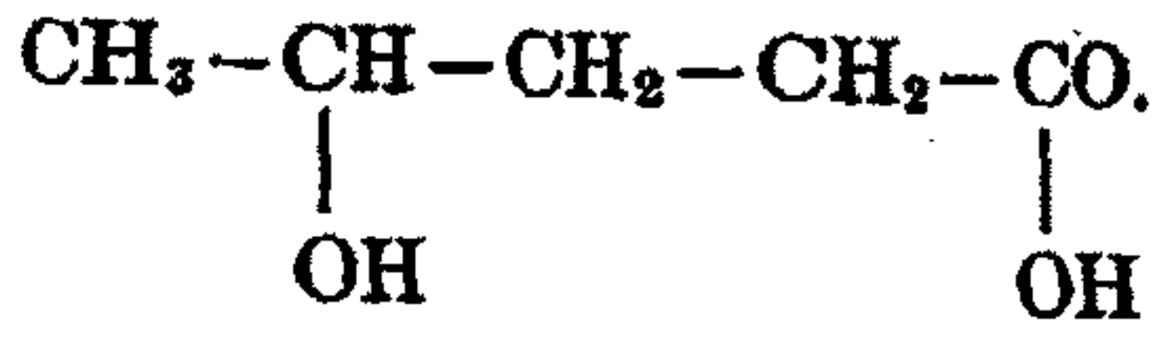
[2] Z. physik. Chem., 10, 96 (1892).

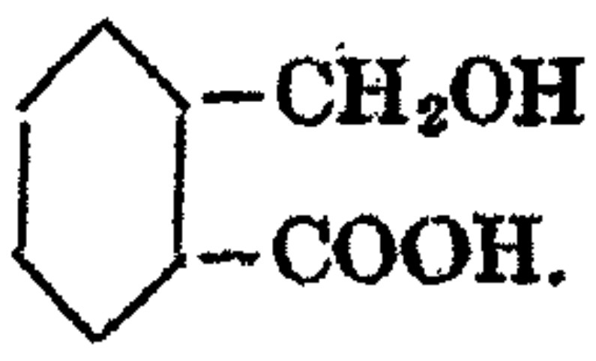
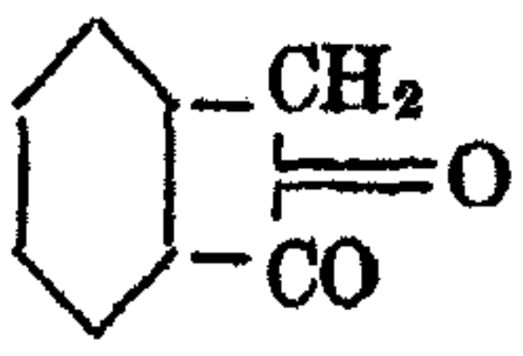
ing in turn each of the following factors:—(a) the nature and concentration of the catalysing acid (b) the nature and concentration of the neutral salt (c) the temperature (d) the solvent.

Experimental

1. *Preparation of Materials.*

a. *Valerolactone.*  $CH_3-CH-CH_2-CH_2-CO$ (CH and CO joined through O). Hydroxyvaleric acid is less stable than its lactone. Consequently, a quantity of the lactone was prepared and was subsequently converted to the hydroxyacid in small quantities as required for each experiment. The lactone was prepared as follows: One hundred grams of cane sugar were heated on a water bath for twenty hours in contact with half a liter of 1:4 hydrochloric acid. This charry mass was then filtered and after the addition of a solution of 35 g. of caustic soda to the filtrate it was evaporated to 100 cc. and the sodium chloride which had separated out was filtered. The crude levulinic acid so obtained was next extracted with ether and fractionally distilled, the quantity passing over between 140° and 170° under a pressure of 15-30 mm. being collected. Thirty cc. portions of this product were then reduced in alkaline solution by use of a 10 percent sodium amalgam. The reduction was carried out in a vessel surrounded by ice and the mixture was constantly stirred. Two hundred grams of amalgam were added in lots of 20 g. every few hours, small quantities of 2:1 hydrochloric acid being also added from time to time as required to prevent the mixture from becoming thick and viscous. The mercury was removed when reduction was completed and 75 cc. of concentrated hydrochloric acid were added. After boiling under a reflux for ten minutes the mixture was cooled and extracted with ether. The ether extract was dried over freshly ignited potassium carbonate, the ether distilled off and the residue repeatedly distilled until a constant boiling point testified to the purity of the product. The valerolactone thus obtained was a colorless sweet-smelling liquid, boiling at 207°.

b. *Hydroxy-valeric Acid.*  $CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_2-\underset{OH}{\underset{|}{CO}}$. The hydroxyacid was prepared by converting the lactone into a soluble salt of the acid, from which the metal was subsequently removed by precipitation, and the free acid liberated. The first method used was to prepare the barium salt and the precipitate the barium as the sulphate. Since this involved the use of sulphuric acid in removing the barium, an alternative method was tried in which the lead salt was prepared by treating the lactone with lead hydroxide and then precipitating the lead with hydrogen sulphide. This was found to give more reproducible results because the hydrogen sulphide could be run in until precipitation was complete, and then the excess entirely removed by shaking under reduced pressure. The method was later simplified by substituting litharge for the lead hydroxide. Litharge can be obtained of more uniform purity and is more stable than lead hydroxide. According to the latter method which was used in all cases except where especially noted to the contrary, three cc. of lactone and seven grams of litharge were warmed with 200 cc. of water and then shaken until the color had practically disappeared. Hydrogen sulphide was then bubbled through until precipitation was complete. After removal of hydrogen sulphide as already described, the solution of hydroxy-valeric acid was used without delay for velocity determinations.

c. *o-Hydroxy-methyl-benzoic Acid.*  This acid was prepared from phthalid  by dissolving the latter in a solution containing a small excess of caustic soda. The solution of the sodium salt of the hydroxy-acid was treated with hydrochloric acid until precipitation was complete. The white precipitate was filtered and washed thoroughly until silver nitrate showed that the chlorides had all been removed. The residue was then sucked dry, transferred to a porus plate, and kept in a vacuum desiccator until used. The dry acid is stable. Titration with alkali showed the acid to be pure.

d. *Ether.* For our purposes it was necessary to use absolute ether and to take all precautions against absorption of moisture. The question as to how well we succeeded in excluding moisture will be referred to later. A good grade of ether was used; was washed three times with dilute caustic soda, and finally eight to twelve times with water. It was then allowed to stand over calcium chloride and subsequently over sodium wire until shortly before it was used. It was then distilled. This ether was kept in a filter-flask with a tightly-fitting, paraffined stopper, and the side tube was closed with a tube of phosphorus pentoxide.

e. *Hydrogen Chloride in Ether.* Into the ether prepared as described a stream of hydrogen chloride gas was led, the gas having previously been dried by passing through two calcium chloride towers followed by a long tube of phosphorus pentoxide. The acid solution was subsequently diluted with absolute ether until it was normal. Precautions against absorption of moisture were taken as in the case of the ether.

2. *Measurement of Reaction Velocity.*

In the case of the hydroxy-valeric acid, 100 cc. of the solution, after removal of the hydrogen sulphide as already described, was placed in a 200 cc. flask, the catalyst added, and the flask filled to the mark. The mixture was immediately transferred to an Erlenmeyer flask and hung in a thermostat, the accuracy of which was ±0.02°C.

At intervals, 20 cc. portions were pipetted off and titrated in the usual way with baryta of convenient strength. Usually seven readings were taken in addition to the initial and final determinations. The time intervals varied, of course, with the speed of the particular reaction. The determinations were always made at least in duplicate and often four determinations were made in cases where the experimental error was unusually large.

When the formula for a simple unimolecular reaction was used in determining the velocity constant of the conversion of hydroxyvaleric acid, the value of the constant was found to fall rather consistently. This was due to the fact, as Henry pointed out, that the conversion to valerolactone is not complete. Consequently the formula for opposed reactions was used and the results obtained were more satisfactory. The following example will serve to illustrate the results obtained by use of the different formulas. The value 1.075 in the second formula was obtained from the observation that equilibrium is established in the reaction when 92.5 per cent of the oxyvaleric acid is changed to lactone.

TABLE I

No. 17 B. Catalyst, .01 N. $HCl+N.CaCl_2$
Jan. 14. Baryta .069 N. Temp. 25°C. a = 13.05cc.

Minutes	Seconds	Time in Minutes	Titer in cc. Baryta	x	$K_1=\frac{1}{t}\log\frac{a}{a-x}$	$K_2=\frac{1}{t}\log\frac{a}{a-1.075x}$
49	40		17.66			
32	5	102.4	15.23	2.43	8.73×10^{-4}	9.45×10^{-4}
5	40	136.0	14.55	3.11	8.68	9.43
52	5	182.4	13.68	3.98	8.66	9.45
25	50	216.2	13.10	4.56	8.63	9.45
9	20	259.7	12.42	5.24	8.58	9.44
39	20	289.7	11.97	5.69	8.58	9.49
23	50	334.2	11.38	6.28	8.53	9.46
End-point			4.61			
Average					8.62	9.45

It is obvious from the above figures that the values for K_1, show a tendency to fall, which is not the case with K_2, in which the effect of the reverse reaction is taken into account.

Experimental Results

Since an example has already been cited which illustrates the method of measurement of the reaction velocity, only the final results need be reported in the tables which follow.

a. *Variation in Catalysing Acid.* Two different catalysing acids of widely differing strengths were used, and in different concentrations. The temperature was also varied. The figures for hydrogen ion concentration are taken either from Kohlrausch and Holborn, from Bray and Hunt[1], or from Dawson and Reiman[2], as indicated in the table.

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[1] J. Am. Chem. Soc., 33, 781 (1911).

[2] J. Chem. Soc., 107, 1426 (1915).

TABLE II

Series and Method	Catalysing Acid	Temp.	K × 10⁴					C_H	Cond. Fig from	$\frac{K}{C_H}$
			1	2	3	4	Mean			
Ser. 1	0.01 HCl	25°	6.82	6.83	6.82	6.84	6.83	0.00971	B+H	703
								0.00989	K+H	691
Lead	0.025 "	"	17.18	17.11	17.14	(16.90)	17.14	0.024	K+H	714
Hydro-	0.05 "	"	34.58	34.04	34.38	34.21	34.30	0.047	B+H	730
xide	0.10 "	"	68.1	67.4	67.1	68.1	67.7	0.092	B+H	736
Method										
Ser. 2	0.01 "	0°	0.51	0.51			0.51	0.00971	B+H	52.5
								0.00989	K+H	51.6
Litharge	0.05 "	"	2.56	2.60			2.58	0.047	B+H	54.9
Method	0.10 "	"	5.28	5.21			5.24	0.092	B+H	57.0
Ser. 3	0.05 $CH_2ClCOOH$	25°	5.83	5.84			5.83	0.0082	D+R	710
Litharge	0.10 "	"	8.76	8.72			8.74	0.0122	D+R	716
Method	0.20 "	"	13.43	13.45			13.44	0.0183	D+R	734

TABLE III

Series and Method	Temp.	Conc. of Neutral Salt	K×10⁴					C_H	Cond. Data from	$\frac{K}{C_H}$
			1	2	3	4	Aver.			
Ser. 1	25°C.	0	33.27	33.82	32.84	32.97	33.23	0.047	K+H	707
		.25N	35.88	36.28	36.07	.	36.08	0.044	K+H	820
.05 N.HCl		.50N	37.73	37.73	37.99		37.87	0.04265	K+H	888
Baryta		1.N	42.48	43.18	43.14		42.93	0.0392	K+H	1095
Method										
Ser. 2	25°C.	0	8.54	8.67			8.61	0.0122	D+R	706
		.005N	7.04	7.13			7.09	0.01035	D+R	685
.1 N		.01N	5.96	6.14			6.05	0.00884	D+R	684
$CH_2ClCOOH$		.02N	4.63	4.57			4.60	0.00667	D+R	690
Litharge										
Method										
Ser. 3	25°C.	0	8.76	8.72			8.74	0.0122	D+R	716
		.005N	7.34	7.40			7.37	0.01035	D+R	712
.1 N		.01N	6.15	6.33			6.24	0.00884	D+R	706
$CH_2ClCOOH$		.02N	4.90	4.80			4.85	0.00667	D+R	727
Litharge										
Method										
Ser. 4	30°C.	0	14.12	14.21			14.17	0.0122	D+R	1161
		.005N	11.67	11.75			11.71	0.01025	D+R	1132
.1 N		.01N	9.87	9.97			9.92	0.00884	D+R	1122
$CH_2ClCOOH$		.02N	7.40	7.46			7.43	0.00667	D+R	1114
Litharge										
Method										

It will be observed that the value of K/C_H rises steadily with increasing concentrations of acid. In other words, the hydrogen ion concentration as determined by conductance methods does not increase with increased acid concentration as fast as the reaction velocity. The conversion of hydroxyvaleric acid to lactone is thus seen to be comparable in this respect to the other examples of acid catalysis, in which, as is well known, the same disproportionality is found.

Variation in Neutral Salt.

(1) *Change in Concentration of Salt.* Table III shows the results obtained when different concentrations of neutral salts were added to reaction mixtures in which the concentrations of the catalysing acid remained constant. Results obtained by different methods are not strictly comparable as it was found that those obtained by the baryta method were consistently somewhat higher than when the lead methods were used.

Considering first the influence of varying amounts of potassium chloride upon the reaction velocity in the presence of .05N. hydrochloric acid, it is obvious that the reaction velocity increases markedly, whereas the hydrogen ion concentration, as determined by applying the principle of isohydric solutions and the law of mass action decreases. The conversion of hydroxyvaleric acid to lactone resembles the other hydrolytic processes in this respect also.

Turning now to the case of monochloracetic acid, it is obvious that addition of sodium acetate, even in very small concentration, produces a marked fall in the reaction velocity. The ratio K/C_H is not constant, there being a tendency for the value of the ratio to fall slightly. In Series 2, a drop in the value of K/C_H as the salt concentration increases is followed by a rise. The series was repeated making some minor improvements in the technique, and when this was done the values shown in Series 3 were obtained. There were considerably higher than those in Series 2, due to the change in method, but again the peculiar minimum was observed. The same concentrations of acid and salt were examined at 30°, in which case a steady drop in the value of K/C_H was observed. Certain it is that the addition of a neutral salt of a weak acid reduces the reaction velocity faster than the hydrogen ion concentration falls. Here again lactone catalysis parallels the other classic examples of catalysis by acids.

(2) *Change in the Nature of the Salt.*

In order to ascertain whether changes in the positive radical of the neutral salt would appreciably alter the reaction velocity, a series of determinations were made using 0.01N. hydrochloric acid, to which were added in turn normal solutions of chlorides of potassium, calcium, and magnesium. These particular salts were chosen in order to see whether either the valence or the condition of hydration has any marked effect. In the crystalline state, potassium chloride contains no water of hydration, whereas calcium and magnesium chlorides crystallize with four molecules of water. Furthermore, calcium chloride tetrahydrate loses two molecules of water and is converted to the dihydrate at 29.8°C., while the corresponding magnesium salt is stable throughout the range of temperatures of these experiments. It was thought that possibly a difference in the relative accelerating powers of calcium and magnesium chlorides would be exhibited as the temperature of the reaction passed through 29.8°C. If this proved to be the case it would be conclusive evidence that hydration was a very important factor in neutral salt action.

TABLE IV

Influence of N Salt upon Reaction Velocity with .01 N HCl

Temp.	0°C.			25°C.			30°C.			30°C.		
Nature of Salt	1	2	Av.	1	2	Av.	1	2	Av.	1	2	Av.
	0.51	0.51	0.51	7.04	6.83	6.94	11.20	11.28	11.24	17.95	17.86	17.91
N.KCl	0.63	0.63	0.63	8.81	8.78	8.79	14.27	14.27	14.02	21.91	22.17	22.04
N.$CaCl_2$				9.45	9.26	9.36	15.23	15.14	15.18	24.23	23.81	24.02
N.$MgCl_2$				9.83	9.64	9.74	16.00	16.01	16.00	25.29	25.00	25.14

TABLE V

Comparison of Action of Various Neutral Salts on
Reaction Velocity of .01 N HCl
.01 HCl = 1.00

Nature of Salt	0°C.	24°C.	30°C.	35°C
	1.00	1.00	1.00	1.00
N.KCl	1.23	1.27	1.26	1.23
N.$CaCl_2$	——	1.35	1.35	1.34
N.$MgCl_2$	——	1.40	1.42	1.40

By reference to the above tables, it is evident that all three salts produce similar effects upon the reaction velocity, but that magnesium is more powerful than calcium, which is in turn more efficient than potassium. The order observed is the same as that of the hydration values of these cations, as determined by Washburn and others, which is an indication that hydration may be the determining factor in the *relative* accelerating power of these neutral salts.

At the same time, changes in temperature make no appreciable difference in the relative accelerating powers of the different salts. Were hydration the predominant factor in determining neutral salt action, it would seem, at first sight, as if a rise in temperature should cause a decrease in the neutral salt effect in aqueous solution. Hydration may, however, be one of the factors involved in neutral salt action, but the influence of temperature upon the hydrating power may be small as compared with the temperature coefficient of the reaction, in which case the latter would prevent the detection of the former.

In particular it should be noticed that no break in the curve for calcium chloride occurs at the transition temperature. This may be because hydration is not an important factor in neutral salt action, or that the condition of a salt in the solid state (that is, as regards hydration) is no criterion of its condition in solution.

c. *Variation in Temperature.* Table VI shows the effect of temperature on the reaction velocity in the presence of hydrochloric and monochloracetic acids both with and without the corresponding neutral salts.

TABLE VI

Influence of Temperature on Reaction Velocity

Catalyst	$K \times 10^4$				Temp. Coefficient Per rise of 5°			Per rise of 10°
	0°	25°	30°	35°	0-25°	25-30°	30-35°	25-35°
0.01 HCl	.510	6.94	11.24	17.91	1.68	1.61	1.60	2.59
0.01 HCl + N.KCl	.627	8.79	14.14	22.04	1.69	1.61	(1.56)	2.51
" N.$CaCl_2$		9.36	15.18	24.02		1.62	1.59	2.57
" N.$MgCl_2$		9.74	16.00	25.13		1.63	1.59	2.58
0.01 N.$CH_2ClCOOH$		8.74	14.17			1.62		
" + .005 N. salt		7.37	11.71			1.59		
" + .01 " "		6.24	9.92			1.59		
" + .02 " "		4.85	7.43			1.53		

It will be noticed from the table that the temperature coefficient is very nearly that of ester hydrolysis, the value of the latter being 2.61. The temperature coefficient decreases somewhat as the temperature rises. Furthermore, the influence of neutral salts on the temperature coefficient is very slight.

d. *Variation of Solvent.* For this purpose, o-hydroxy-methyl-benzoic acid was used instead of hydroxyvaleric acid, because the former is easily obtained in the crystalline form and is stable if kept dry. It is soluble in alcohol, ether, acetone, pyridine and water, at least to a sufficient extent to be suitable for reaction velocity measurements. The two solvents chosen were ether and water since they show markedly different ionizing powers. The hydroxy-acid is converted to its lactone in precisely the same way as is hydroxyvaleric acid, the reaction being very slow indeed in either of these solvents in the absence of a catalyst, but when an acid is present the conversion goes on at a very much faster rate. The preparation of the materials has already been described. About a gram of the hydroxy-acid was carefully weighed out and dissolved, the catalyst added, and the flask filled to the mark. The solution was then quickly transferred to an Erlenmeyer flask and immersed in a thermostat at 0°C. Portions were removed at convenient intervals, the catalysing acid neutralized by quickly running in an equivalent amount of the dilute caustic soda from a pipette, and the unconverted hydroxy-acid then determined by titration in the usual way. The immiscibility of water and ether and the high volatility of the latter made a large experimental error inevitable. The results obtained are best shown graphically by plotting the amount of hydroxy-acid converted against the time.

In the first place it was evident that the reaction was proceeding rather rapidly, although the number of hydrogen ions in an absolute ether solution of hydrogen chloride must be very small indeed. On closer examination, it was evident that the reaction velocity was not decreasing, as it should in an ordinary unimolecular reaction, but remained practically constant as far as the reaction had been followed. One possible explanation of the fact that the reaction progressed at all and that the velocity remained almost constant would be that the undissociated hydrogen chloride is catalytically active, and that the water produced in the reaction breaks down these undissociated acid molecules into ions, the hydrogen ions thus produced being more powerful catalytically than the undissociated molecules. It was perfectly clear, in any case, that water was playing an important role, and therefore it seemed wise to repeat the work, taking greater precautions against contamination by moisture.

Consequently some ether was washed very thoroughly as before, dried over calcium chloride and later over sodium wire. This latter operation was performed three times, after which the sodium remained bright for half a day. The ether was then distilled into a vessel surrounded by a freezing mixture. The outlet tube was closed by a phosphorus pentoxide tube. After sufficient ether had distilled over, some hydrogen chloride gas, which had been dried by passing through two calcium chloride towers and a long tube of phosphorus pentoxide, was led in for a time. The hydroxy-acid was then added to the mixture, still retained in the same flask, and the latter immersed in a thermostat. The course of the reaction was followed as usual by pipetting off the samples from time to time. The fall in the titer showed that the reaction was going on, but at a rate *less than two-thirds* that observed in the previous experiment. The fact that the velocity was reduced to such an extent by taking the extra precautions against moisture seemed to throw some doubt on the assumption that the undissociated molecule was active catalytically. One thing it proved conclusively, namely, that traces of water have a tremendous effect.

It was then determined to run a series of experiments in which very small but increasing amounts of water were deliberately added, all the other factors in the case being kept constant. The results are shown graphically in Figure 1.

Curve No. 1 represents the course of the reaction in 200 cc. of ether dried as above indicated. Nos. II, III, and IV represent mixtures containing .25 gm., .5 gm., and 1.25 gms., of water respectively. In the last case, the ether was saturated with water and the reaction was completed *in less than five minutes.*

The conductivity of all the ether-water mixtures containing both substrate and catalysing acid (except No. IV, which by mistake was not measured) was found to be less than that of conductivity water.

An examination of the curves in Fig. 1, will show that Curve 1, is slightly concave upwards, in Curve II the addition of .25 gm. of water to 200 cc. of ether has made the curve concave downwards. Further additions of water have changed the reaction velocity enormously and have completely changed the shape of the curve. It seems highly probable, therefore, that if *every trace* of water were excluded the reaction would not proceed at a measurable rate. The fact that the greater the precautions taken against moisture the slower the velocity, indicates that in all probability the undissociated molecule is not the active agent in the catalysis.

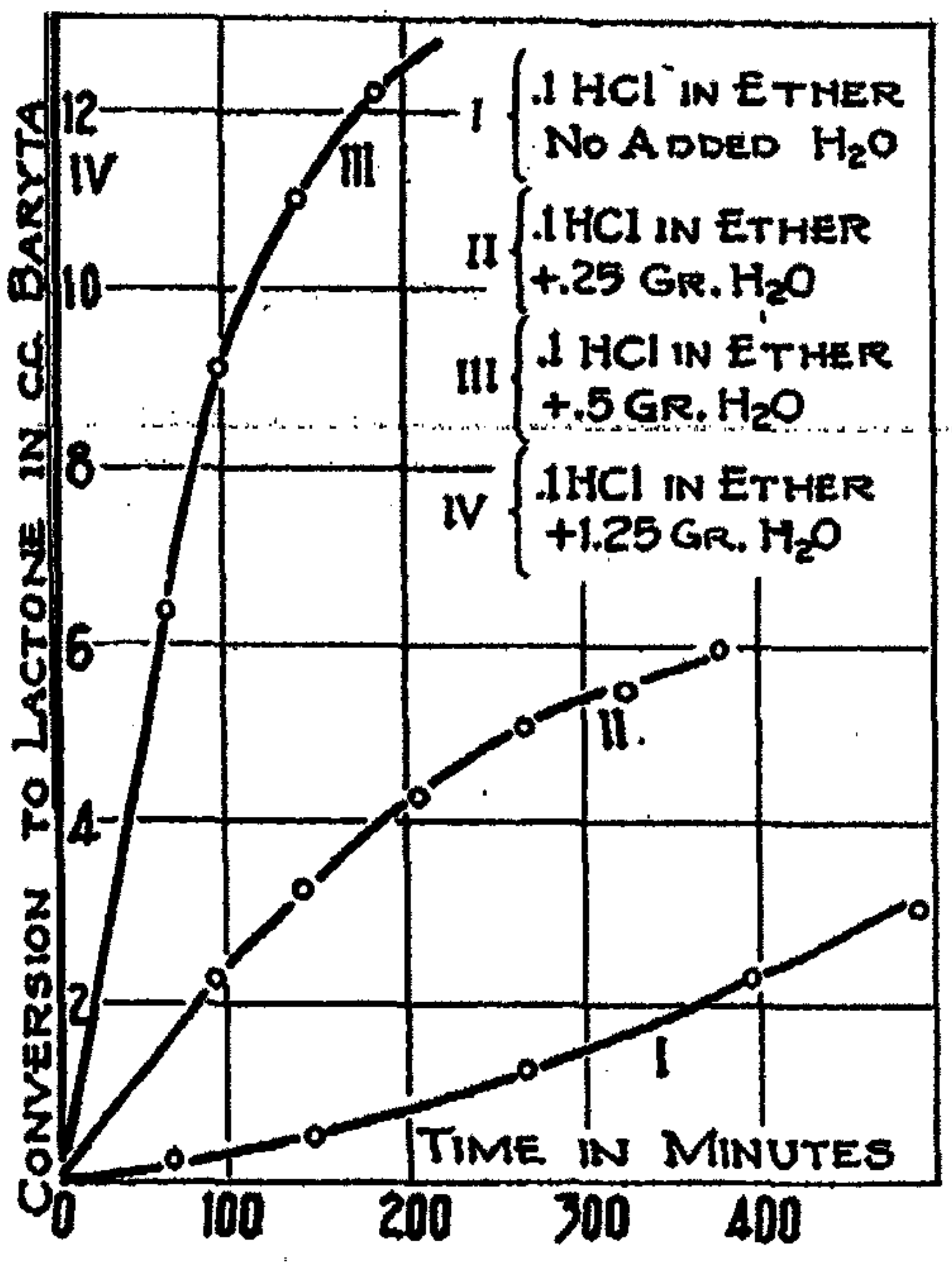

FIG. 1

Experiments were next conducted in water solution to which varying amounts of ether were added. The results showed that the reaction proceeds about 2.6 times as fast in aqueous hydrogen chloride solution as it does in ethereal hydrogen chloride which has been dried as described. Also, it was noted that the addition of ether to the water solution caused a slow but steady increase in the reaction velocity. The velocity-composition curve has the form shown in Fig. 2. The distances the curves can be followed are, of course, limited by the mutual solubilities of ether and water. Were they miscible in all proportions, the curve would undoubtedly rise to a maximum and then descend to the value for pure water.

The facts that have been brought out by these experiments involving change in solvent are these:—

1. The less water in the ethereal hydrogen chloride, the slower the velocity.

2. Very small amounts of water increase the reaction velocity in ethereal hydrogen chloride tremendously.

3. The reaction velocity in presence of 0.1 N. hydrochloric acid is very much greater in ether solution containing less than one mol. percent of water than it is in aqueous solution with the same concentration of catalysing acid, although the conductance of the former solution is immeasurably less.

4. The reaction proceeds faster in 0.1 N. hydrochloric acid than in 0.1 N ethereal hydrogen chloride, and the admixture of ether in small quantities to the water solution causes a slow but steady rise in reaction velocity.

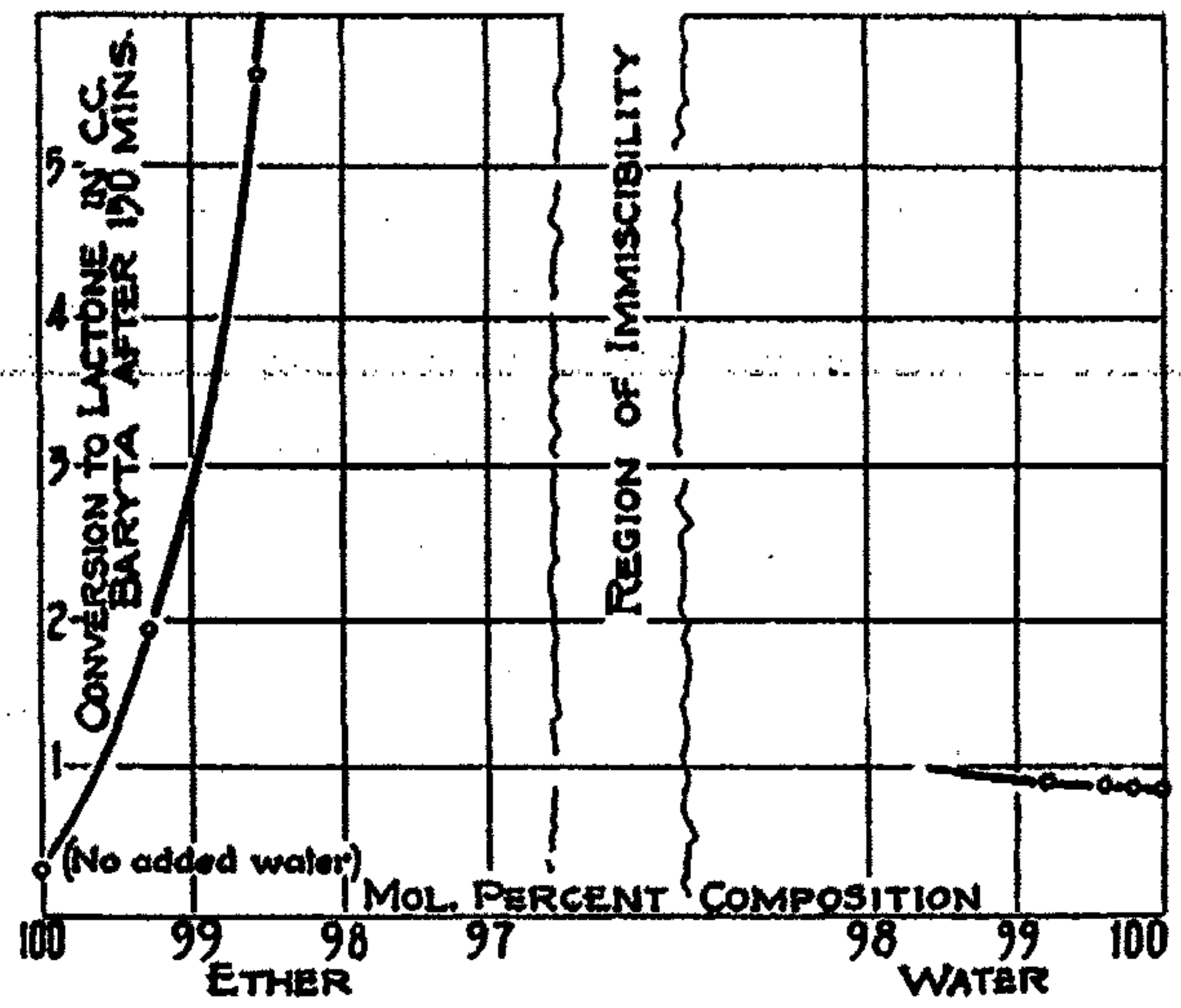

Fig. 2

Discussion of Results

The experimental results may now be considered in comparison with other work on the same reaction. They are in good agreement with the earlier results of Taylor and Close[1], on hydroxyvaleric acid conversion to lactone in acid solutions and solutions of acid and salts. The earlier results established the similarity between acid catalysis in lactone formation and in ester hydrolysis, so far as deviations from proportionality to hydrogen ion concentration and also the influence of neutral salts are concerned. In the present series, this work has been extended to a wider range of salts and to a temperature range from 0°-35°C. as contrasted with a single temperature of 25°C. in the former work. In this respect the results may be compared with some measurements of Garrett and Lewis[2], published since the completion of this work. There is a good agreement between our data and those of Garrett and Lewis, although we found (p. 1088) that the use of the formula for opposed reactions was necessary in order to eliminate a slight drift in our unimolecular constant.

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[1] J. Am. Chem. Soc., 39, 422 (1917).

[2] J. Am. Chem. Soc., 45, 1091 (1923).

Garrett and Lewis did not find this necessary, from which we judge that our data are somewhat more precise than theirs. For this reason our numerical data are not directly comparable with theirs since our formula was

$$K_2 = \frac{1}{t}\log\frac{a}{a - 1.075X},$$

whereas the unimolecular formula contains the term a-x in the denominator.

Garrett and Lewis emphasize that the reaction is only apparently unimolecular and is in reality bimolecular, involving a bimolecular complex between undissociated hydroxy acid and hydrogen ion. The agreement between the two sets of results would imply an identical conclusion in our case. Instead of the hydrogen ion concentration, Garrett and Lewis used hydrogen ion activities, as determined in W. C. McC. Lewis' laboratory from electromotive force measurements, making corrections also for the viscosity of the solutions at their two working temperatures, namely 25° and 35°C. They conclude, also, that water of hydration of the salts is available as solvent water, whereas, from experiments in presence of sucrose, water of hydration of sucrose is not found to be available as solvent water. Were we to apply the same methods of calculation to our results we should reach conclusions identical with theirs. We have not done so for the reason that we feel that the quantitative data on hydrogen ion activities, their variation with temperature, viscosity, hydration of added non-electrolytes and salts, are altogether too arbitrary and uncertain, as yet, to yield any conclusions holding other than an illusory satisfaction. Exact reaction velocity data of this kind must await a more satisfactory basis for the determination of ion activities in solutions. There are indications that such may be found in the theory of Debye and Hückel[1] which in its recent developments[2] seems applicable to concentrated solutions without any assumptions as to water of hydration and the like.

We believe that in the influence of the solvent as displayed in our wet ether solutions we have found a more decisive index of the factors controlling reaction velocity. In this regard we can supplement our own observations with others by Kailan and Neumann[3] who have studied the reaction velocity of lactone formation in alcohol and alcohol-water solutions. These authors find that in 99 per cent alcohol the formation of valerolactone, either with hydrogen chloride or without catalyst, proceeds much faster than in water. With increasing water content, the reaction velocity in presence of hydrogen chloride falls rapidly and passes through a minimum before the aqueous acid solution is reached. This behavior is similar to that occurring in velocity of esterification measurements and also in the decomposition of diazo esters in alcoholic solutions. In each case, water exerts this inhibitive effect, most pronounced, however, in the lactone experiments.

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[1] Physik. Z., **24**, 185, 305 (1923).

[2] Ibid., (1925).

[3] Z. physik. Chem., **93**, 111 (1920); **101**, 63 (1922).

The behavior in our ether experiments is in striking contrast to that manifested in the alcoholic solutions of Kailan and Neumann. Whereas they observed a depression of velocity on addition of water, we observe, in ether, a tremendous acceleration, to a velocity many times greater than that in aqueous hydrogen chloride. Any completely satisfactory theory of the mechanism of lactone formation must be able to account for all these varied phenomena in water, alcohol and ether solutions. We believe that such is possible and that a new point of view with regard to the general problem of ion activity in solutions, aqueous and non-aqueous is thereby gained. This point of view is most readily presented in a survey of our results in wet ethereal solutions.

Several decisive conclusions may be reached, at once, from our experiments in ether. The high velocity of lactone formation in wet ethereal hydrogen chloride as opposed to that in aqueous acid solutions is not due to the ether, since, in dry ether solutions, the reaction velocity is negligibly small. The extreme slowness of the reaction velocity in well dried ethereal hydrogen chloride disposes effectively of any claim that undissociated molecules of the hydrogen chloride have catalytic activity. Nor can the catalytic activity be directly proportional to the acid concentration or to the hydrogen ion concentration as determined by conductance measurements since the conductance of the ethereal solutions was a very minute fraction of that of the aqueous solutions, while the reverse is true of the reaction velocity.

Since the catalytic activity is therefore not directly dependent on the solvent, the undissociated molecules of acid, the acid concentration or the hydrogen ion concentration, it is necessary to relate the observed activity to some other function of the acid catalyst. The experimental data seem to us to offer better qualitative evidence than has hitherto been offered that the reaction velocity is proportional to the hydrogen ion activity as defined in the thermodynamic sense. From the activity concept, it is predictable that the velocity in ethereal solutions of hydrogen chloride saturated with water should be many times that of aqueous solutions of the same concentration of hydrogen chloride saturated with ether. For, hydrogen chloride distributes itself between ether-water mixtures in such a way that the chloride is mainly in the water layer, only slightly in the ethereal layer.

If the reaction velocity is proportional to the thermodynamic activity of the hydrogen ion, the reaction velocity should be the same in ether-water hydrogen chloride solutions in distribution equilibrium with one another. This point is under test in the laboratory at the present time. The experimental results in the present case, however, are evidence for the correctness of this view, since, in the ether solutions, which were many times the hydrogen chloride concentration of such an equilibrium solution, the reaction velocity was many times that of the aqueous acid solutions. Qualitatively, therefore, the experimental results of the present work are in agreement with the demands of the activity theory, which supplies, at the same time, a reason for the abnormal reactivity in wet ether solutions which we have recorded.

We may venture a few words, in conclusion, with respect to the original theory of Lapworth that it is the non-hydrated hydrogen ion which is responsible for catalytic activity, with the quantitative aspects of which Rice and his co-workers have recently been interested[1]. The results of the present work give qualitative support to the theory though quantitatively the evidence is of small value. It is evident that the results in ether are in agreement with the following assumptions. In dry ether, the hydrogen chloride is but feebly dissociated and, consequently, the hydrogen ions are negligibly small. As water is added, ionisation increases tremendously even with amounts of water such as ether will dissolve. The ions produced, by reason of the low water concentration, will be relatively much less hydrated than the ions higher in concentration but more hydrated in aqueous solutions; to this is to be ascribed the higher catalytic activity. On this basis, we should conclude that the non-hydrated hydrogen ion concentration of wet ether solutions of the acid is many times greater than that of the same species in aqueous acid solutions of the same concentration. Whether the thermodynamic activities of such solutions are, in reality, a measure of such concentrations of non-hydrated hydrogen ions as already suggested by Kendall[2] is a problem to which kinetic and thermodynamic measurements must contribute the answer.

Summary

The velocity of lactone formation from γ-hydroxyvaleric acid has been studied in aqueous acid solutions, in presence and absence of salts, over a temperature range of 0-35°C.

The velocity of lactone formation from o-hydroxy-methyl-benzoic acid has been studied in various ether-water mixtures in presence of hydrogen chloride.

In aqueous solutions the reaction shows the same characteristics as the hydrolytic reactions with esters, showing abnormal variation with acid concentrations, neutral salt effect and a temperature coefficient of the usual magnitude, namely 2.56 per ten degree interval, 25-35°C.

In wet ether solutions containing hydrogen chloride the reaction velocity is enormously faster than in water solutions of the same acid strength.

The results indicate that the velocity is not dependent either on the acid concentration, the undissociated acid molecule concentration or on the hydrogen ion concentration as determined by conductance methods. They suggest a proportionality between reaction velocity and the thermodynamic activity of the hydrogen ions.

A method of testing this activity theory has thereby been suggested and such a test is now being undertaken.

Princeton, New Jersey.

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[1] J. Am. Chem. Soc., 45, 2808 (1923); 46, 2405 (1924); 47, 379 (1925).

[2] Proc. Am. Acad. Sci., 7, 56 (1921).

THE HEATS OF OXIDATION OF CARBON MONOXIDE AND OF HYDROGEN BY MANGANESE DIOXIDE AT 0°C*

BY J. C. W. FRAZER AND C. E. GREIDER

It has been shown by Frazer and Whitesell,[1] working in this laboratory, that manganese dioxide can be prepared in a form sufficiently active to powerfully catalyze the oxidation of carbon monoxide to dioxide in a dilute carbon monoxide-air mixture at 0° and below. These authors have further shown that when pure carbon monoxide is brought into contact with this active manganese dioxide, it is taken up by the catalyst and presumably either is adsorbed or reacts chemically with it. Whichever is the case, when attempt is made to remove the gas, only carbon dioxide results, the carbon monoxide being oxidized at the expense of the oxygen of the catalyst.

It was therefore decided to measure the heat attending this adsorption and oxidation, in the hope that it might throw some light on the mechanism of the reaction.

Apparatus and Materials

Except as noted below, the apparatus and the method of its operation were the same as has been illustrated and described by Patrick and Greider.[2] The source of carbon monoxide was a generator which permitted formic acid to drop sulphuric acid previously heated to any desired temperature, thus generating the gas as needed. The gas was purified by passage through a tube containing alternate layers of course and fine soda-lime. The generating flask and drying train, which contained also an open manometer in order better to regulate the admission of the gas, was sealed to the system at E, Fig. 1. The manganese dioxide was prepared from potassium permanganate and nitric acid as described by Frazer and Whitesell, pressed and dried at 150°-160° in vacuo. The source of hydrogen was a tank of the commercial compressed gas, which was freed of oxygen by passage through a U-tube filled with heated platinized asbestos, followed by a second U-tube filled with phosphorus pentoxide.

Procedure

Preliminary experiments with carbon monoxide showed that a large amount of heat was liberated during the admission of the gas to the manganese dioxide, indicating that the oxidation was practically immediate. Equilibrium was not attained at the end of several hours, however, due to the slow diffusion of carbon dioxide out of the adsorption or reaction bulb and of carbon monoxide into it.

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*Contribution from the Chemical Laboratory of Johns Hopkins University.

[1] J. Am. Chem. Soc. 45, 2841 (1923); also Whitesell: Dissertation, Johns Hopkins University (1923).

[2] J. Phys. Chem., 29, 1031 (1925).

The following procedure was therefore adopted. The system was evacuated as described in the preceding article, including the adsorption bulb, which contained one gram of pressed and dried manganese dioxide. The stopcock at H was then closed, pressure equalized, and the bulb detached and weighed. It was then placed in the calorimeter and attached to the system, which was re-evacuated, while at the same time the drying train was being swept out with carbon monoxide, which escaped at F. When evacuation was complete, the bulb had come to the temperature of the calorimeter, which was then made ready for a heat measurement.

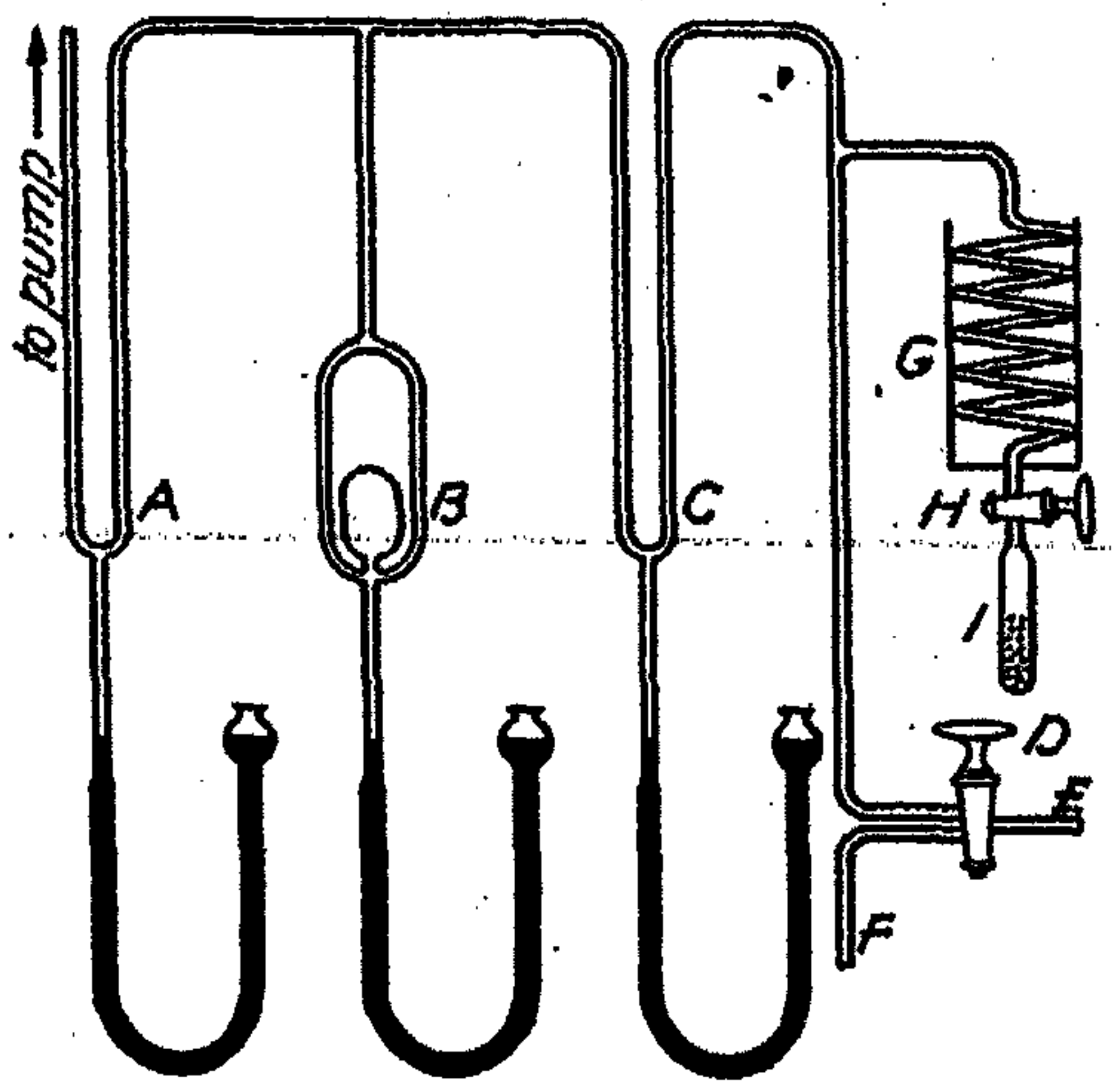

FIG. 1

The stopcock H was then opened and the stopcock D so turned that a slow current of carbon monoxide was admitted to the system. The rate of admission of the gas was so regulated that it required five minutes for the pressure to reach 650-700 mm. When this pressure was reached, the stopcock was closed and the three-way stopcock D so turned that carbon monoxide was no longer admitted to the system, in order to prevent diffusion to and from the adsorption or reaction bulb. Under these conditions thermal equilibrium was established in about half an hour. Measurements of equilibrium pressure could not be made by this method.

When no more heat was given off, the total heat was recorded, the stopcock to the bulb (H) was closed, the pressure equalized, and the bulb again detached, dried and weighed,—the increase in weight being recorded as carbon monoxide taken up. The bulb was then replaced in the calorimeter, and after it had acquired the temperature of the latter, it was attached to the system and evacuated for one hour, and the heat of desorption of the carbon dioxide measured. The bulb was then closed, the pressure equalized, and the bulb detached and weighed,—the loss in weight on evacuation being recorded as carbon dioxide removed, which included both that which had been adsorbed and that in the free space of the bulb. Calculation of the total loss in weight as carbon dioxide necessitates the assumption that at equilibrium the carbon monoxide is practically completely oxidized, which is justified both by the observations of Whitesell, to which reference has already been made, and by the magnitude of the heat effect as measured.

At the end of the run, particles of manganese dioxide near the top of the bulb had changed from black to orange in color. When this sample is heated over night at 150° in a current of air, the orange color disappears. This treatment does not, however, restore the original activity of the sample, and a second run shows only about half of the amount of oxidation shown on the first run. A third run with the same sample after the same treatment shows still further falling off in activity. Heating in a current of oxygen is much more efficient in restoring the activity of the sample.

The results of the above measurements are recorded in Table I.

Measurements with Hydrogen

It had been observed in the dynamic method used by Whitesell that hydrogen in an air mixture was not catalytically oxidized by manganese dioxide at this temperature. It was thought that this might be due to poisoning of the catalyst by the water formed from the oxidation of the first portions of hydrogen admitted, since it is known that water poisons the catalyst for the oxidation of carbon monoxide. Runs were therefore made using hydrogen in place of carbon monoxide. The hydrogen was admitted to the system in the same manner as was the carbon monoxide, except that the stopcock H was left open after the hydrogen was admitted.

It was found that a slow but continuous fall in the pressure of the gas in contact with the catalyst took place. However, the heat given off at the end of an hour, as well as the increase in weight of the bulb, was negligible, indicating that the amount of water formed during this time had little if any effect on the catalyst.

TABLE I

Oxidation of Carbon Monoxide

	Sample III	Sample IV		
	Run 1	Run 1	Run 2	Run 3
Heat on admission of CO—calories	67.1	67.7	37.7	45.2
Heat on desorption of CO_2—calories	7.3	6.3	3.5	5.4
Millimols CO taken up	1.17	1.17	0.67	0.80
Millimols CO_2 removed	0.97	0.97	0.53	0.64

The fact that a slow but continuous fall in pressure of the gas in contact with the catalyst occurred, indicated that oxidation of the hydrogen was apparently taking place, but its slowness made it impracticable to follow the heat of the reaction. A bath of ice and water was therefore substituted for the calorimeter, and measurements made with the bulb immersed therein, no attempt being made to determine the heat of the reaction. Hydrogen was admitted to the system, the initial pressure read, and the change in pressure of hydrogen over the catalyst over a number of days was read and recorded, the results being given in Table II. The recorded temperatures are room temperatures, the bulb containing the manganese dioxide being kept at 0° throughout.

TABLE II

Oxidation of Hydrogen

Time hours	Pressure mm.	Temperature
0	612.7	25.7
3	596.2	26.0
19.5	560.5	24.3
27	555.7	25.5
50	537.2	25.8
70	529.0	26.3

Discussion

The work of Frazer and Whitesell, and of Patrick and Greider, already referred to, makes it seem very probable that carbon dioxide is rather easily desorbed from manganese dioxide at 0°. The observed decrease in weight of the bulb after evacuation for one hour did not, however, correspond to as much carbon dioxide as could have been formed from the carbon monoxide taken up. This might be explained by assuming the oxidation of the carbon monoxide to be incomplete, but this assumption agrees neither with the observations of Whitesell nor with the magnitude of the heat effect observed, which is shown below to be greater than that calculated on the assumption that all the carbon monoxide entering is oxidized.

It is assumed therefore that a portion of the manganese dioxide is reduced to MnO, which would with the CO_2 then form $MnCO_3$. This also accounts for the orange color shown by a portion of the catalyst after it is reduced It is assumed that for every mol of carbon dioxide pumped off a corresponding amount of manganese dioxide has been reduced to Mn_3O_4. It is further assumed that all the carbon monoxide entering is oxidized; therefore the number of mols of carbon monoxide undergoing the reaction

$$CO + MnO_2 \longrightarrow CO_2 + MnO + MnCO_3$$

is the difference between the number of mols of CO entering and of CO_2 removed.

The heats attending these reactions were evaluated from the heats of formation,—the heat of adsorption of carbon dioxide being taken as numerically equal to its heat of desorption as measured. It should be noted that this heat of adsorption corresponds, not to the total amount of carbon dioxide removed, but to this minus the undetermined amount present in the free space of the bulb. It is possible also that some manganous carbonate is decomposed by the evacuation, since manganous carbonate probably has an appreciable carbon dioxide pressure even at this temperature.

All the heats of reaction corresponding to the weights of carbon monoxide and dioxide observed were summed up, together with the heat of adsorption of the carbon dioxide, and were compared with the total heat observed. These data are given in Table III.

TABLE III

Heat Data for Carbon Monoxide Oxidation

Reaction	Heat—cal.			
	Sample III	Sample IV		
	Run 1	Run 1	Run 2	Run 3
1	−7.0	−7.0	−4.9	−5.6
2	−23.2	−23.2	−12.7	−15.3
3	5.5	5.5	3.9	4.4
4	79.7	79.7	45.7	54.6
CO_2 adsorbed	7.3	6.3	3.5	5.4
Total heat calc.	62.3	61.3	35.5	43.5
Total heat obs.	67.1	67.7	37.7	45.2
Difference-percent	7.2	10.4	6.3	3.8

Reaction 1—$MnO_2 \longrightarrow MnO\ (+O)$
Reaction 2—$1\frac{1}{2}MnO_2 \longrightarrow \frac{1}{2}\ Mn_3O_4\ (+O)$
Reaction 3—$MnO + CO_2 \longrightarrow MnCO_3$
Reaction 4—$CO\ (+O) \longrightarrow CO_2$

The results given by Sample IV, Table III, indicate that when the catalyst is reduced with pure carbon monoxide it is reoxidized with considerable difficulty. After the first run the sample was heated over night in a current of dry air, as described under "Procedure". Its oxidizing power on the second run, after this treatment, was only about half of that shown on the first run, indicating that it had not been completely reoxidized. It was then heated over night at the same temperature—150°-160°—in a current of oxygen. The third run, after this treatment, showed a greater oxidizing power than the second, the extent of the oxidation being about two thirds of the value obtained on the first run. Continued heating in a current of oxygen should therefore completely restore the activity of the sample, by completing the reoxidation of the catalyst.

Calculations were made to see if the change in pressure of hydrogen over the catalyst, Table II, was proportional to either the pressure or the square of the pressure of the hydrogen over the sample. Values of K for different values of t were obtained for the equations

$$-\frac{dP}{dt} = KP$$

$$-\frac{dP}{dt} = KP^2$$

In either case the values of K fell off considerably with increasing values of T. In case the reaction had been proportional to the amount of hydrogen adsorbed by the catalyst, K as calculated would have increased with increasing time and decreasing pressure, since the ratio of the amount of a gas adsorbed to the pressure increases as the pressure decreases. In other words, the adsorption is relatively greater at lower pressure.

The decrease in value of K with increasing time is probably due to changes in surface of the catalyst, brought about by the slow oxidation of the hydrogen, which cause the reaction rate to decrease.

Summary

1. The oxidation of carbon monoxide and of hydrogen by active manganese dioxide has been studied, and the heat of the former reaction has been measured.

2. A mechanism has been proposed for the oxidation in the case of carbon monoxide.

THE ADSORPTION OF GASES BY GRAPHITIC CARBON

BY H. H. LOWRY AND S. O. MORGAN

Charcoals used in all the previous studies of adsorption of gases by "carbon" reported in the literature have been prepared by the thermal decomposition of carbonaceous materials. The data given in a previous paper[1] indicate (1) that such so-called "carbons", or charcoals, are not pure carbon but hydrocarbons, in which the carbon hydrogen ratio is dependent on the temperature history of the specimen considered; and (2) that, within the range studied, the amount of gas adsorbed varies with the hydrogen content of the charcoals. This gave rise to the question as to whether or not pure carbons, such as graphites, could be prepared with adsorptive capacities similar to those of charcoals. It was pointed out in this earlier paper that the data contained therein together with those reported in the literature on the adsorption of gases by charcoals are not inconsistent with the view that the large adsorptive capacities of charcoals are due to a combination of a large ratio of surface to mass and to what may be described as the degree of unsaturation of the forces holding the atoms together in the solid. Both of these conditions were likewise found to be directly related to the hydrogen content of the charcoals. From these considerations the low adsorptive capacity of ordinary graphite may be regarded as due both to the small ratio of surface to mass and to a relatively low degree of the unsaturation of atomic forces; and, therefore, if graphite could be prepared by some means whereby these conditions might be made to approach those of ordinary charcoals, the adsorption capacity should be very greatly increased.

The preparation of "pyrographitic acid", which has been shown by Burns and Hulett[2] to be graphite in a fine state of division, seemed to offer the possibility of preparing graphites of different degrees of fineness, that is, with different ratios of surface to mass. "Pyrographitic acid" results from the explosion of "graphitic acid" which has been shown by Hulett and Nelson[3] to be an oxide of carbon, probably C_3O or $C_{11}O_4$. Therefore by oxidizing graphite, in the preparation of "graphitic acid", to different extents, and then exploding the resulting "oxide", it should be possible to prepare a series of graphites each with a different degree of unsaturation of the atomic forces, as well as a different fineness. The data in this paper will show that graphites may indeed be so prepared which have a maximum adsorption capacity of about one-third to one-fourth of that of the best adsorptive charcoals. Further the adsorptive capacities of these graphites vary in the same order as the extent of oxidation of the original "graphitic acid".

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[1] H. H. Lowry: J. Am. Chem. Soc. 46, 824 (1924).

[2] J. Am. Chem. Soc. 45, 572 (1923).

[3] Trans. Am. Electrochem. Soc. 37, 103 (1920).

Preparation of Samples

Ceylon graphite, obtained in large lumps, was filed to a powder, treated with hydrofluoric acid for several hours in order to reduce the ash content, washed and dried. Small batches of the graphite powder were digested with fuming nitric acid, washed and heated according to the method described by Luzi[1]. This method, besides further reducing the ash content, increases the volume of the material ten to twelve times and makes the material more susceptible to oxidation in the preparation of "graphitic acid". The "Luzied" graphite was converted to "graphitic acid" by the Brodie[2] method using fuming nitric acid and potassium chlorate following the detailed procedure of Selvig and Ratcliffe[3]. The degree of oxidation was controlled by the number of treatments given the material. Three "graphitic acids" were prepared using two, four, and seven treatments respectively. The oxidation could be carried further only with great difficulty on account of the fact that the "graphitic acid" becomes colloidal and swells in water resulting in a gelatinous material which cannot be washed readily.

The graphitic acids so prepared were analyzed[4] by the method described by Hulett and Nelson by gently heating a known weight of the material in vacuo, which causes it to explode, and collecting and analyzing the gases evolved. The results of the analyses gave ratios of carbon to oxygen 3.98 ±0.04 (2), 3.61 ±0.06 (6), and 3.12 ±0.05 (8) for the "graphitic acids" prepared with two, four and seven treatments respectively. The plus and minus values represent the probable error of the mean as calculated from the individual analyses and the figures in parentheses the number of analyses made.

"Pyrographitic acid" was prepared from each of the "graphitic acids" by exploding them in vacuo in the same way as for the analyses. In the following discussion the "pyrographitic acids" obtained from the "graphitic acids" which received two, four, and seven treatments with fuming nitric acid and potassium chlorate will be designated graphites I, II, and III, respectively. The fine powders resulting from these explosions were collected and pressed into discs 5/8" in diameter and 1/32" thick, using a pressure of 50,000 lbs. per sq. in. Discs of Graphite I gave a laminated fracture which had much the appearance of the original graphite. This was less marked in the case of Graphite II, while discs of Graphite III did not have sufficient strength to lift whole from the die. Experiments made on Graphite I, as will be seen later, showed that the pressed and unpressed samples had *identical* adsorptive capacities.

An attempt was made to prepare a "graphitic acid" from graphite II without success owing to the fact that the material took fire even at 80°C in the atmosphere above the mixture of fuming nitric acid and potassium chlorate

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[1] Ber. 24, 4085 (1891); 25, 214 (1892).

[2] Phil. Trans. 149, 249 (1859).

[3] Trans. Am. Electrochem. Soc., 37, 121 (1920).

[4] We wish to acknowledge our gratitude to Mr. W. R. Erickson for making these analyses as well as for the preparation of Graphite III.

This observation indicates how great an increase in chemical reactivity has been brought about by the change in form of the graphite, since ordinary graphite burns only with considerable difficulty at temperatures much below 1000°C.

Description of Apparatus and Method of Measurement of Adsorptive Capacity

The apparatus used for measurements of adsorptive capacity is shown in Fig. 1 and was designed primarily for the measurement of the adsorption of small amounts of gas by small amounts of material with the elimination of all stop-cocks in the adsorption system and thereby preventing the possibility of contamination of the material by grease. Several novel features of the apparatus seem to warrant a description of its construction and method of manipulation.

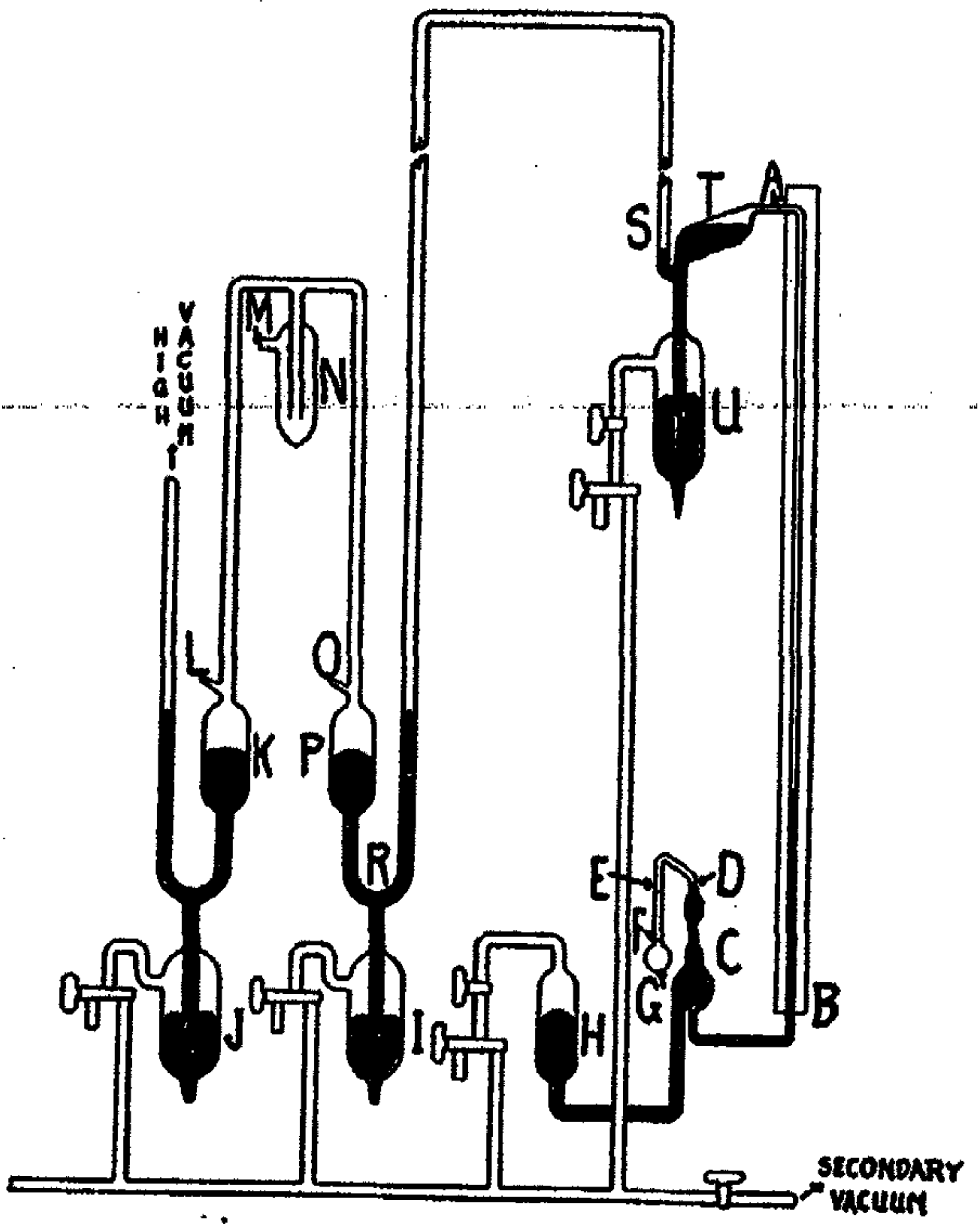

Fig. 1

Apparatus for the Measurement of the Adsorption of Gases.

Preliminary to a "run", a sample of the material to be used was weighed in air, evacuated at 200° C in a stoppered weighing bottle to <0.001 mm. at 200° C and weighed again; the loss in weight which represents the weight of adsorbed gas and moisture was applied as a correction to the weight of the sample when weighed into sample tube G of the apparatus. The volume of the sample tube to the etched mark F, together with the volumes of the other calibrated parts of the apparatus, was determined by weighing the amount of mercury necessary to fill it; and the free space, i.e., that not occupied by carbon, was calculated to be the volume of the tube empty less the volume of the graphite (density = 2.215[1]). The tube was sealed in place and since the connecting tube FED was of only 4 mm. O.D. this could be done without a significant change in volume. The tube FED was calibrated in two parts from F to E and E to D. After sealing on the tube, the whole apparatus was evacuated, by means of a mercury condensation pump with liquid air trap, for 36 to 48 hours while the sample was heated to about 250°C. During evacuation the mercury in the traps was kept in the bulbs H, I, J, and U so that all parts of the apparatus were thoroughly evacuated. The sample was allowed to cool before the pump was cut off by means of the mercury trap R. Evacuation being completed the mercury was forced into the cut-out R so that the system to P could be let down to atmospheric pressure. The tips of the tubes L, M, and O were then broken[2], and the mercury in P and K forced up to just below the tubes L and O. The gas[3], the adsorption of which was to be studied, was then passed through M for several hours and without interrupting the flow of gas the tips were sealed off at L and O and the tube M sealed at a constriction. Gas at atmospheric pressure was now enclosed in the system LMNO and to get to the sample had to pass the trap R. Since it is impossible to allow gas to pass up a large column of mercury without carrying some mercury with it, the two bulbs K and P were sealed into the system so that the pressure in the closed system could be reduced to about $^1/_5$ atmosphere. Before allowing any gas to pass R, the mercury was raised in the Töpler pump T and in C to the etched mark D. The position of the mercury in the tube AB was read off on a fixed meter stick by means of a simple cathetometer[4]. This position was used as the zero point for calculating the subsequent pressures in G. A couple of bubbles of gas were now allowed to pass R and by means of the Töpler pump brought into the calibrated tube AB. This displaced the mercury below its original position by an amount equal to the pressure of the gas in the tube, and hence a reading of the new position gives the data necessary for calculating both the pressure and volume of gas present while the temperature is readily determined by a thermometer hanging along the tube AB. Before this gas can be driven over onto the sample by the Töpler pump, the mercury in C must be lowered so that mercury will not be carried over with the gas. (It is necessary to first lower the mercury in the Töpler pump in order that the gas in the tube AB be not drawn over on lowering the mercury in C.) On drawing the mercury back into the large bulb of

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[1] Burns and Hulett: loc. cit.

[2] Except in the case of hydrogen, which was admitted through a palladium valve.

[3] *Carbon dioxide* was prepared by dropping 1:1 H_2SO_4 on a saturated solution of $KHCO_3$ and was dried over P_2O_5 before entering the apparatus. *Nitrogen* was prepared by gently warming a solution of 100 gr. $NaNO_2$ and 100 gr. NH_4Cl in 500 c.c. of water, passing the gas through a red hot quartz tube to decomprose oxides of nitrogen, then through dilute H_2SO_4 to remove NH_3 and finally over P_2O_5. Liquid air was kept on the trap N during the experiments with N_2 and H_2 and solid acetone during the experiments with CO_2.

[4] H. H. Lowry, to be published.

the Töpler, after driving the gas into the sample tube, the column of mercury breaks leaving a Torricellian vacuum above the mercury in the tube AB. Therefore on raising the mercury in C once more to the mark D and reading the new position of the mercury in AB, the pressure of the gas in the sample tube is directly obtained as the difference of the two readings. Then with this value together with a knowledge of the volumes and temperatures of the separate parts, the amount of "free" gas can be calculated. The difference between this amount and the total quantity of gas admitted to this closed system represents the amount of gas adsorbed. In practice the sample tube and connecting tube to the mark E are kept in a constant temperature bath—ice for 0°; boiling ether vapor for 35.0°; acetone 56.7°; benzene 80.4°, and water 100°; and liquid air for −191°—while the remainder of the connecting tube is at room temperature. After each admission of gas, the pressure at each of the several temperatures is read, allowing time (1-2 hours) for equilibrium to be attained, and thus several isotherms are determined concurrently. Actually the apparatus was designed so that two samples could be run together, the changes necessary for this being obvious.

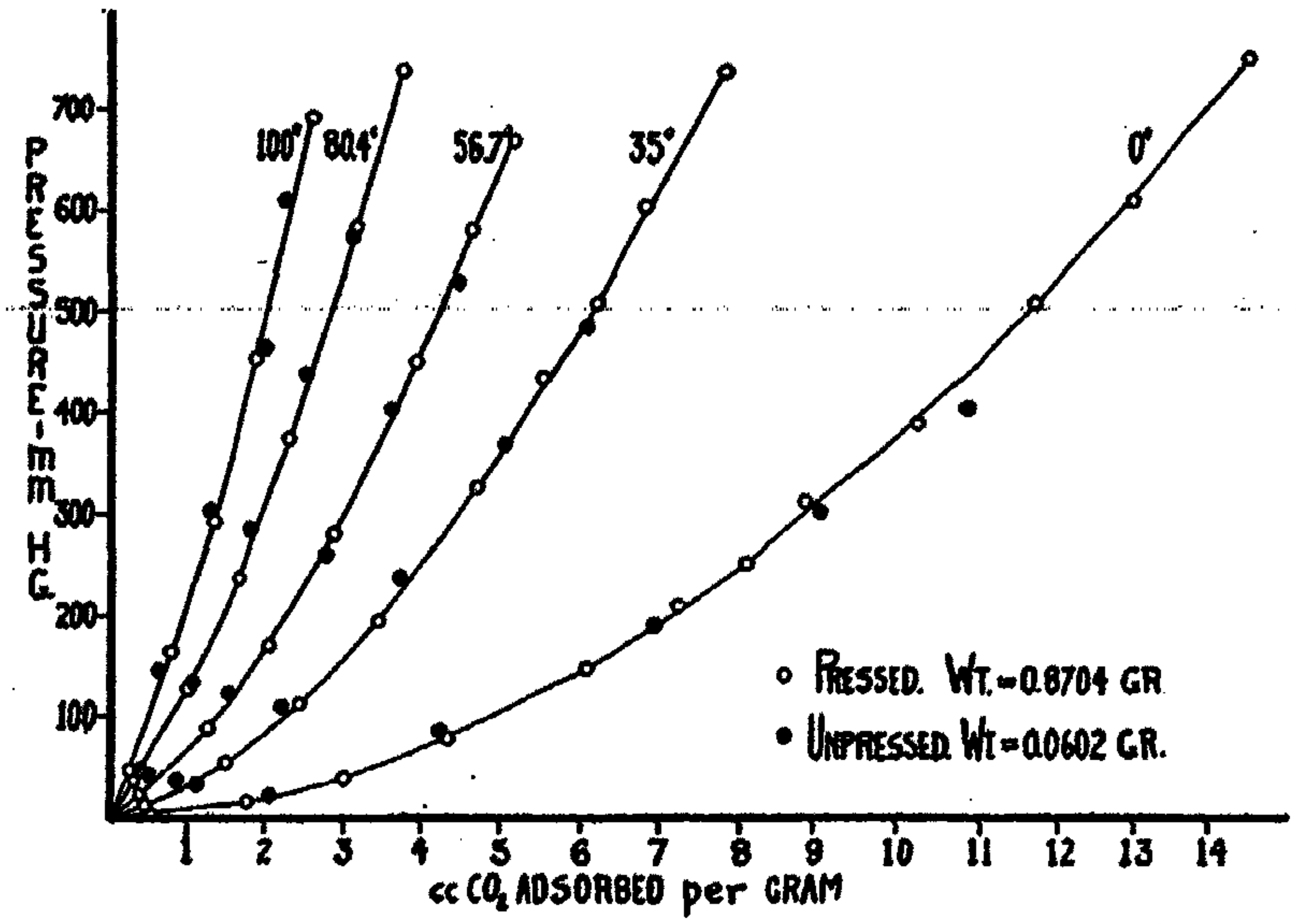

Fig. 2

Adsorption Isotherms of Carbon Dioxide on Pressed and Unpressed Graphite at 35°, 56-7°, 80-4°, and 100°C.

Experimental Results

The adsorption of carbon dioxide at 0°, 35°, 56.7°, 80.4° and 100° by Graphite I, both pressed and unpressed, was determined up to pressures of one atmosphere by the method described above. Similarly measurements of the amounts of nitrogen adsorbed by the three graphites, I, II and III, were made at 0°, 56.7°, and 100° and pressures up to one atmosphere. There is also included data on the adsorption of hydrogen at the temperature of liquid air (−191°) by Graphites I and II. These data are given in Table I, II and III and graphically in Figs. 2, 3, 4, 5, and 6. The accuracy with which the individual measurements can be made and reproduced can be seen, from inspection of the Tables and Figures 2 and 3, to be highly satisfactory, and in fact is equal or superior to the accuracy which may be obtained by any method hitherto described. The fact that even though the data are plotted on scales ranging from 40 to 0.4 c.c. adsorbed per gram per unit length in the Figures with no significant difference between the regularities of the data, is itself good evidence of the accuracy with which the measurements can be made by the method described. This fact also justifies the inclusion in the Tables of at least three significant figures in presentation of the data regarding the amount adsorbed. Also since the results are reported as c.c. N. T. P. of gas adsorbed per gram of material, it is obvious that the calculated error in the case of the unpressed Graphite I, Table 1B, where only 0.0602 grams of material was used, is more than 13 times that in the case of the pressed sample Table 1A, where 0.8074 grams was used, yet the difference of the calculated amounts of CO_2 adsorbed per gram for the same temperature and pressure differ at no time by more than 0.2 c.c. Also in the case of N_2 on Graphite I where two runs at 0° were made on the same sample, the difference in amount adsorbed at any given pressure is always less than 0.01 c.c. per gram. Duplicate runs were also made at 56.7° and 100° with just as satisfactory agreement, though the data are not included in order to economize space. However, no significant value can be assigned to the absolute accuracy of this or any other method of

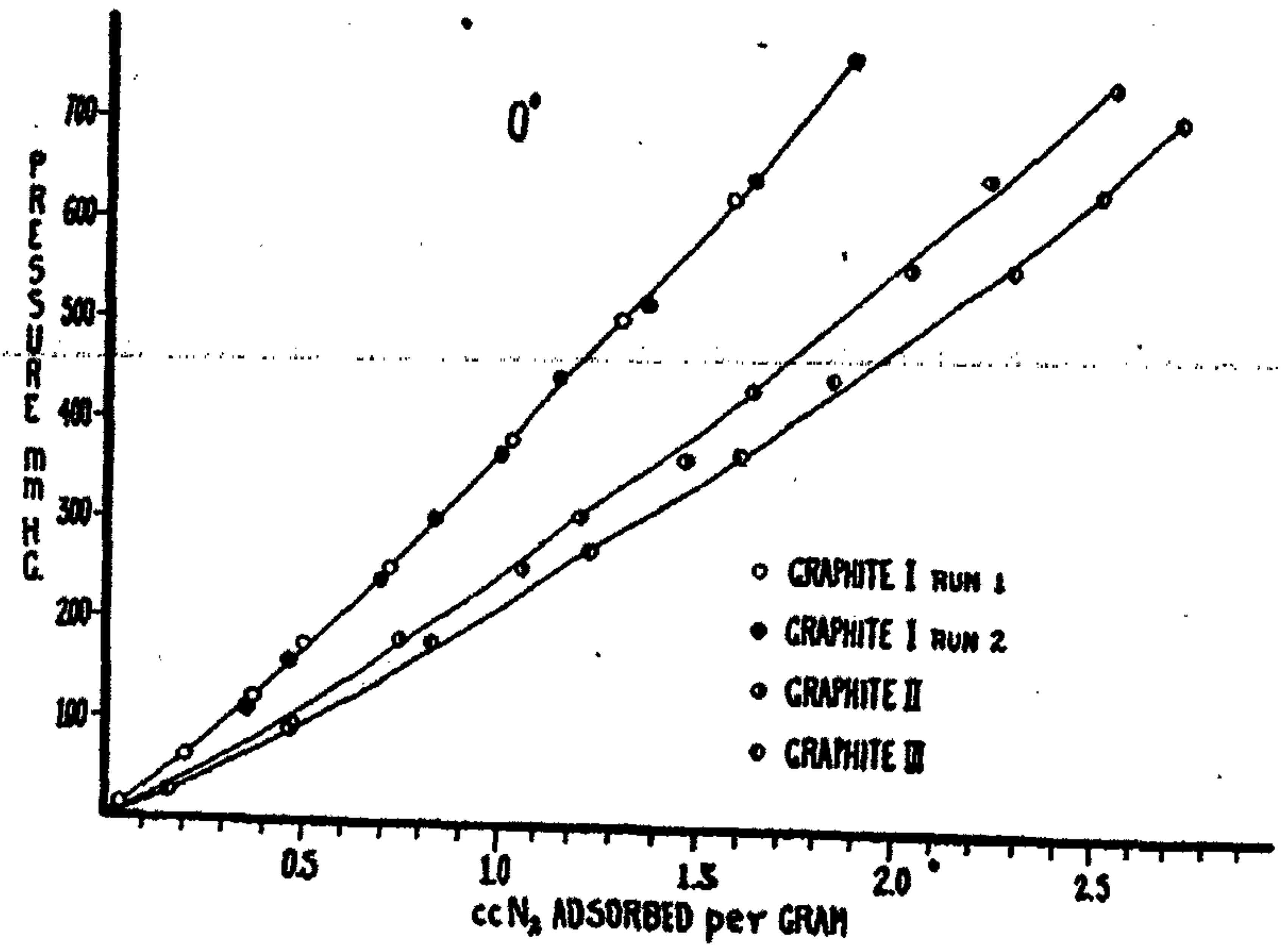

Fig. 3
Adsorption Isotherms of Nitrogen on Three Graphites at 0°C.

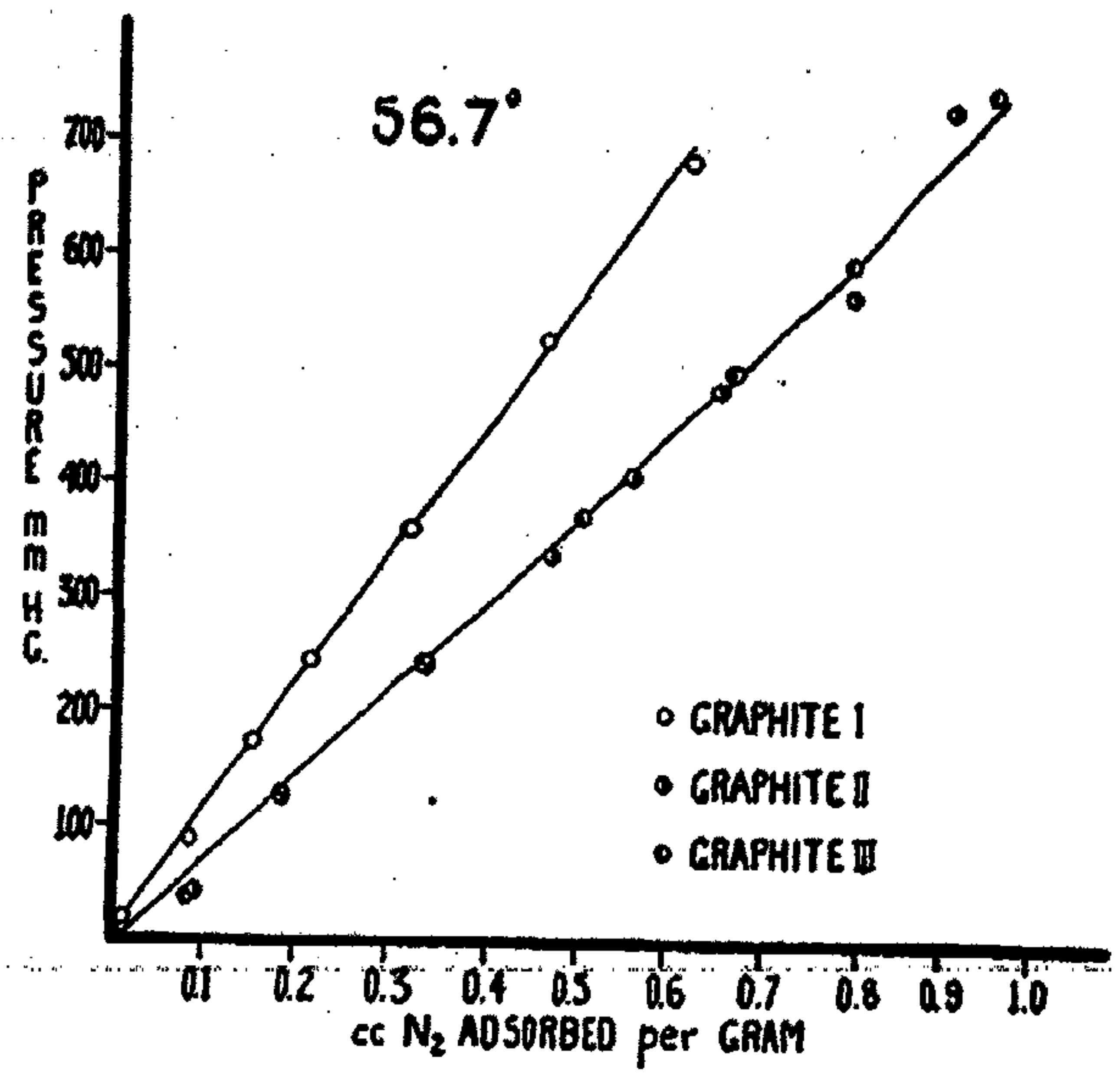

FIG. 4
Adsorption Isotherms of Nitrogen on Three Graphites at 56.7°C.

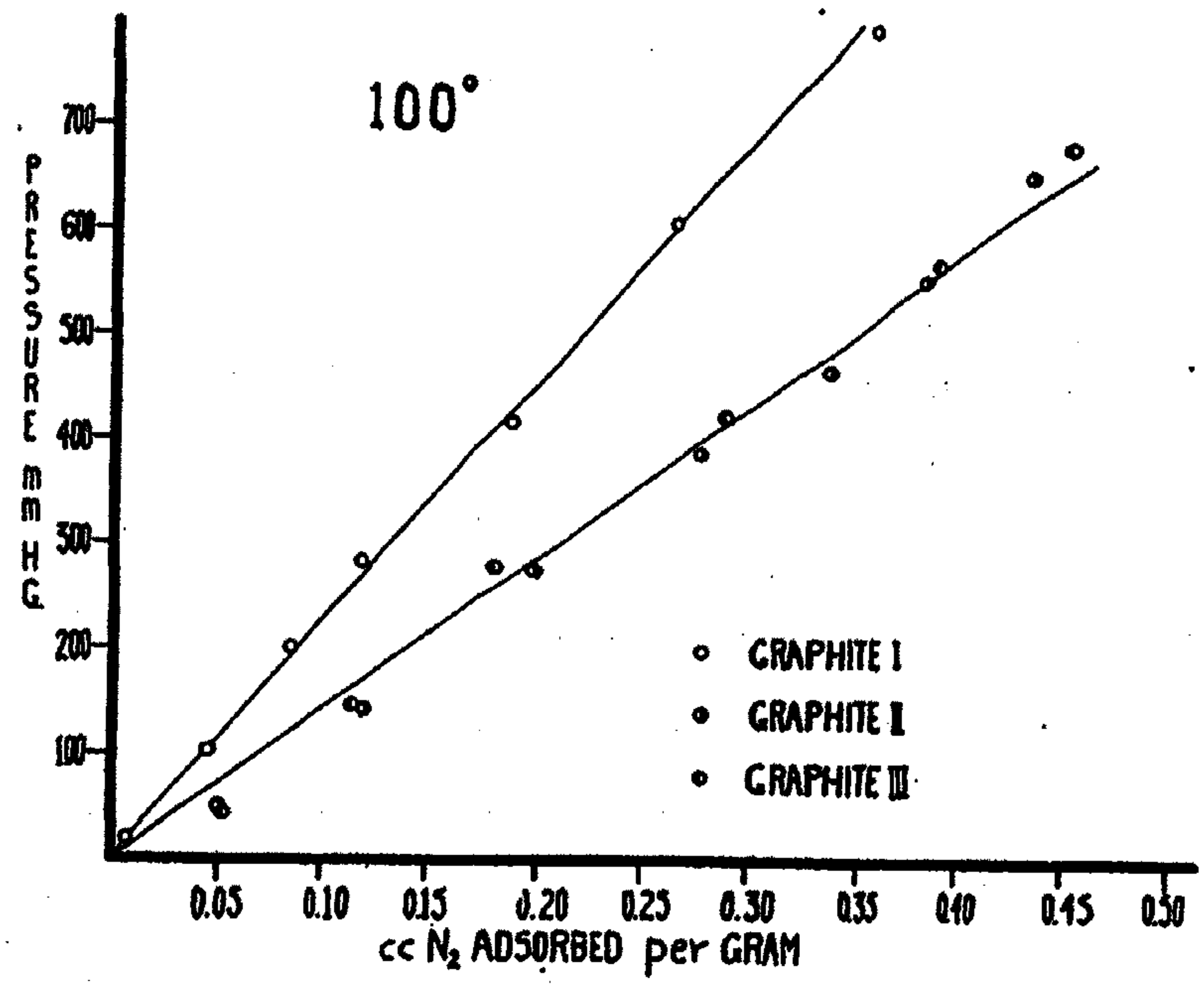

FIG. 5
Adsorption Isotherms of Nitrogen on Three Graphites at 100°C.

measuring adsorption of gases by carbon or charcoals, since the uncertain factors of the true density, the rate of penetration of the microcapillaries, and the sampling must enter into all calculations.

The data given in the Tables and in Figures 3, 4, and 5 show that the adsorption of nitrogen is proportional to the pressure except at 0°, which is in agreement with other investigations over the same temperature and pressure range. However, although the data are qualitatively in accord with the idea that the amount of adsorption should be proportional to the degree of oxidation of the original "graphitic acid", quantitatively there is no strict relationship. For instance, the amount of gas adsorbed at 0° and 760 mm. per gram are in the ratios[1] 1:1.38:1.53 for Graphites I, II, and III respectively, while the ratios of the degree of oxidation, given in the same order, are 1:1.10:1.28. This may mean that either the degree of unsaturation of the resulting graphite or the ratio of surface to mass, or both, are not directly proportional to the degree of oxidation of the original graphite.

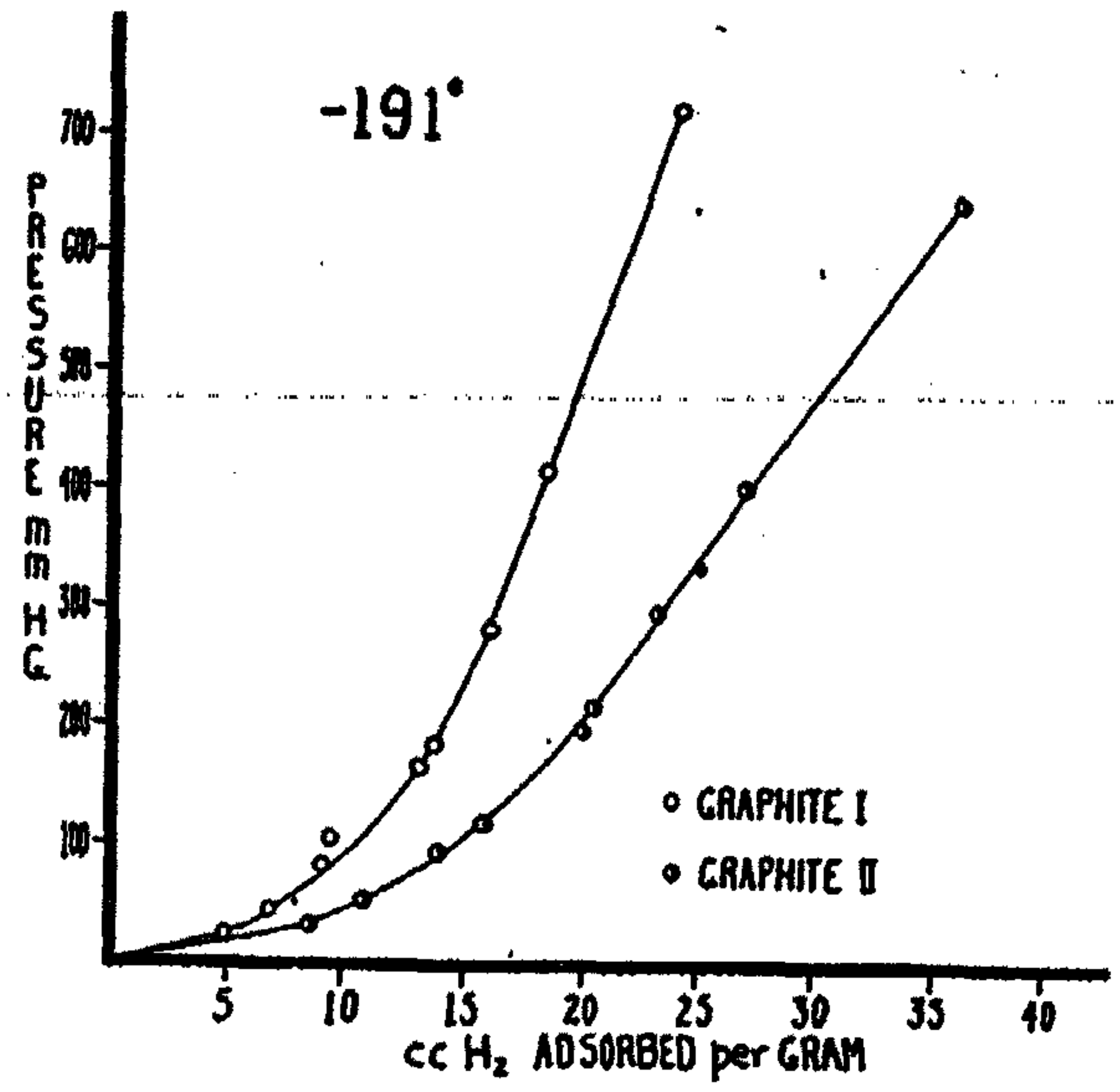

Fig. 6

Adsorption Isotherms of Hydrogen on Two Graphites at −191°C.

The fact that graphites may be prepared with adsorptive capacities as high as described in this paper is in agreement with the interpretation of the experiments on "The Relation of the Hydrogen Content of Certain Charcoals to Some Other Properties".[2] In this earlier paper it was pointed out that the decrease in the adsorptive capacity and in the hydrogen content of charcoals with increasing temperature of preparation may well be due to the form-

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[1] The absolute values of these ratios have no significance, however, since the ratios are quite different at other temperatures and pressures, or with another gas, as may be seen from an inspection of the Figures or Tables.

[2] H. H. Lowry: J. Am. Chem. Soc. 46, 824 (1924).

ation of larger crystal aggregates at the higher temperatures which would decrease the degree of unsaturation of the atomic forces, and, to some extent, the exposed surface. That by destroying these large crystal aggregates by oxidation, the adsorptive capacity may again be increased, is indicated by the experiments described above.

TABLE I

Graphite I.

A. Pressed Sample: Wt. = 0.8074 gr.

Carbon Dioxide

T =	0°		35.0°		56.7°		80.4°		100°	
	mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr
	2.9	0.562	13.0	0.483	23.0	0.414	36.4	0.329	47.3	0.267
	16.1	1.785	55.1	1.485	88.1	1.259	127.9	1.011	163.4	0.808
	39.4	3.010	112.5	2.456	170.0	2.068	236.9	1.660	292.8	1.349
	77.8	4.336	195.4	3.448	280.5	2.883	375.4	2.322	454.0	1.895
	147.0	6.073	328.1	4.742	451.0	3.955	585.4	3.183	693.6	2.626
	208.6	7.247	436.2	5.595	582.6	4.675	740.3	3.794		
	252.0	8.080	510.1	6.220	672.4	5.220				
	313.1	8.940	607.2	6.861						
	391.2	10.31	741.3	7.850						
	511.4	11.75								
	614.4	13.04								
	756.1	14.54								

Nitrogen

T =	0° (1)		0° (2)		56.7° (1)		100° (1)	
	mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr
	13.9	0.039	110.5	0.355	19.7	0.013	22.6	0.007
	62.3	0.201	159.5	0.462	88.1	0.086	103.1	0.046
	123.3	0.370	242.1	0.692	173.1	0.152	201.6	0.084
	176.3	0.499	304.5	0.832	243.9	0.213	283.7	0.118
	264.4	0.716	370.6	1.003	360.8	0.321	418.4	0.188
	385.2	1.033	449.8	1.170	527.0	0.462	611.7	0.266
	508.4	1.319	526.0	1.378	687.0	0.622	798.5	0.360
	632.8	1.582	652.8	1.637				
			777.0	1.899				

Hydrogen

T =	−191°	
	mm.Hg	cc/gr
	23.7	4.928
	45.0	6.880
	83.0	9.152
	104.6	9.480
	165.7	13.13
	184.9	13.72
	282.0	16.03
	417.0	18.39
	729.0	24.12

(*Table I continued on page 1114*)

B. Unpressed Sample: Wt. = 0.0602 gr.

Carbon Dioxide

T = 0°		35°		56.7°		80.4°		100°	
mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr
23.4	2.068	33.3	1.142	37.5	0.882	42.8	0.556	46.0	0.422
85.7	4.236	111.1	2.224	123.7	1.520	135.7	1.058	145.9	0.652
191.3	6.964	238.0	3.739	261.0	2.775	285.8	1.828	304.1	1.296
303.9	9.126	370.0	5.085	404.3	3.622	439.3	2.543	464.5	2.027
406.1	10.88	487.0	6.098	530.3	4.487	575.9	3.123	611.8	2.278

TABLE II

Graphite II.

Wt. Sample = 0.4300 gr.

Nitrogen						Hydrogen	
T = 0°		56.7°		100°		−191°	
mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr
		43.0	0.093	50.6	0.051	32.5	8.646
91.8	0.463	125.0	0.187	143.5	0.120	53.7	10.92
182.5	0.746	240.3	0.337	276.4	0.198	94.4	13.92
256.4	1.062	338.4	0.470	389.7	0.279	119.3	15.91
311.8	1.225	408.6	0.558	469.0	0.337	198.3	20.01
370.0	1.467	485.6	0.653	557.7	0.386	217.8	20.47
441.1	1.632	571.3	0.791	658.6	0.437	299.1	23.29
565.6	2.043	736.5	0.907			404.6	27.20
658.3	2.236					650.1	36.50
752.3	2.564						

TABLE III

Graphite III.

Wt. Sample = 0.4314 gr.

Nitrogen

T = 0°		56.7°		100°	
mm.Hg	cc/gr	mm.Hg	cc/gr	mm.Hg	cc/gr
28.0	0.163	38.1	0.083	44.2	0.053
93.7	0.468	128.6	0.186	147.0	0.114
179.2	0.829	242.9	0.336	279.4	0.181
275.6	1.248	372.4	0.503	426.2	0.290
375.1	1.602	501.8	0.667	572.9	0.392
452.8	1.848	600.9	0.790	686.9	0.454
565.7	2.298	752.2	0.955		
644.4	2.530				
720.7	2.749				

Summary and Conclusions

1. A method for the preparation of graphites of different adsorptive capacities from "graphitic acids", oxidized to different degrees, has been given.

2. An accurate method for measuring the adsorption of gases, eliminating the use of stop-cocks, has been described.

3. Adsorption data for three samples of graphite of different adsorptive capacities are given for carbon dioxide (at 0°, 35°, 56.7°, 80.4°, 100°), nitrogen (at 0°, 56.7°, 100°) and hydrogen at −191°, and at pressures up to one atmosphere.

4. The data show that while graphite from the "graphitic acid" which was least oxidized (C:O = 3.98:1) adsorbed the least gas and the graphite from the "graphitic acid" which was most oxidized (C:O = 3.12:1) adsorbed the most, there was no quantitative proportionality between the degree of oxidation and the amount of gas adsorbed.

5. The graphite showing the highest adsorptive capacity adsorbed one-third to one-fourth the amount of nitrogen at 0° and 760 mm. pressure that the best adsorptive charcoal will adsorb.

6. The data are in general agreement with the hypothesis proposed earlier that any treatment which will increase the ratio of surface to mass or the degree of unsaturation of the atomic forces of a solid adsorbent, or both, will increase its adsorptive capacity.

Bell Telephone Laboratories, Incorporated,
New York

THE PHYSICAL STATE OF CATALYSTS

BY ROBERT CHRISTIE SMITH

It is stated by Spring[1] that polished platinum does not decompose hydrogen peroxide. He prepared his platinum by polishing till a mirror surface was obtained, and subsequently washed with alcohol and ether to remove any grease. Results obtained by the author modify Spring's conclusions to a very considerable extent.

The author found that polished platinum did decompose hydrogen peroxide but that washing with alcohol and water inhibited the effect, as also did the presence of a surface of grease. Exposure to the air of the freshly polished platinum surface for considerable periods, also inhibited the decomposition. It is, of course, well known that clean surfaces exposed to the air collect a film of grease[2]. Inhibition in the rate of decomposition also took place after heating the polished metal until the surface became crystalline, suggesting a difference in catalytic activity depending on the state of the surface.

It has been suggested that the activity of the finely divided metals used as catalysts is due to the specific surface, but from the experiments of the author the conclusion seems justified that the activity is also dependent on the state of the catalyst. In other words, that an amorphous surface is more active than a crystalline surface. Experiments with platinum, gold and palladium give concordant results bearing out this conclusion. It seems reasonable to suppose that the bonds, secondary valencies, or forces which hold the atoms or molecules in their correct crystallographic position in a crystal will be directed inwards towards the centre of the crystal, whereas in a "glass" or amorphous form of the substance (supercooled liquid) these bonds or forces will be directed at least, partially outwards, and that it is these bonds or forces which will take part in the formation of these unstable intermediate compounds by which catalytic reactions are generally explained. Surface catalysts such as platinum, nickel, cobalt etc. are always prepared by a method which gives principally the amorphous form, and in general the lower the temperature of preparation (usually by reduction) the greater the activity. If however the temperature reaches the sintering temperature[3] a crystalline variety will be obtained. Thomas[4] discusses the factors affecting the catalytic activity of nickel when used for hydrogenation, and points out that if the

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[1] Z. anorg. Chem. 10, 161 (1895).

[2] Cf. Lord Rayleigh: "Scientific Papers", 3, 523 (1902).

[3] Wright and Smith: J. Chem. Soc. 119, 1683 (1921); Smith: 123, 2088 (1923).

[4] J. Soc. Chem. Ind. 42, 21T (1923).

nickel is prepared by reduction with carbon at 600°C it is active, whereas if it is prepared at 650°C it is practically inactive. This result could have been predicted from a knowledge of the sintering temperature of nickel. Vavon[1] studying the hydrogenation of limonene with platinum black states that its activity is decreased if heated from 300°-350°C. The sintering, i. e. growth or formation of crystals in the finely divided metal, inhibits its action. This was experimentally confirmed by the author.

Experimental

A plate of platinum (similarly gold and palladium) one centimetre square and one half millimetre thick was mounted on a brass cube of slightly over one centimetre side. The platinum was thoroughly polished on a wheel till no scratches were visible even under the microscope (550 mag.). A series of various strengths of peroxide were made up ranging 0.2, 0.4 . . . . 1.0, 2.0, 4.0 . . . . 10.0 volumes. After the plate was polished a drop of the weakest solution was placed on the platinum, and the time taken for the first bubble of gas to appear was noted. A drop of the next strength, and after rinsing the plate in water and drying with filter paper, was placed on and time again noted. Repetition with the same plate gave quite concordant results, even with different observers. The metal was then heated above the sintering temperature so that crystallisation took place, and the amorphous surface was transformed to crystalline. The same tests were then applied. The time taken for the gas to be evolved showed a marked increase, showing a decreased

TABLE I

Strength of Peroxide	Platinum					Gold			Palladium		
	A	B	C	D	E	A	D	F	A	D	F
.2 vol	25	>3 min.	>3 min.	>3 min.	>3 min.	20	30	45	40	18	25
.4 ”	11	30	do.	60	165	15	12.5	40	15	11	20
.6 ”	6	18	do.	36	27	4	7	30	4	8	18
.8 ”	6	11	do.	32	30	3	6	20	3	5	17
1 ”	7	8	50	23	25	3	4	13	2.5	3	14
2 ”	4	4	30	22	60	2	<1	7	2	<1	13
4 ”	4	2	6-7	15	55	<1	2	4	<1	3	9
6 ”	3	2	3	13	34	<1	2	4	<1	3.5	8
8 ”	2	<1	2	9	28	<1	3	4	<1	2	5
10 ”	2	<1	2	6	40	<1	2	4	<1	2.5	4

Figures given represent time in seconds for first bubble of oxygen to appear.
A—Polished, amorphous metal.
B—Pt polished and washed C_2H_5OH and $(C_2H_5)_2O$.
C—Pt polished and slightly greased.
D—After heating metal.
E—After etching and heating.
F—After etching alone

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[1] Compt. rend. 158, 409 (1914).

activity of the crystalline state. The amorphous surface was also transformed into the crystalline state by etching and similar results were obtained. In the case of the platinum tests were also made after washing the polished surface with absolute alcohol and anhydrous ether, and also after lightly greasing with vaseline the polished surface, with the results already stated. In considering the result the whole series of the different volume strengths must be taken into account, and the general effect considered. Experimental difficulties prevented more exact quantitative measurements being obtained. The polishing agents had no catalytic effect on the peroxide. For some of the preliminary experiments "perhydrol" was used which is known to contain some preservative as uric or barbituric acid; but the whole experiments were repeated with hydrogen peroxide, free from any preservative, and obtained specially from British Drug Houses, London. The results are given in Table I.

Conclusions

1. Polished platinum decomposes hydrogen peroxide.
2. The amorphous state gives a more active catalyst than the crystalline.

The author desires to express his thanks to the Carnegie Trust for a Grant which enabled this work to be carried out.

The University
Glasgow. May 6, 1926.

THE DECOLORIZATION OF CARBON DISULPHIDE SOLUTIONS OF IODINE BY RED PHOSPHORUS

BY RALPH N. TRAXLER AND FRANK E. E. GERMANN*

Sestini[1], working in 1871, observed that when he added 10 g. of red phosphorus, previously washed with *water* and ether, to 100 cc. of carbon disulphide containing 1 g. of iodine the violet color of the carbon disulphide solution changed to reddish brown and later to yellowish red. After 24 hours he filtered off the red phosphorus and washed it with carbon disulphide until the solvent showed no more color. He recognized the presence of phosphorus iodide in the filtrate. Upon treating this red phosphorus with warm water he obtained a solution which gave a test for iodine with nitric acid. He also found that 6 or 8 g. of freshly washed red phosphorus completely decolorized 30 cc. of carbon disulphide containing "a little" iodine. From these experiments he was led to believe that red phosphorus removed iodine from carbon disulphide solution, just as charcoal and other finely divided solids remove other substances from solution.

It has been suggested[2] that it would be of interest to determine adsorption isotherms using red phosphorus and iodine in carbon disulphide. With such an aim in view the following experiments were performed, the results of which show that adsorption is not the primary cause of the changes observed by the previous investigator.[3]

When the above experiments were repeated, similar results were obtained. A more complete examination was made, however, of the aqueous solution resulting from the washing of the red phosphorus which had effected the whole or partial decolorization of a carbon disulphide solution of iodine. This examination showed that the aqueous solution contained a large amount of hydrogen iodide and phosphorous acid but no free iodine. Since the washing with carbon disulphide before treatment with water would remove practically all phosphorus iodide, the hydrogen iodide and phosphorus acid must have resided upon the red phosphorus before treatment with water. The presence of hydrogen iodide and phosphorous acid on the red phosphorus can be explained as follows: The slightly moist red phosphorus which Sestini used reacts with the iodine present to form phosphorus iodide which is soluble in carbon disulphide giving a reddish brown color. The iodide is then acted upon rather slowly by the small amount of water adhering to the red phosphorus, yielding hydrogen iodide and phosphorous acid both of which being

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*Contribution from the Department of Chemistry of the University of Colorado.

[1] Gazz. chim. ital. 1, (1871) 323 (1873).

[2] Bancroft: Nat. Res. Council Reprint No. 13, problem No. 53.

[3] Gordon and Krantz: J. Am. Pharm. Assoc. 13, 906 (1924) carry on a series of experiments of decolorization of iodine solutions from various solvents and assume they get adsorption as Sestini did. They have, however, missed entirely the real explanation of the phenomenon.

insoluble in carbon disulphide are precipitated upon the red phosphorus. Washing with carbon disulphide removes any phosphorus iodide which is not decomposed by the water but not the hydrogen iodide and phosphorous acid. These are then removed by the treatment with water. Thus the presence of iodine in *washed* red phosphorus after adding to carbon disulphide-iodine solutions depends primarily upon the insolubility of hydrogen iodide in carbon disulphide and not upon the adsorbing power of red phosphorus toward iodine. It should be noted at this point that 0.15 g. of water will react completely with the 1 g. of iodine used in Sestini's experiments. This is an amount which could very easily be present in 10 g. of washed red phosphorus.

A series of experiments were performed using *dry* red phosphorus which had not been opened to the air for any length of time. The solutions of iodine used varied in strength from 0.015% to 10.000% by weight. Only in the case of the most dilute solutions was complete decolorization obtained, the color of the other solutions after treatment with red phosphorus varied from yellow to dark reddish brown according to the strength of the original iodine solution. The decolorization of the very dilute solutions may have been due (1) to the presence of traces of moisture or, (2) to the fact that phosphorus iodide does not have as high a coloring power toward carbon disulphide as does iodine. The second hypothesis is suggested by the fact that the decolorized dilute solutions gave, upon concentration, a pink colored solution and finally upon complete evaporation a small but dark colored residue.

When *dry* red phosphorus was added to iodine in carbon disulphide contained in a flask which had been rinsed but not dried the red phosphorus flocculated and was found to contain hydrogen iodide and phosphorous acid which could be removed by washing with water. Water is practically insoluble in carbon disulphide and thus would be taken up by a substance such as red phosphorus which it is capable of wetting. This water adhering to the red phosphorus reacted with the phosphorus iodide present to give hydrogen iodide and phosphorous acid which in turn are left adhering to the phosphorus due to their insolubility in carbon disulphide.

Samples of the dry red phosphorus used were washed very thoroughly with carbon disulphide and small amounts of iodine added to the washings. No decolorization or change in color was noted. The washed red phosphorus reacted with iodine as readily as the unwashed. Carbon disulphide could not remove from red phosphorus any material capable of reacting with iodine in carbon disulphide and therefore the possibility was eliminated that a portion of the red phosphorus had changed to ordinary white phosphorus after leaving the factory.

A number of experiments were performed to determine the percentage of the red phosphorus which would react with iodine in carbon disulphide. Weighed amounts of dry red phosphorus were added to weighed amounts of iodine in this solvent. After allowing sufficient time for reaction to take place the red phosphorus was filtered off, washed with carbon disulphide and again added to a fresh iodine solution. This procedure was followed for each sample of red phosphorus until the phosphorus would no longer affect a solution of iodine. It was found that the red phosphorus would react with iodine until 18.5% of its original weight had been used, beyond that point it became inactive toward iodine under the conditions of the experiments (22°C and 630 mm. Hg). This was later repeated at 22° and 760 mm. with 18.5% reacting. Since the so-called red phosphorus prepared by heating white phosphorus, varies in its properties (color, vapor, pressure, etc.) with the temperature to which and the length of time during which it is heated, it seemed advisable to attempt other methods than mere solution of any residual white phosphorus by carbon disulphide. Red phosphorus was therefore heated in a tube, provided with a very small opening, by a Meeker burner. This drove off considerable yellow phosphorus vapor, which burned at the opening. After about two hours of heating the tube was allowed to cool and opened under carbon disulphide which dissolved out any residual white phosphorus which might have condensed in cooler parts of the tube. The remaining red phosphorus was somewhat darker than the original. It reacted to the extent of 18.5% with the iodine.

Ordinary red phosphorus was boiled with sodium hydroxide followed by hydrochloric acid according to Chapman's method. Not enough of the violet phosphorus was obtained for a quantitative determination, but a qualitative test showed that it acted quite strongly on iodine. The treated material as a whole reacted to the extent of 18.7% with iodine. Other experiments of a similar nature show that bromine reacts with red phosphorus almost quantitatively. This must be due to the greater chemical activity of bromine. It would therefore seem that our experiments with iodine exclude the possibility of any pseudo-equilibrium, but rather point to the existence of at least two constituents in violet phosphorus in the percentages of 18.5 and 81.5. The progressive addition of fresh solutions of iodine to the treated red or violet phosphorus certainly exclude any possibility of a mass action equilibrium. The inactive red phosphorus had a slightly darker color than the original, the difference being so slight however as to escape notice except under close comparison with the original material.

In all of the above experiments the reddish-brown solution resulting from the addition of red phosphorus to iodine in carbon disulphide yielded upon evaporation of the solvent red crystals which fumed in moist air. These crystals upon analysis gave an average of 7.52% phosphorus and 92.5% iodine. Upon treatment with distilled water the crystals dissolved, giving a water white, acid solution which contained hydroiodic acid and phosphorous acid. The crystals melted at 55°C. From the analyses, action toward water and melting point the crystals were identified as phosphorus tri-iodide.

Phosphorus tri-iodide was prepared by dissolving 10 g. of yellow phosphorus and 123 g. of iodine in carbon disulphide adding the solutions and evaporating. The crystals melted at 55°C. This is the value given by Abegg[1]

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[1] "Handbuch der anorganischen Chemie" 3, III p. 419. Quoting L. Ouvrard: Ann. Chim. Phys. (7), 2, 224 (1894).

for the melting point of phosphorus tri-iodide. Carbon disulphide was used as the crystallizing medium in the preparation quoted by Abegg.

55° C. is also the melting point given by Snape[1] for phosphorus tri-iodide prepared by the following reaction:

$$3\ KI + PCl_3 = 3KCl + PI_3$$

followed by extraction with carbon disulphide and crystallization from that medium.

The commonly accepted value for phosphorus tri-iodide is 61° C. given by Landolt-Börnstein based upon the work of Besson[2] and Jaeger and Doornbosch[3]. Besson prepared phosphorus tri-iodide by passing hydrogen iodide into carbon tetrachloride which contained phosphorus trichloride. Carbon disulphide was not used by Besson for recrystallization. Jaeger and Doornbosch[4] prepared their phosphorus iodide by Besson's method. They also sublimed the material and recrystallized from carbon disulphide which had been shaken with mercury and then thoroughly dried. To remove all adhering carbon disulphide they heated the iodide to 65° C. under reduced pressure meanwhile bubbling nitrogen through the molten mass.

A number of experiments were performed to ascertain the cause of the lowering of the melting point of phosphorus tri-iodide when crystallized from ordinary carbon disulphide. Consideration was given to the possibilities that from carbon disulphide the phosphorous tri-iodide crystallized in a form different from that obtained from carbon tetrachloride or that some of the carbon disulphide ordinarily remained in loose combination with the iodide. Freshly prepared phosphorus tri-iodide crystallized from carbon disulphide was placed in a tube connected with a vacuum pump. The crystals were melted and kept just above the melting point for 20 minutes, meanwhile maintaining a quite low pressure in the tube. After cooling the mass was ground to a powder in an agate mortar and melting points taken immediately. The determinations gave a melting point of 55° C. for the powder. From this it is to be concluded that the lowering of the melting point is not due to a particular crystal form resulting from crystallization from carbon disulphide or to the presence of solvent loosely combined with the iodide.

The presence of slight impurities in the phosphorus iodide crystals obtained from ordinary carbon disulphide was next considered as a cause of the lowering of the melting point. Upon shaking carbon disulphide with mercury, a black powder is formed which can be recognized as mercuric sulphide. Since carbon disulphide always contains small amounts of free sulphur such a reaction would be expected. Highest grade carbon disulphide when freed from sulphur by this method and used as the solvent for preparing phosphorus tri-iodide yielded crystals which melted at 61° C. The carbon disulphide must be

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[1] Chem. News, **74**, 27 (1896).

[2] Compt. rend. **124**, 1347 (1897).

[3] Z. anorg. Chem. **75**, 270 (1912).

[4] Personal communication from Prof. Jaeger.

used soon after purification for slight decomposition of the solvent will take place on standing, giving a liquid containing small amounts of free sulphur.

By adding 0.1 g. of sulphur to 100 cc. of purified carbon disulphide and using this as the solvent for the preparation of phosphorus tri-iodide a product was obtained which melted at 53° C. Crystals prepared by Besson's method from carbon tetrachloride when recrystallized from impure carbon disulphide gave a product which melted at 55° to 56° C. The conclusion is reached that the low melting point obtained by Corenwinder, Ouvrard, and Snape for phosphorus tri-iodide is due to the presence in the crystals of small amounts of sulphur compounds, very probably one or more of the compounds of phosphorus, sulphur, and iodine, and that these impurities may be avoided by the use of carbon disulphide freshly purified by shaking with mercury.

Gmelin-Kraut lists PSI, $P_2S_2I_2$; P_2SI_2, P_2SI_4, PS_xI_3 and $P_4S_3I_2$. The melting point of the P_2SI_2 is given at 75° C. and of the $P_4S_3I_2$ is given at 119.5° C. $P_2S_2I_2$ and $P_4S_3I_2$ can each be made by dissolving the three elements in carbon disulphide in molecular proportions. P_2SI_2, $P_2S_2I_2$ and $P_4S_3I_2$ are all soluble in carbon disulphide, but $P_4S_3I_2$ is given as being less soluble than $P_2S_2I_2$. Since phosphorus is present in excess, comparatively small amounts of iodine, and only traces of sulphur, we would expect to have either P_2SI_2 or $P_4S_3I_2$ formed. The former, being more soluble in carbon disulphide would probably not be as readily formed as the less soluble $P_4S_3I_2$. It therefore becomes evident that PI_3 crystals melting below 61° C. must be contaminated with a salt of P, S, and I, this salt probably being $P_4S_3I_2$, which when pure melts at 119.5°C.

The preparation of pure phosphorus tri-iodide directly from purified carbon disulphide is much shorter and less complicated and tedious in execution than the usual method of preparation from phosphorus trichloride in carbon tetrachloride. For these reasons it is believed that, knowing the cause of the difficulties usually encountered and the means for their removal, the method will be of distinct value to any one wishing to prepare the pure compound. Finally the method offers another verification of the now well established melting point of phosphorus tri-iodide.

Summary

1. Sestini's work dealing with the action of washed red phosphorus on iodine in carbon disulphide was repeated and checked. The red phosphorus was found to contain hydrogen iodide and phosphorous acid but no free iodine.

2. Adsorption has little or nothing to do with the appearance of these substances on the red phosphorus. Their insolubility in carbon disulphide offers the best explanation.

3. Experiments using dry red phosphorus yielded decolorization only in very dilute solution. More concentrated solutions gave phosphorus tri-iodide in abundance.

4. Experiments using wet containers yielded results quite similar to those obtained by Sestini.

5. Carbon disulphide cannot remove any substance from red phosphorus which is capable of reacting with iodine in carbon disulphide.

6. Red phosphorus agitated with iodine in carbon disulphide was found to lose 18.5% of its original weight before becoming inactive toward iodine. This was also true for red phosphorus heated for two hours.

7. Phosphorus tri-iodide prepared using both red and yellow phosphorus in carbon disulphide gave a melting point of 55°C. This melting point was not changed by melting the original crystals in a vacuum, cooling and grinding to a powder. Thus the low melting point of such phosphorus tri-iodide is not caused by the presence of a different crystal form or to the presence of carbon disulphide loosely held by the phosphorus iodide.

8. Phosphorus tri-iodide prepared in carbon disulphide which had been purified by shaking with mercury gave a melting point of 61°C.

9. The lowering of the melting point of phosphorus tri-iodide as usually prepared from carbon disulphide was found to be due to the presence of sulphur probably in the form of $P_4S_3I_2$ which melts at 119.5°C.

10. The preparation of phosphorus tri-iodide using carbon disulphide freshly purified with mercury is recommended as a distinctly shorter and more convenient method of preparation than those usually used to obtain the pure product.

Boulder, Colorado

TITANIA JELLIES*

BY SIMON KLOSKY AND CHRISTOPHER MARZANO**

The first mention of a titania gel was made by Rose[1]. He fused titanium dioxide with an alkali carbonate. The product was treated with hydrochloric acid. The filtered solution upon standing gave a very soft mass with supernatant liquid. In 1861, Thomas Graham[2] dialyzed a solution of titanic acid in hydrochloric acid. The hydrochloric acid readily diffused, while hydrated titanic acid in a gelatinous and insoluble form was left upon the dialyzer. About the same period, Knop[3] was able to obtain a transparent gel of very soft structure by adding ammonium hydroxide to an acid solution of titania. Towards the end of the nineteenth century, Pfordten[4] repeated the work of Rose. The filtered solution separated gradually into a gelatinous part and a liquid part.

Theoretical

As titanium is a very near neighbor to silicon in the periodic table, it was thought that a jelly (jelly is used in this paper to mean the product obtained when a solution "sets" to give a vibrant solid without any separation of supernatant liquid although subsequently on standing the jelly may show slight syneresis[5]) might be found if titisna could be precipitated at a "suitable rate"[6] It was further thought that this could best be done by the "slow neutralization"[7] of an acid solution of titanium dioxide.

Experimental

In the preparation of sodium titanate from sodium carbonate and titanium dioxide, very carefully prepared, acid treated graphite crucibles were employed. The materials used were chemically pure, except the titania which was obtained from the Titanium Pigment Company, Niagara Falls, New York. The titanium dioxide was tested for iron, but negative results were obtained.

Sodium titanate was prepared by the thorough fusion of sodium carbonate and titanium dioxide[8] in the ratio of mole per mole. The fused product was poured into cold water. A very fine sandy substance was obtained. The titanate was washed till there was no basic reaction with litmus.

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*An extract from a dissertation presented by Christopher Marzano in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

**Contribution from the Martin Maloney Chemical Laboratory of The Catholic University of America.

[1] Gilbert's Ann. 73, 76 (1823).

[2] Phil. Trans. 151, 213 (1861).

[3] Ann. 123, 351 (1862).

[4] Ber. 17, 727 (1884).

[5] See Weiser: Bogue's "Colloidal Behavior", Chap. XV, p. 377 (1924).

[6] Weiser: "First Colloid Symposium Monograph," p. 42.

[7] Holmes: "First Colloid symposium Monograph", p. 28.

[8] O. P. Smith: Z. anorg. Chem. 37, 332 (1903).

TABLE I

Titanium Solution	Coagulant in: cc.	Immediate results	Later observations.
	K_2CO_3		
5.00 cc.	(30 g/100cc)		
5.00 cc.	7.60	clear solution	24 hours clear solution.
5.00 cc.	7.80	" "	18 hours fair jelly
5.00 cc.	7.85	" "	sets to jelly in 6 hours, vibrant.
5.00 cc.	7.90	" "	sets to jelly in 15 minutes
5.00 cc.	8.00	sets to jelly immediately.	
	Na_2CO_3 20g in 100cc. of solution.		
5.00 cc.	10.2	clear solution	24 hours clear solution.
5.00 cc.	10.4	" "	18 hours fair jelly
5.00 cc.	10.6	" "	8 hours good jelly, vibrant.
5.00 cc.	10.9	sets to jelly immediately	
	$(NH_4)_2CO_3$ 20g. in 100 cc. of solution.		
5.00 cc.	12.8	clear solution	24 hours clear solution
5.00 cc.	13.0	" "	18 hours set to firm jelly
	$(NH_4)_2CO_3$ 20g. in 100 cc. of solution.		
5.00 cc.	13.15	set to jelly immediately	

TABLE II

Ti. Sol.cc.	Fe Sol. cc.	Coagulant in cc.	Immediate results.	Later observations.
		K_2CO_3		
5.00	2.00	7.9	clear solution	24 hours clear solution.
5.00	2.00	8.1	” ”	18 hours fair jelly.
5.00	2.00	8.5	” ”	18 hours good jelly, vibrant.
5.00	2.00	9.0	set to jelly immediately.	
		Na_2CO_3		
5.00	2.00	10.4	clear solution	24 hours clear solution.
5.00	2.00	10.8	” ”	18 hours fair jelly opalescent.
		Na_2CO_3		
5.00	2.00	11.3	opalescent reddish sol.	18 hours good jelly, vibrant.
5.00	2.00	11.7	set to jelly immediately	
		$(NH_4)_2CO_3$		
5.00	2.00	13.1	clear solution	24 hours clear solution.
5.00	2.00	13.4	” ”	18 hours fair jelly.
5.00	2.00	13.7	” ”	18 hours good jelly, vibrant
5.00	2.00	14.1	set to jelly immediately.	

The thoroughly washed product was treated with 800 cc. of concentrated hydrochloric acid (sp. gr. 1.18-1.19, 35% HCl). Upon filtering the mixture, a lemon-canary colored solution was obtained.

After preliminary experiments, it was found that the solution was too dilute to produce a jelly. A milky solution with a precipitate was the usual result. Upon concentrating the solution at 50° C., a product was obtained that gave excellent results. Analysis of this solution gave the following:

Titanium dioxide	1.81 mols/1 liter
Total acid	1.89 mols/1 liter
Sodium	0.43 mols/1 liter
Chloride	7.00 mols/1 liter

from these data, it was reasoned that the solution contained HCl, TiO_2 $(H_2O)_x$ and $TiCl_4$(?).[1]

Since the solution was acid in nature, it was necessary to add a neutralizing agent to bring about the desired conditions. Although sodium and ammonium hydroxides were tried, the best results were obtained when potassium, sodium and ammonium carbonate were used as the coagulating agents. The clearest jellies were obtained with potassium carbonate.

The acid titanate solution was measured into a pyrex Erlenmeyer flask and the coagulating agents were added drop by drop. The mixtures were carefully shaken so as to peptize any precipitate and were then poured into test-tubes. The volumes employed were measured from graduated burettes.

Hundreds of different combinations were tried. Table I represents a few of the successful series.

Ferric Oxide—Titanium Dioxide Jellies

It occurred to the authors that mixtures of metallic oxides and titania might be produced similar to those prepared with silica[2]. Table II shows the results.

The ferric chloride solution used in the following experiments contained one mole of ferric oxide per liter.

All of the vibrant jellies were capable of being readily washed with water. Upon drying, these washed jellies showed good structure.

Their catalytic properties and adsorptive capacity are being investigated.

Summary

1. The production of titanium dioxide jellies which possess good structure has been accomplished, and

2. Ferric oxide—titanium dioxide jellies with structure have also been obtained.

April, 1926.

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[1] For the composition of solutions of TiO_2 in HCl see Morley and Wood: J. Chem. Soc. 125, 1633 (1924).

[2] Klosky: Dissertation. Johns Hopkins University (1921).

THE SURFACE CONCENTRATION OF SODIUM OLEATE AND OF COLLOIDAL SULPHUR

BY J. M. JOHLIN

The soaps have been more thoroughly investigated than any of the colloids which occur in a similar state of dispersion. The various points of view concerning theories and speculation derived from surface tension measurements of soaps are best reviewed in recent textbooks on colloidal behavior. The formation of stable foams and emulsions is generally thought to depend merely upon a lowering of the interfacial tension and upon the formation of surface films at the interface in question. Such speculation is limited largely to soaps and to the possible effect of the spacing of molecules at the interface as influenced by the atomic volumes of the metallic radicals. There is no reference to the influence which a change in the complexity of the disperse phase might have upon the manner of the surface concentration and its effect upon the surface tension and the stability of the foam or emulsion.

Lord Rayleigh[1] first showed that, even in the case of a soap solution, a measurable period of time must elapse before a quantity of the solute is adsorbed at a freshly formed interface in sufficient amount to affect the surface tension appreciably and that the surface tension will then decrease with extreme rapidity so as to reach a very low value in a few seconds. That the surface tension of soap solutions changes with time but that the equilibrium values which are obtained do not vary directly with the concentration has been demonstrated repeatedly since. Milner[2] found in using the capillary rise method that the surface tension of sodium oleate solutions decreases progressively with time and that the equilibrium values which are reached in the case of solutions of different concentrations do not vary with the concentration.

Harkins, Davies and Clark[3] found by the drop weight method that, at concentrations greater than 0.002 normal, uniform equilibrium values are obtained. The uniformity of these values is ascribed to the formation of a closely packed monomolecular layer at the interface, the formation of which terminates further adsorption. Berczeller[4] showed by means of a stalagmometer that, in the case of a sodium oleate solution of 0.1 percent concentration, the surface tension decreased as the time of drop formation was increased from 0.71 to 10 seconds. duNoüy[5] recently showed by the ring method that, in measuring the surface tension of extremely dilute solutions of sodium oleate, certain minima in the equilibrium values were obtained at three definite concentrations. He assumed that at the end of two hours after the formation

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[1] Proc. Roy. Soc. 47, 281 (1890).

[2] Phil. Mag. (6) 13, 96 (1907).

[3] J. Am. Chem. Soc. 39, 541 (1917).

[4] Int. Z. Biol. 1, 241 (1914).

[5] Phil. Mag. (6) 48, 264 (1924).

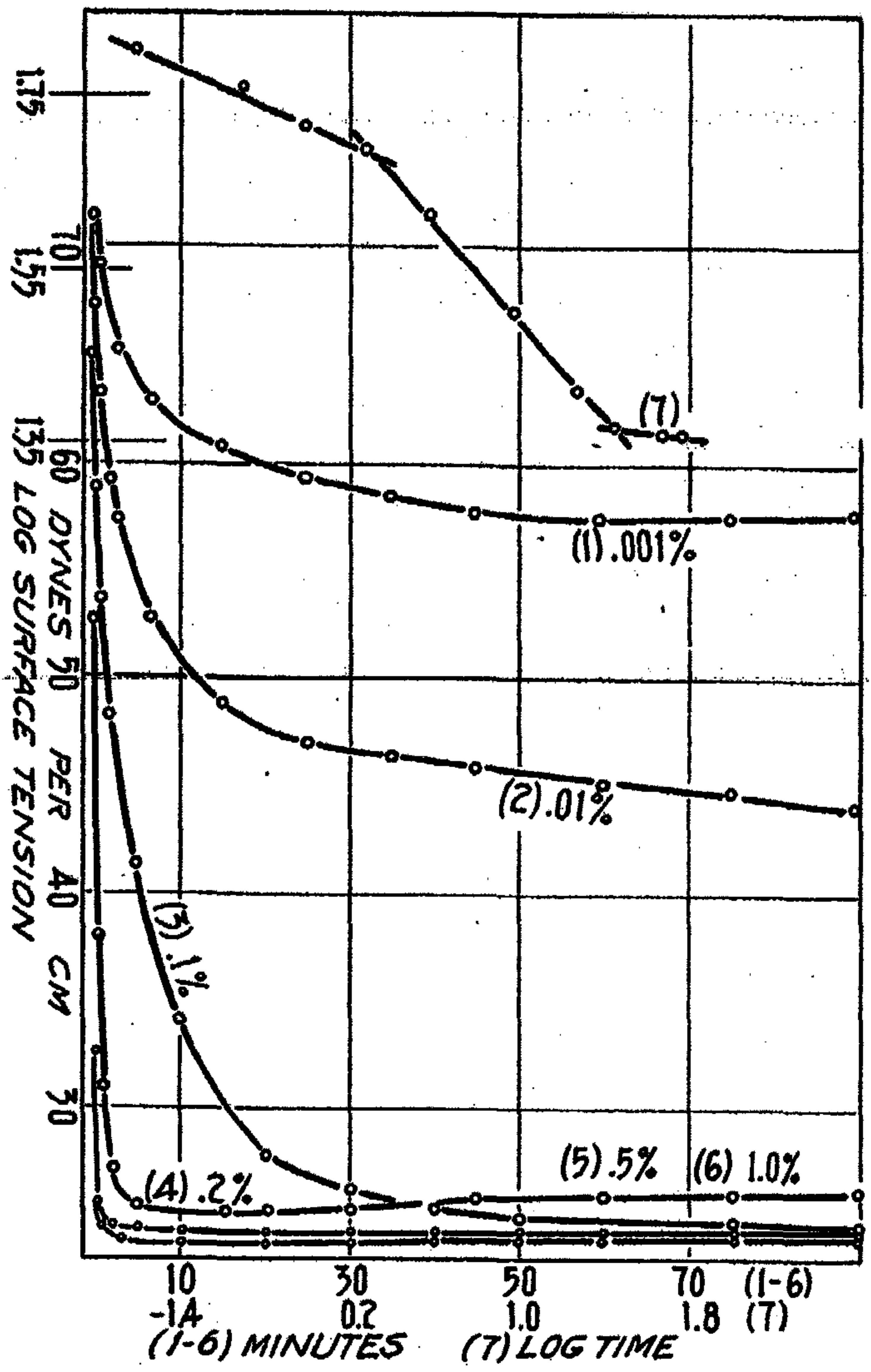

Fig. 1

Illustrating the change of surface tension with time in the case of solutions of sodium oleate of varying concentration.

of the interface, when measurements were made, all of the soap had been adsorbed either upon the glass or at the interface, that the minima were due to the formation of monomolecular layers in which the molecules were differently oriented, and that the higher equilibrium values which were obtained at all other concentrations were due to a heterogeneous arrangement of the molecules at the interface. These minima do not, however, represent the lowest surface tension values obtainable for a solution of sodium oleate.

The sodium oleate used in the present investigation was prepared from Kahlbaum's best grade of oleic acid and from caustic soda which had been prepared from metallic sodium. A one percent stock solution was kept in a tightly stoppered hard glass flask. This solution did not color phenolphthalein but was alkaline toward methyl red. The technique employed was the same as that employed in the case of gelatine solutions which were measured by the capillary rise method[1]. The temperature of the thermostat was 25°C.

Table I

Percent Concentration

Time	1.0 Dynes per cm.	0.5 Dynes per cm.	0.2 Dynes per cm.	0.1 Dynes per cm.	0.01 Dynes per cm.	0.001 Dynes per cm.
10 sec.	25.56	32.45	52.62	64.87	70.94	71.36
30 "	24.66	25.23	37.97	58.77	67.29	71.36
1 "	24.50	24.39	30.87	53.67	63.23	69.20
2 "	24.41	24.02	27.15	48.15	59.21	66.59
3 "	24.33	23.91	25.80	44.98	57.41	65.32
5 "	24.28	23.78	25.35	41.28	54.82	63.94
7 "	.....	.....	.....	37.09	52.81	62.89
10 "	24.22	23.69	25.13	34.05	50.91	61.72
15 "	24.17	23.62	25.11	30.72	48.86	60.72
20 "	24.15	23.60	25.15	27.85	47.35	59.95
25 "	24.14	23.60	25.20	26.78	46.96	59.34
30 "	24.13	23.70	25.22	26.11	46.54	58.93
35 "	.....	23.78	25.44	25.72	46.30	58.48
40 "	24.12	23.83	25.56	25.26	46.07	58.12
45 "	.....	23.86	25.73	25.09	45.76	57.68
50 "	24.12	23.89	25.78	24.89	45.44	57.34
60 "	24.12	23.93	25.84	24.69	45.03	57.38
75 "	24.12	23.95	25.87	24.55	44.56	57.38
90 "	24.12	23.95	25.99	24.36	43.90	57.54

(Data obtained at 25° C, by the capillary rise method with solutions of sodium oleate of varying concentration.)

Two series of measurements were made. In the first series solutions of 1.0, 0.5, 0.2, 0.1, 0.01, 0.001 and 0.0001 percent concentration were used. In the second 0.1 percent solutions, to which sufficient caustic soda had been added so that they were 1/10, 1/70, 1/140, 1/280, and 1/560 normal with respect to this reagent, were used. The nature of the results obtained is shown by the data of Tables I and II, and by the curves of Figures 1 and 2. In the first of these it is shown that the surface tension of a 1.0 percent solution had almost reached an equilibrium value by the time the first reading was taken at the end of ten seconds. These results were reproducible many times with remarkable consistency. The corresponding values in successive series of determinations varied but one or two hundredths of a dyne per cm. This was also true of 0.5 per cent solutions. As the solutions became more dilute the

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[1] Joblin: J. Phys. Chem. 29, 271 (1925).

results were reproducible with less consistency. No definite cause can be given for this effect which has been observed in the case of dilute solutions of all the materials which have been thus far investigated.

In the case of solutions between 0.2 and 1.0 percent concentration, apparent equilibrium values were reached in an hour or less. Although these vary between 24 and 26 dynes per cm., they do not change directly with the concentration. A similar observation was made by Milner[1].

It is to be noted that the initial values, taken ten seconds after the formation of an interface, became higher as the concentration decreased and that the decrease of surface tension with time was not nearly so rapid. The logarithmic curve is that representing a 0.1 percent solution. It is evident that here too the change of surface tension with time takes place according the equation,

$$\sigma = a/t^n.$$

Although the time curve appears quite smooth, the logarithmic curve indicates a repeated change in the rate at which the surface tension is changing with time.

In the case of a 0.001 percent solution it was observed that an initial period of inactivity, lasting for thirty seconds, preceded the decrease of the surface tension. This was repeatedly observed even when the walls of the tube had been in contact with the solution for a longer time. The initial value is, however, not quite as high as that for the surface tension of water. A similar phenomenon was observed in the case of casein solutions which had been made alkaline, but the data were omitted because the phenomenon could not be consistently repeated. In the case of 0.0001 percent soap solutions data are also omitted because of the apparent irregularity of results. Here the period of inactivity was sometimes quite prolonged. A regular decrease of the surface tension with time was, however, repeatedly observed.

The data of Table II and IIa illustrate some of the results which were obtained with 0.1 percent solutions to which varying amounts of caustic soda were added. It is to be noted that curve 1a(Figure 2), which was obtained from data representing a solution which was 0.1 normal with respect to sodium hydroxide, has several maxima and minima in the eight hour period. The maximum reached at the end of eight hours was followed by a further decrease which, at the end of forty two hours had reached 30 dynes per cm. This rise and fall is similar to that which was previously observed in the case of solutions of egg-albumin to which alkali had been added and to the lesser fluctuations which may be observed in the case of colloidal solutions in which the solute is present in the form of larger aggregates. A similar fluctuation was observed in the case of emulsions by Joshi[2]. In the case of solutions which contain larger aggregates it cannot be stated to what extent these fluctuations might be due to the coagulation of the colloid at the very curved surface of the meniscus in the fine capillary tube.

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[1] Phil. Mag. (6) 13, 96 (1907).

[2] Kolloid-Z. 39, 198 (1923).

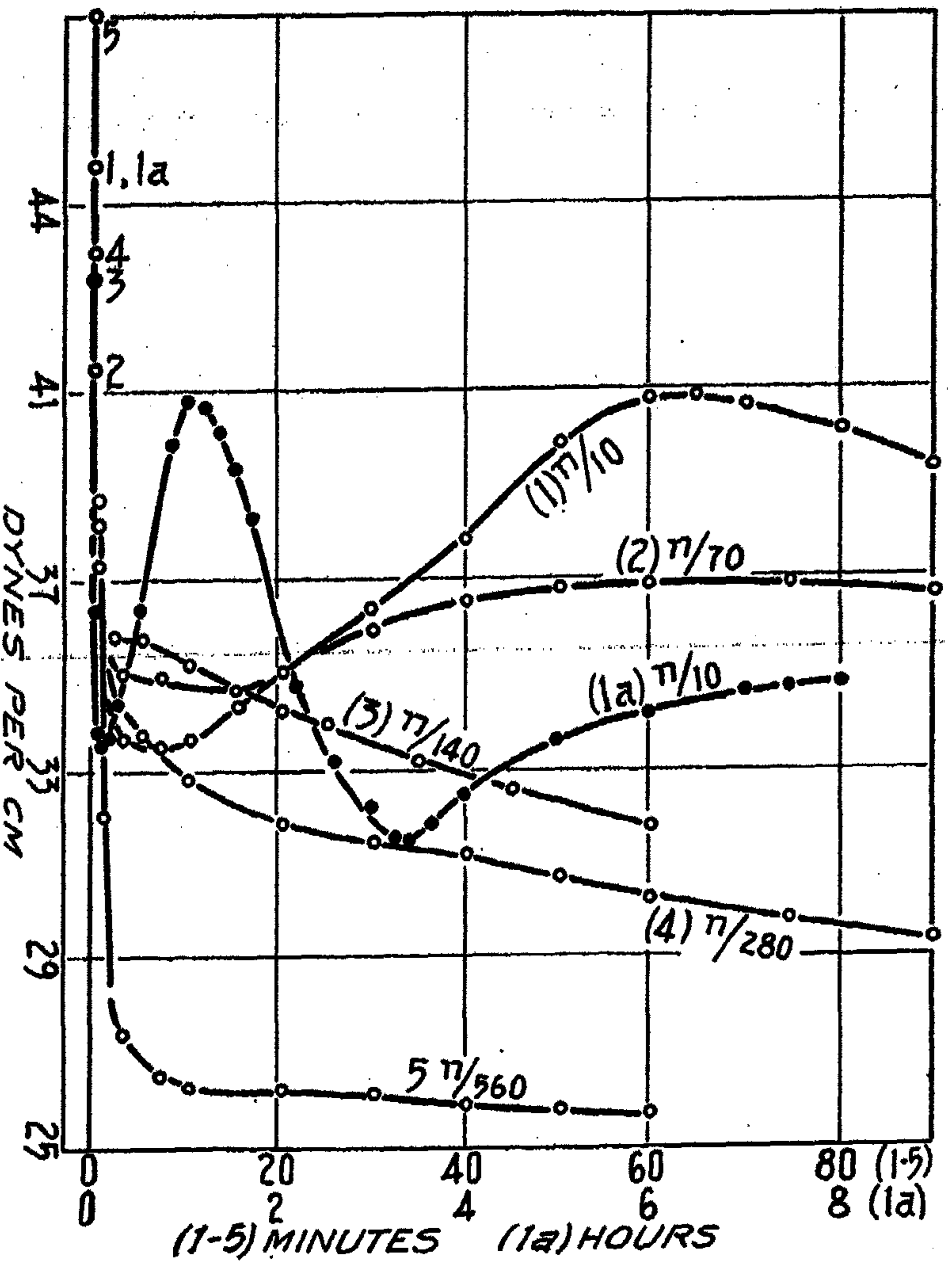

Fig. 2

Illustrating the effect of adding increasing amounts of sodium hydroxide to 0.1 percent solutions of sodium oleate.

Of may colloidal solutions which were tested in a preliminary study, one of silicic acid best illustrates the gradual deviation from a regular decrease in the surface tension with time. It was noted in the case of a freshly prepared solution of silicic acid that the change with time deviated considerably from the change as expressed by the given equation and that this deviation became more marked as the solution grew older until eventually the change was but a negligible one. As shown by Graham and other investigators since, the state of aggregation of silicic acid increases with time.

Farrow[1] and McBain, Taylor and Laing[2] have shown that, in the case of more concentrated soap solutions, the addition of alkali increases their colloidal properties. Irrespective of whether a comparison should be made between the behavior of the more concentrated solutions and the dilute ones used in the present investigation, it is an observed fact that the behavior at the surface of these dilute solutions, as increasing amounts of alkali are added, approaches that of a colloidal solution which is known to contain complex aggregates. This behavior suggests the possibility that the change of surface tension with time takes place according to the given equation only in the case of solutions in which the solute is present in a highly dispersed condition more similar to that to be found in the case of true-solutions.

TABLE II

Normality with respect to sodium hydroxide

	1/10	1/70	1/140	1/280	1/560
Time	Dynes	Dynes	Dynes	Dynes	Dynes
10 sec.	45.84	41.53	43.36	44.01	48.99
30 "	38.27	37.39	38.30	38.53	38.75
1 min.	36.38	35.97	36.85	36.14	32.05
2 "	33.97	35.17	35.91	34.76	28.37
3 "	33.77	35.06	35.83	34.25	27.49
5 "	33.50	35.03	35.83	33.78	26.92
7 "	33.55	35.01	35.68	33.32	26.57
10 "	33.67	34.83	35.28	32.86	26.33
15 "	34.40	34.73	34.69	32.36	.....
20 "	35.15	35.04	34.29	31.92	26.29
25 "	.....	35.63	33.97	31.62	.....
30 "	36.43	36.02	33.63	31.48	26.23
35 "	.....	36.44	33.22	31.40	.....
40 "	37.88	36.62	32.91	31.24	25.95
45 "	.....	36.75	32.58	31.00	.....
50 "	39.94	36.85	32.30	30.77	25.85
60 "	40.83	36.93	31.83	30.31	25.77
65 "	40.90	.....	.....	.....	.....
70 "	40.71	.....	.....	.....	.....
75 "	.....	36.93	.....	29.87	.....
80 "	40.17				
90 "	39.40				

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[1] J. Chem. Soc. 100, 347 (1912).

[2] J. Chem. Soc. 121, 621 (1922).

TABLE IIa

Time	Dynes	Time	Dynes	Time	Dynes
10 sec.	45.84	65 min.	40.90	240 min.	32.50
30 "	38.27	70 "	40.71	270 "	33.21
1 min.	36.38	80 "	40.17	300 "	33.61
2 "	33.97	90 "	39.40	330 "	33.92
3 "	33.77	100 "	38.36	360 "	34.20
5 "	33.50	120 "	36.42	390 "	34.42
7 "	33.55	140 "	34.80	420 "	34.56
10 "	33.67	160 "	33.20	450 "	34.73
15 "	34.40	180 "	32.23	460 "	34.81
20 "	35.15	195 "	31.55	470 "	34.81
30 "	36.43	205 "	31.49	475 "	34.81
40 "	37.88	210 "	31.59	480 "	34.81
50 "	39.94	220 "	31.84	42 hrs.	30.04
60 "	40.83	240 "	32.50	...	.....

(The data of Tables II and IIa were obtained at 25°C, by the capillary rise method with 0.1 percent solutions of sodium oleate to which varying amounts of sodium hydroxide had been added. The data of Table IIa are the continuation of those of column 1 of Table II.)

It was observed that the addition of increasing amounts of alkali decreased the tendency of these soap solutions to form stable foams. The more dilute solutions where there was an initial period of inactivity did not foam at all even when no alkali had been added. This would again support the point of view that for a stable foam to exist there should be an immediate and rapid decrease in the surface tension after the formation of the interface.

Experiments with Colloidal Sulphur

The experiments which were made with colloidal sulphur are of a more preliminary nature than any for which data have been given. Of the inorganic solutions which were tested, colloidal sulphur solutions were the only ones which were found to lower the surface tension progressively with time to a marked degree. It cannot be stated to what extent this effect might be due to the presence of pentathionic acid.

The solutions of colloidal sulphur were some which had been prepared for another investigation carried on in his laboratory by Dr. Rinde. The writer gratefully acknowledges Dr. Rinde's kindness in placing several samples of these solutions at his disposal. Two types of solutions were studied. One of these had been dialysed until nearly all of the hydrochloric acid, the peptizing agent, had been removed so that the sulphur just began to be precipitated. The second consisted of solutions which were so strongly acidified that the sulphur just began to be precipitated. The latter were about 0.5 normal with respect to hydrochloric acid. They contained, both at the bottom of the container and at the surface of the solutions, considerable amounts of coagulated crystalline sulphur. The surface consisted of an invisible film interspersed with these particles of sulphur as could be shown by shaking the solution to break up the film. All the solutions were transparent, slightly opalescent and had a yellow color.

The more acid solution had a density of 1.0070 and contained 2.50 percent of sulphur and 0.10 percent of nonvolatile matter. The surface tension measurements were made at 25°C, by the capillary rise method. The first reading was taken ten seconds after the formation of the interface.

In the case of the less acid solution the change with time took place exceedingly slowly in a manner shown by the data of Table III and by the upper curve of Figure 3. A similar change was noted in repeated experiments.

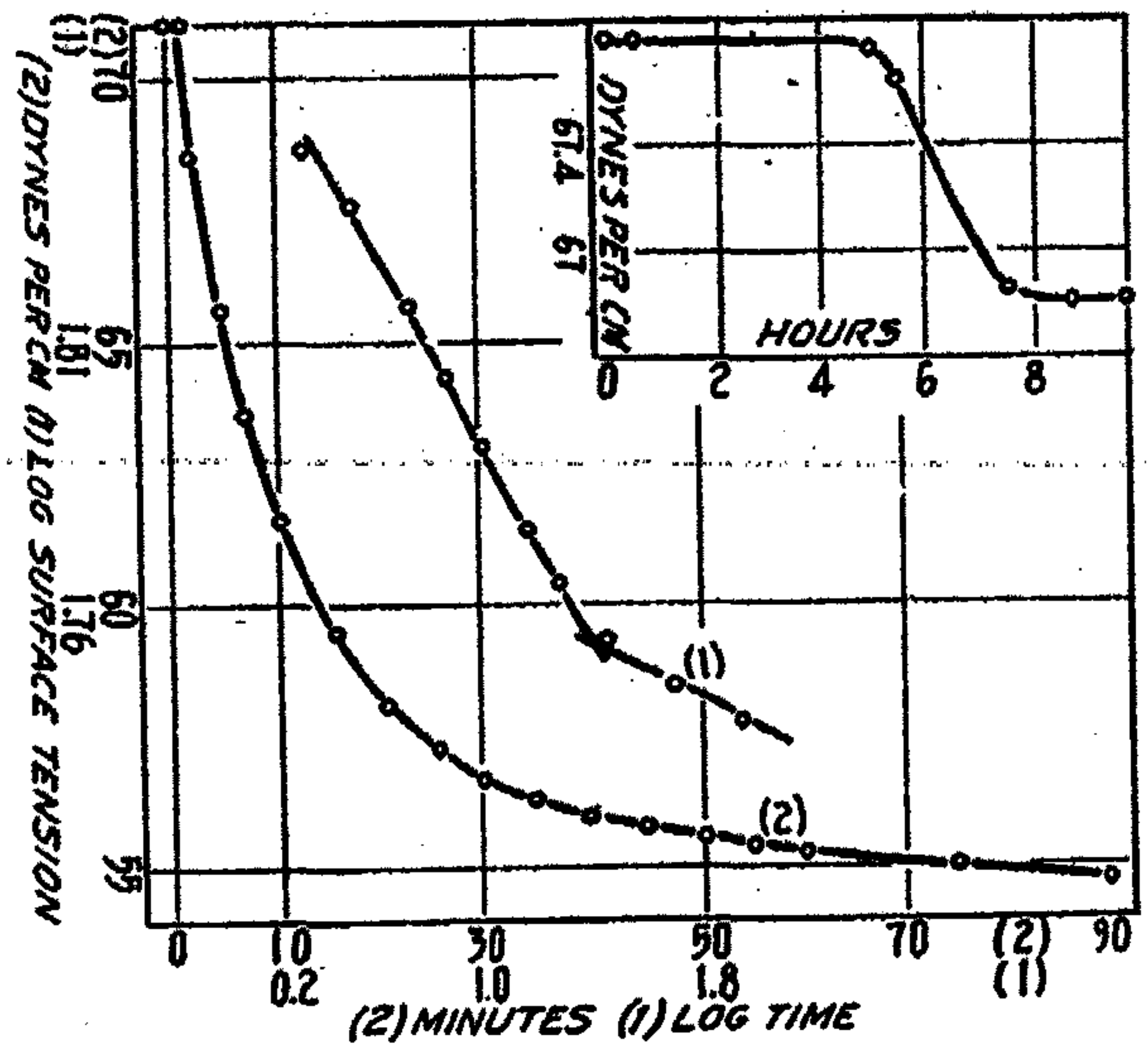

Fig. 3

The upper curve illustrates the change of surface tension with time for a solution of colloidal sulphur from which nearly all acid has been removed, the lower curve the same phenomenon in the case of a highly acid solution.

The nature of the change with time in the case of the acid solutions was found to depend upon the manner in which the sample used for measurement was taken from the container. If any of the surface film was included, a slow irregular and comparatively small decrease took place. The decrease was usually 0.5 to 0.6 dynes per cm. during a period of 24 hours as compared with a decrease of 15 dynes per cm. in 90 minutes when the sample was taken from the bulk of the solution so as to exclude the surface film. The results obtained in the latter case are illustrated by the data of Table IV and by the lower curves of Fig. 3. There was a period of initial inactivity, lasting from one to three minutes, which was followed by a rapid decrease in a manner expressed by the given equation as shown by the logarithmic curve. Equilibrium values varying about one dyne per cm. were usually reached in about three hours. When the interface was disturbed the surface tension rose to its original value. The capillary had to be cleared before an experiment could be repeated.

TABLE III

Time	Dynes per cm.
10 sec.	73.04
30 min.	73.01
5.00 hrs.	72.97
5.50 ”	72.85
7.50 ”	72.05
8.75 ”	72.01
10.00 ”	72.01

(Data obtained with the less acid solution of colloidal sulphur. No change took place for several hours following the 10 hour period.)

TABLE IV

Time	Dynes per cm.	Time	Dynes per cm.
10 sec.	71.02	20 min.	58.08
30 ”	70.99	25 ”	57.23
60 ”	70.99	30 ”	56.64
90 ”	70.99	35 ”	56.28
105 ”	70.56	40 ”	55.94
2 ”	70.18	45 ”	55.74
3 ”	68.47	50 ”	55.53
5 ”	65.57	55 ”	55.37
7 ”	63.57	60 ”	55.26
10 ”	61.63	75 ”	55.00
15 ”	59.44	90 ”	54.73

(Data obtained at 25° C, by the capillary rise method with a solution of colloidal sulphur which was 0.5 normal with respect to hydrochloric acid and contained 2.50 grams of sulphur per 100 ccm. of the solution.)

Summary

The following summary includes three papers on the surface concentration of colloids.

A simple but efficient method has been devised for preparing "ash-free" gelatine. The procedure which was developed makes it possible to remove practically all mineral matter by an electrolytic process without previous dialysis of the gelatine. It was found that all traces of iron cannot be removed from gelatine.

A convenient method has been devised for the manufacture of mechanically perfect glass tips to be used in measuring the surface tension of liquids by the drop-weight method. The tips which were repeatedly prepared by this method were free from any imperfections which were visible under a mangification of forty diameters.

The surface tension of solutions of ash-free, iso-electric gelatine was measured by the drop-weight method, at 40°C. Solutions of 0.01, 0.1, 0.5, 1.0, 2.0 and 9.45 percent concentration were used. It was shown that the surface tension changes with time and that the relationship which exists between these two variables is given by the equation

$$\sigma = a/t^n$$

but that this equation does not hold as the values for t approach zero. It was proved by the data of three independent methods that this equation well expresses the change which takes place with time. It was shown that equilibrium values are not soon reached by the drop-weight method and that data obtained by this method with solutions of gelatine have no significance unless the time of drop formation is taken into account and even then values are but relative ones. Data obtained relative to definite periods of time fluctuate considerably in the case of dilute solutions.

A much larger series of measurements was also made by the capillary rise method with gelatine solutions of 0.01, 0.1, 0.5, 1.0, and 2.0 percent concentration. The relationship existing between the two main variables, time and surface tension, was found to be even more precisely that expressed by the given equation. There was frequently, however, a change in the rate at which the surface tension changed with time. It was found that, when the hydrogen-ion concentration was changed by adding either an acid or a base, the surface tension was a minimum at the iso-electric point. Measurements made at 20°, 30°, and 40°C were similar but the values rose very considerably as the temperature decreased. The effect of hydrolysis by heating was found to be that of greatly increasing the rate at which the surface tension decreased with time. The decrease with time was found to be more rapid with a wider tube. Equilibrium values were not soon reached and measurements can, therefore, be relative ones only. It was shown that the equation frequently used by duNoüy for denoting a similar change is incorrect and that the change denoted by his data is better expressed by the writer's equation.

Tests made by the ring method showed that this method should not be used with solutions which readily foam so as to cause a film of liquid to adhere to the ring after it is detached.

It was shown that denatured casein has a solubility of 0.021 grams per liter at room temperature, and that casein solutions of this concentration change their surface tension with time in the same manner as gelatine solutions. The addition of acid did not affect the nature of the change but alkali in increasing amounts caused increasing irregularities and caused the solutions to foam less readily. Casein prepared by different methods showed the same behavior.

The surface tension of solutions of crystalline egg-albumin was found to change with time in a manner similar to that of the other proteins. Sodium hydroxide added to give 0.1 percent solutions a greater normality than 1/11200 with respect to this reagent was found to cause the surface tension to fluctuate up and down periodically without causing any great ultimate decrease and to decrease the tendency of these solutions to foam. Potassium chloride and sulphuric acid did not produce a similar effect.

The surface tension of solutions of crystalline oxy-haemoglobin, and that of solutions of reduced haemoglobin and of haemoglobin carbon monoxide was found to change with time in a manner similar to that of the other proteins which were investigated.

The surface tension of sodium oleate solutions of 1.0 to 0.0001 percent concentrations was measured. It was found that in the case of the stronger solutions the change with time was exceedingly rapid but took place according to the given equation. Alkali added to 0.1 percent solutions was found to cause a decreasing irregularity as the amount of alkali was increased until the change with time fluctuated periodically up and down. Alkali was found to cause a decreased tendency to foam.

It has been shown that it appears probable that the change of surface tension with time in a regular manner according to the given equation only takes place in the case of colloidal solutions in which the solute is highly dispersed in a manner similar to that of true solutions.

In preliminary experiments it was shown that the surface tension of colloidal sulphur solutions will under certain conditions change with time according to the given equation. No other inorganic colloid was found to behave similarly. This behavior cannot be reconciled with the assumption of the preceding paragraph and it cannot be stated to what extent the phenomenon is due to the presence of pentathionic acid.

The writer is greatly indebted to Professor F. G. Donnan F. R. S. for much helpful criticism.

The Sir William Ramsay Laboratories of Inorganic and Physical Chemistry.
University College, London.
April 15, 1925.

THE REACTIONS OF HYDROGEN ACTIVATED BY EXCITED MERCURY ATOMS*

BY HUGH STOTT TAYLOR AND ABRAHAM LINCOLON MARSHALL

Studies in contact catalysis have shown that reactions occur at contact surfaces and that the properties of the surface are fundamental to both the velocity and the nature of the reaction occurring. These studies have, however, failed to reveal, as yet, what is the mechanism of the activation of the reacting species, induced by association with the contact agent. It has, on several occasions, been pointed out by Bancroft[1], that the solution to the problem of how activation occurs might be reached through a comparison of the results of catalytic and photo-chemical studies. Bancroft illustrated this point by reference to various decomposition processes which organic molecules undergo in contact with catalysts and also under the influence of ultraviolet light. There are, however, several reasons why such a comparison may involve problems of very great difficulty. A considerable body of experimental work in recent years[2] has shown that catalytic decomposition of organic compounds at surfaces are complex processes, very sensitive in their progress to the catalyst preparation and the purity of the reacting species. The photochemical studies, also, show a wide variety of processes occurring simultaneously, involving not only decompositions but syntheses of new substances from the initial products of decomposition. It seems, therefore, worth while to attempt a comparison of catalytic and photo-effects in reactions which, from their simplicity and the smoothness with which they proceed catalytically, offered greater prospects of successful issue. Processes of hydrogenation seemed to present such an opportunity. Several catalytic hydrogenations have been shown to occur quantitavely, without complicating side reactions, and with measurable velocities. Recent research has shown that at least two methods exist by which hydrogen can be brought in to the atomic condition by physical agencies. In one method, the passage of a powerful high tension discharge through molecular hydrogen at low partial pressures was shown by Wood[3] to yield hydrogen atoms. In the other method, the resonance radiation absorbed by mercury vapor from the light of a cooled mercury vapor arc can be transferred, as was shown by Cario and Franck[4], to hydrogen present in the illuminated system with the production of atomic hydrogen.

Such methods of production of atomic hydrogen seemed to offer a very interesting opportunity to learn more concerning the activation necessary in

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*Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] First Report, Committee on Contact Catalysis, National Research Council; See also, Ind. Eng. Chem., 16, 270 (1924).

[2] See especially that of Adkins and his co-workers: J. Am. Chem. Soc., 44, 385, 2175 (1922); 45, 809 (1923); 46, 130 (1924); 47, 807 (1925).

[3] Proc. Roy. Soc., 102A, 1 (1922).

[4] Z. Physik, 11, 162 (1922).

catalytic hydrogenation processes, from a study of the reactivity of such hydrogen atoms with a variety of materials known to be subject to catalytic hydrogenation. Reactivity with hydrogen atoms would indicate that adequate activation of hydrogen alone was a sufficient preliminary to reaction. Non-reactivity with the atoms would suggest that the catalytic process must involve activation of both molecular species.

Marshall and Taylor have shown[1] that hydrogen atoms by Wood's method will produce hydrogen chloride when led into unilluminated chlorine. Further work by Marshall[2] has shown that more hydrogen chloride is produced than corresponds with hydrogen atoms introduced and that therefore some chain mechanism, as in the photochemical combination of hydrogen and chlorine, is involved. Bonhoeffer[3] has studied the reactivity of such hydrogen atoms with a number of solid substances such as sulphur, phosphorus and arsenic as well as with an unsaturated oil, showing that hydrogenation occurs in each instance. Oxides, sulphides, halides and oxygen salts were reduced by the atomic hydrogen.

For kinetic studies with gases, the activation of hydrogen by the resonance radiation of mercury is more amenable to experimental manipulation. Cario and Franck showed that hydrogen atoms so produced would reduce copper oxide and tungstic oxide at room temperatures and would 'clean up' on the walls of the containing vessel. Dickinson has shown[4] that oxygen and hydrogen atoms so produced will react at 45°C. W. A. Noyes, Jr., has recently indicated[5] that at the temperature of boiling mercury a nitrogen-hydrogen mixture in the presence of mercury vapor illuminated by the necessary radiation produces minute quantities of ammonia. In the experiments recorded in this paper we have studied the reaction of hydrogen activated by excited mercury atoms with ethylene, carbon monoxide, nitrous oxide and carbon dioxide. For comparison with the results of the work already recorded we have also made measurements with oxygen and nitrogen.

Our experiments differ from those which have preceded in the working pressures over which the observations extend. Cario and Franck studied the rate of 'clean up' at hydrogen pressures of 0.2 mm. Dickinson showed that, with an initial pressure of 0.18 mm., an hourly pressure decrease of 0.06 mm. was obtained. Our normal initial pressures have been in the neighbourhood of atmospheric pressure and the reaction concentrations have been suitably varied so that the reaction rates over wide pressure intervals and with varying ratios of reactants have been ascertained.

Experimental Procedure

The reaction vessel consisted of a horizontal transparent fused quartz tube, 175 ccs. in volume, connected to a manometer and also to a burette

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[1] Nature, 112, 937 (1923).
[2] J. Phys. Chem., 28, 842 (1925).
[3] Z. physik. Chem., 113, 199 (1924).
[4] Proc. Nat. Acad. Sci., 10, 409 (1924).
[5] J. Am. Chem. Soc., 47, 1003 (1925).

system and oil pump for evacuation. A 7cm. Hanovia quartz mercury vapor arc was mounted horizontally and in contact with the reaction tube throughout its length. The whole system was kept in a water bath through which water at approximately 15°C. was rapidly passing. In this manner the mercury arc system was kept cold, a necessary precaution if the radiation, $\lambda = 2536.7$ Å, is to be obtained from the arc. In a hot mercury arc all the radiation of this frequency is absorbed by the mercury vapor in the arc and none is transmitted. We have specially verified this point by illuminating our reaction system with the light from the hot arc transmitted through a quartz window in our water bath. In such circumstances none of the effects recorded below were obtained. The reaction vessel always contained as much as 1cc. of liquid mercury.

Compressed ethylene, oxygen, nitrous oxide and carbon dioxide were used as the source of these gases in the experiments, without any special purification. Nitrogen and hydrogen from cylinders were freed from oxygen. Carbon monoxide was prepared from formic acid and concentrated sulphuric acid.

All the reactions studied proceed with a decrease in the number of molecules so that the rate of the reaction could be followed manometrically at constant volume.

In all of the experiments the arc burned at approximately 25 volts and consumed some 200 watts. The deviations from these magnitudes never exceeded 20 percent.

Experimental Results

Hydrogen and Ethylene. The data for the hydrogenation of ethylene at 15.5°C. are shown in Table I. The mercury arc burned at 28 volts and consumed 210 watts with variations amounting to ± 10 percent.

TABLE I

$C_2H_4 + H_2 = C_2H_6$, at 15.5°C.

Initial Hydrogen Pressure 34.5 cm.		Initial Ethylene Pressure 32.3 cm.	
Time in Hours	Pressure Decrease	Time in Hours	Pressure Decrease
0.25	1.05 cm.	10.05	24.95
0.90	2.8	11.07	27.25
1.35	4.25	12.66	30.5
2.38	6.85	13.05	31.3
4.08	10.8	13.47	32.0
5.92	15.5	13.73	32.25
7.28	18.7	14.0	32.3
9.18	23.0	14.25	32.3

Since the decrease in pressure corresponds exactly to the initial ethylene pressure it is evident that the reaction proceeds smoothly according to the usual equation. It will be noted that over the first thirteen and one quarter hours the change in rate with time is relatively small. Initially the rate of pressure decrease amounts to 3 cm. per hour. From the tenth to the thirteenth hours the rate averages 2.15 cm. decrease per hour. Between 13.25 and 13.75 hours the velocity falls suddenly to zero. A further experiment in which ethylene was present in excess (27.8 cm. C_2H_4; 21.5 cm. H_2) showed the same initial rate as the above. Measurements were discontinued after 1.5 hours.

We have already pointed out that the above reaction was quite absent when the mercury arc was operated hot, outside the water bath and illuminating the reaction system through a quartz window in the water-bath. This result can be further emphasized by our experimental observation that a hydrogen-ethylene mixture containing mercury vapor and maintained at 100°C. showed no change in pressure when illuminated by the hot mercury arc for 15 hours.

Hydrogen and Oxygen: In Table II are recorded experimental data for the reaction between hydrogen and oxygen. In this experiment, results were first obtained with an initial total pressure of 36 cm. After a steady value for the rate had been determined the pressure was reduced by evacuation and the rate at the end of the reaction was observed. This latter rate is recorded in the right half of the following table.

Table II

$2H_2 + O_2 = 2H_2O$ at 15.5°C.

Initial Hydrogen Pressure, 20.15 cm.		Initial Oxygen Pressure, 16.0 cm.	
Time in Hours	Pressure Decrease	Time in Hours	Pressure Decrease
0.32	0.05	0.66	0.4
1.15	0.55	1.02	0.65
1.66	0.85	1.65	0.9
2.92	1.25	2.0	1.1
3.55	1.85	4.0	1.4
4.93	2.55	5.0	1.4
6.07	3.05		

Within the experimental error the velocity of reaction was, in this case, constant over the whole pressure range covered by the experiment. It is to be noted, however, that the rate is considerably less than was found in the case of the hydrogen-ethylene reaction. The reaction system contained liquid water, so that, throughout the experiment, water vapor was present at the saturation concentration.

Hydrogen and Carbon Monoxide: The data in Table III present the experimental results obtained when hydrogen and carbon monoxide in the presence of mercury vapor were exposed to the resonance radiation of mercury from the arc. In the first case the gases were present in approximately equal concentrations. In the second case hydrogen was present in pronounced excess.

TABLE III

$H_2 + CO = HCHO$ etc. at 15.5°C.

Initial Hydrogen Pressure 30.2 cm. Initial Carbon Monoxide Pressure 32.3 cm.		Initial Hydrogen Pressure 44.35 cm. Initial Carbon Monoxide Pressure 25.25 "	
Time in Hours	Pressure Decrease	Time in Hours	Pressure Decrease
0.25	0.85 cm.	0.23	0.60 cm.
0.55	1.70	0.42	2.0
0.77	2.3	0.73	4.35
1.16	3.3	1.0	7.45
1.89	5.05	1.58	10.35
2.37	6.15	2.08	13.05
3.35	7.9	2.66	15.5
3.96	8.75	3.0	16.85
4.69	9.65	3.96	19.45
5.60	10.85	4.98	21.45
5.96	11.35	6.0	23.05
7.0	12.45	6.75	24.15

These reactions have not been followed to their end. Test showed that the reaction was complex, formaldehyde, solid polymerised products and methane being among the identified reaction products. A further study of this reaction is deferred until a method has been devised of protecting the products of reaction against further action of the ultra-violet light and of hydrogen atoms. The experiments performed suffice to settle the immediate problem of interest, namely, that unactivated carbon monoxide will react readily with hydrogen atoms. Formaldehyde is undoubtedly the primary reaction product and this synthesis represents a new method of achieving its production at atmospheric pressure and room temperature. That the carbon monoxide was not activated by the light employed is suggested by the experimental observation that mixtures of carbon monoxide and oxygen when illuminated gave no reaction, in marked contrast to the case of hydrogen and oxygen already considered. The data for ethylene, oxygen, and carbon monoxide are presented graphically in Figure 1.

Hydrogen and Carbon Dioxide: Two experiments were carried out, one with 32.7 cm. CO_2 and 21.1 cm. H_2 as dry gases, the other with 35.8 cm. CO_2 and 28.1 cm. H_2 in presence of a small amount of liquid water. In neither case was any pressure change detectable over a period of several hours exposure to the resonance radiation, although the manometric system permitted a change of 0.5 mm. to be very definitely recorded.

Hydrogen and Nitrogen: Mixtures of nitrogen with excess hydrogen in presence of mercury vapor showed no measurable pressure change when illuminated with resonance radiation, the working temperature being 17°C. Any pressure change occurring was less than 0.5 mm. of mercury in a system at atmospheric pressure containing 20 percent nitrogen. No special attention was paid in these experiments to secure thoroughly dry gases. In some of the experiments, the reaction vessel was screened from the lamp by a quartz mantle carrying ethyl alcohol, with a view to cutting out the radiation from the mercury arc capable of decomposing any ammonia that might be formed. Tests with Nessler's reagent upon completion of a run failed to reveal any ammonia formed.

Hydrogen and Nitrous Oxide: A mixture of hydrogen and nitrous oxide reacted more rapidly when illuminated with resonance radiation than did similar mixtures of hydrogen and oxygen. That water vapor is one of the reaction products is evident from the initial slow rate of pressure decrease during the first hour as shown in Table IV and in Fig. 2, during which time a water film was forming. The reaction is complicated by the fact that

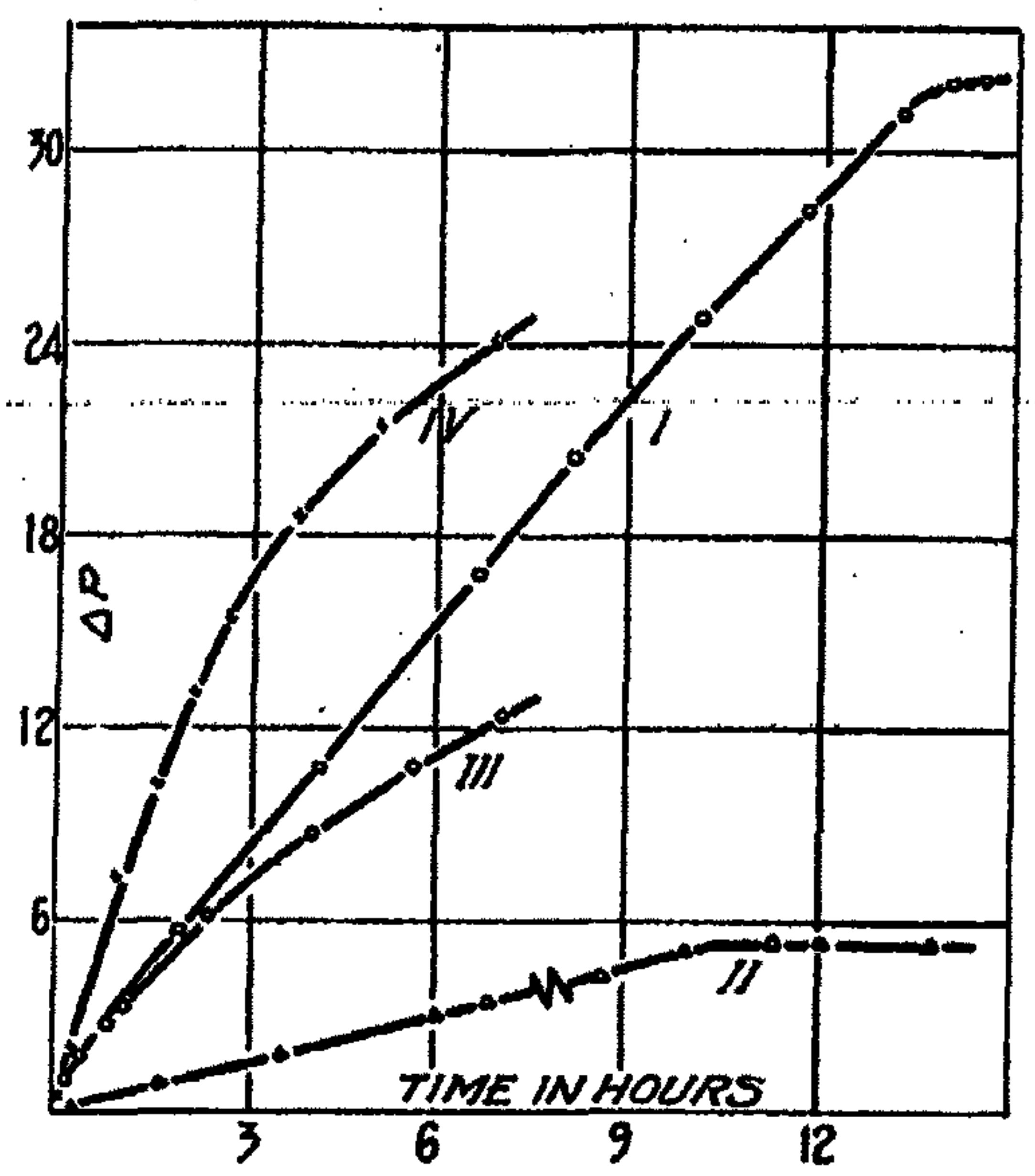

Fig. 1

(I) Hydrogen-Ethylene; (II) Hydrogen-Oxygen; (III) and (IV) Hydrogen-Carbon Monoxide.

TABLE IV

$N_2O + H_2$ at 15°C.

Initial Hydrogen Pressure 9.7 cm.
Initial Nitrous Oxide Pressure 8.85 cm.

Time in Hours	Pressure Decrease
0.5	0.35 cm.
0.86	1.1
1.0	1.4
1.62	2.8
2.0	3.4
2.58	4.25
3.5	5.5
4.84	6.95
5.84	7.3

Initial Nitrous Oxide Pressure 42.5 cm.

Time in Hours	Pressure Increase
0.20	0.45 cm.
0.50	1.1
0.75	1.4
1.75	3.0

nitrous oxide alone in presence of mercury vapor is decomposed by the light of the cooled mercury arc, an increase in pressure resulting. We are planning a special study of the photochemical decomposition of this gas.

Discussion of Results

The experimental results with ethylene, carbon monoxide, and oxygen show decisively that the hydrogenation or reduction of these compounds can be attained by activation of the hydrogen alone to the atomic condition. Activation of the compound reduced is not necessary if the hydrogen be brought into the atomic state. The hydrogenation of carbon dioxide and of nitrogen does not appear to be so readily achieved, a conclusion of importance in respect to the production of methane and, of ammonia from these respective gases by contact catalytic methods.

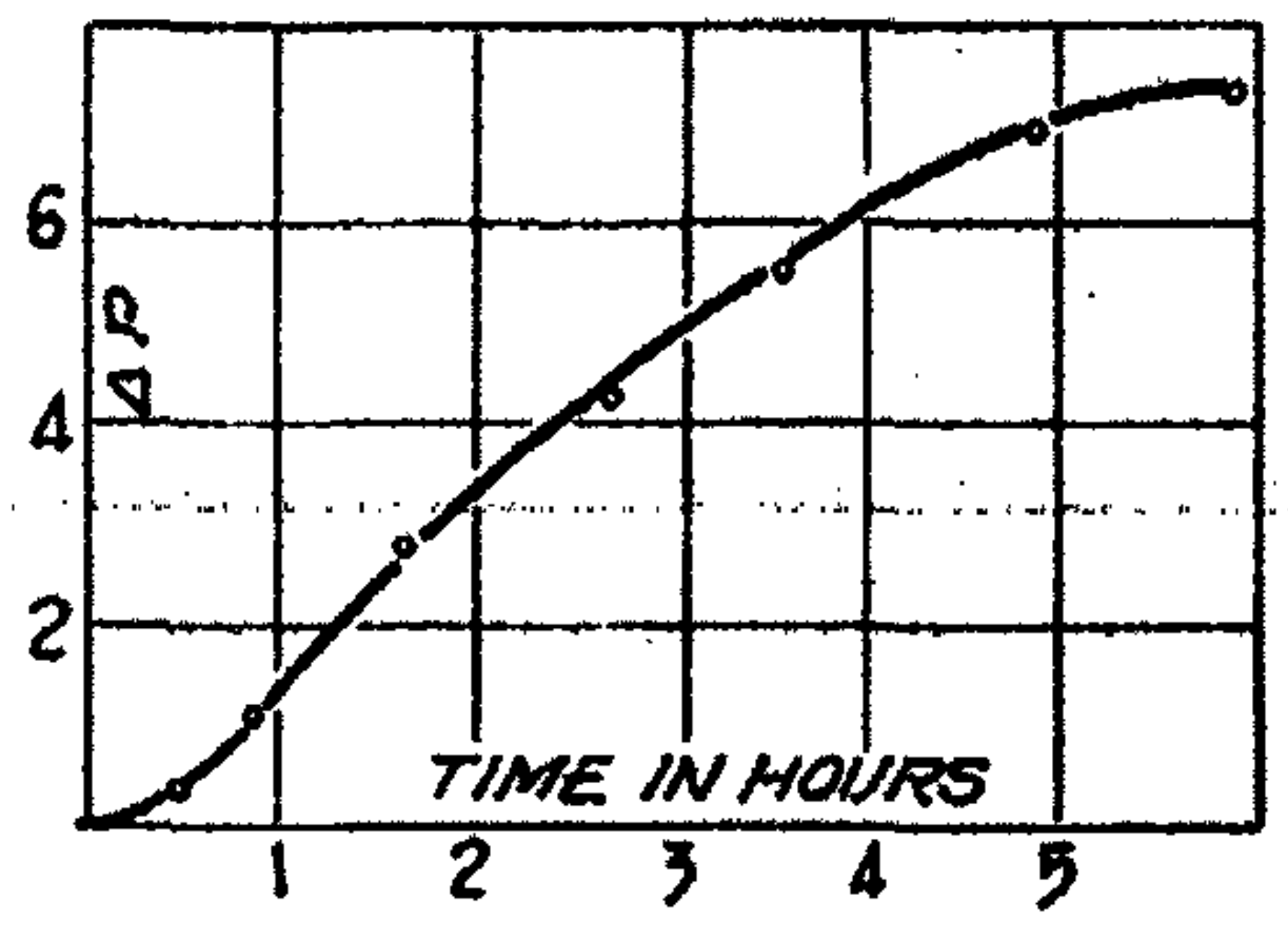

Fig. 2
Hydrogen-Nitrous Oxide

On the quantitative side, the experimental results disclose a state of affairs for which there is little precedent in the earlier work. We refer to the relative rapidity with which the hydrogenation processes are taking place. Turner has calculated[1] from the data of Cario and Franck that in their experiments, using an air-cooled arc, the decrease in pressure, by reaction with copper oxide, can attain at a maximum 8×10^{-4} mm. per minute or approximately 0.05 mm. per hour in a vessel 7.5 cc. in volume. This also is the order of pressure drop in Dickinson's experiments with oxygen using an air-cooled arc where an observed pressure decrease of 0.06 mm. per hour at a working pressure of 0.18 mm. was obtained. These reaction rates are negligible when compared with those recorded in the present paper. With carbon monoxide a maximum rate of 70 mm. pressure decrease per hour was recorded. With ethylene the rate attained 30 mm. per hour. With oxygen it was 5 mm. per hour. Our reaction vessel had a volume of 175 ccs. These velocities range, therefore, from 100 to 40000 times those recorded in the earlier work. The reason for this extraordinary divergence we have not as yet elucidated. It is improbable that there is this degree of difference in the intensity of the exciting radiation. We are planning, however, to extend our studies to a quantitative determination of the intensity and its relation to the reaction rate. There is a possibility that, under the experimental conditions chosen, the high yields are to be attributed to a chain mechanism of the type now familiar in discussions of the photochemical hydrogen-chlorine combination[2]. If such

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[1] Phys. Rev., (2) 23, 466 (1924).

[2] See for example, Photochemistry, Chapter 18, p. 1222-1230, Treatise on Physical Chemistry, Van Nostrand, 1924. Cario and Frank, Z. Physik, 17, 209 (1923) discuss the possibility, even with their low reaction yields, of a chain mechanism in the reduction of metallic oxides.

existed in the present case we should have the entirely parallel case of hydrogen atoms functioning as a photochemically produced catalyst for the combination of hydrogen and a reducible gas. The decision on such matters must await a more quantitative study of the reactions. To that end we are employing a more refined technique and a more suitable arrangement of reaction system and exciting arc. With the new experimental arrangement it will be possible greatly to extend the range of reactions studied, the temperatures at which they proceed and the sensitising energies at our disposal.

We wish to acknowledge our indebtedness to Professor Karl T. Compton for advice and assistance which led to the right choice of experimental conditions.

Summary

Ethylene, carbon monoxide, oxygen and nitrous oxide have been shown to react at room temperatures with hydrogen atoms produced by collisions of molecular hydrogen with mercury atoms excited by illumination with the resonance line, $\lambda = 2537.6$ Å. of the mercury arc. Carbon dioxide and nitrogen do not react with hydrogen atoms so far as can be observed under the given experimental conditions.

The velocities of reaction measured are some 100-40000 times more rapid than in previous studies of the same type. The present experiments were conducted at pressures averaging 0.5 atm. as opposed to earlier work with pressures of a few mm. or less.

It is suggested that these high yields may result from a chain mechanism of the type obtaining in the photochemical hydrogen-chlorine combination.

The reactions studied form additional examples of photosensitisation, with mercury atoms as the sensitiser. One of the reactions, that between hydrogen and carbon monoxide, yields, *inter alia*, formaldehyde, by a new process of photosynthesis at room temperatures.

The bearing of these photochemical studies on the problem of mechanism in contact catalysis has been indicated.

Princeton, New Jersey.

THE CONDUCTIVITY OF PHOSGENE SOLUTIONS OF ALUMINIUM CHLORIDE AT 25°, 0° AND −45°

BY ALBERT F. O. GERMANN

In a short paper entitled "Carbon Monoxide, a Product of Electrolysis"[1], presented at the Stanford University meeting of the Pacific Division of the American Association for the Advancement of Science, the author announced that solutions of aluminium chloride in liquid phosgene conduct electricity, the solvent being decomposed in the process into carbon monoxide and chlorine. Because the production of carbon monoxide by electrolysis is unique, and because the solution of aluminium chloride in phosgene has unusual chemical properties, it became important to know something about the conductivity of this solution.

Conductivity Cell. The cell used is shown diagrammatically in Figure 1. The body of the cell consisted of two principal portions, A, 22 mm. in diameter, containing the electrodes E, and B, 30 mm. in diameter, containing the electrode supports, c, c. Surmounting B were the filling and emptying devices: F was a tube of 12 mm. bore through which weighed samples of aluminium chloride were introduced, and which was then sealed off; J was a flat joint by means of which the cell could be attached to the phosgene purification apparatus, and the cell evacuated, or filled with phosgene; S was a stopcock to which was adapted a brass stopcock clamp to prevent the stopper from blowing out at the highest temperature with the more dilute solutions[2]. D was a capillary tube extending to the bottom of the cell, sealed off at the upper end; by breaking the tip of this tube, the liquid contents of the cell could be syphoned off, and the walls washed free of solution—with the judicious use of freshly distilled phosgene. The electrodes were constructed of heavy platinum foil, 20 mm. × 28 mm., coated with platinum black. Electrical contact was made by means of a few drops of mercury placed in each supporting tube c, and copper wires extending down into the mercury.

The *procedure* adopted was to begin with an amount of solution large enough to fill the cell approximately to the level at which the electrode supports were sealed in by introducing a weighed amount of aluminium chloride, sealing off the filling tube F, evacuating the cell, weighing, distilling in an excess of pure phosgene, distilling off the excess after effecting solution of the aluminium chloride, and weighing again. Conductivity measurements were then made at 25°, 0° and −45°. The solution was then concentrated to approximately double the previous concentration by distilling off some of the solvent, weighing again, etc. Three or four measurements could thus be made with a single sample of aluminium chloride, after which the solution was discarded by discharging through the capillary tube D, as already indicated.

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[1] Science, 60, 434 (1924).

[2] Germann and McIntyre: J. Phys. Chem. 29, 102 (1925).

Conductivity Measurements. The method used was the well known Kohlrausch method, using the alternating current produced by a simplified Vreeland Oscillator, except for a few of the last measurements, when a microphone hummer controlled by a tuning fork attachment was used, each capable of producing an alternating current with a frequency of 1000 cycles per second. For the highest resistances two special L. & N. boxes each containing five coils of one hundred thousand ohms each were used, and for the smaller resistances, a number of L. & N. two and four dial resistance boxes were connected in series. The bridge readings were made with the slide wire of an L. & N No. 7651 Student's Potentiometer, with the end coils in series. The cell constant and the conductivity of the pure solvent were determined on two different occasions, at the beginning of the measurements, and after half the measurements had been made by Mr. Russell Timpany on the first occasion, and by the author on the second, using fiftieth-normal solutions of thrice recrystallized potassium chloride made up with carefully prepared conductivity water. The value of the cell constant at zero was considerably lower than the value at 25°, probably due to the construction of the cell. Following are the values obtained, and the value assumed for the lowest temperature:

at $25°$, $C=0.0133$
at $0°$, $C=0.0130$
at $-45°$, $C=0.0125$

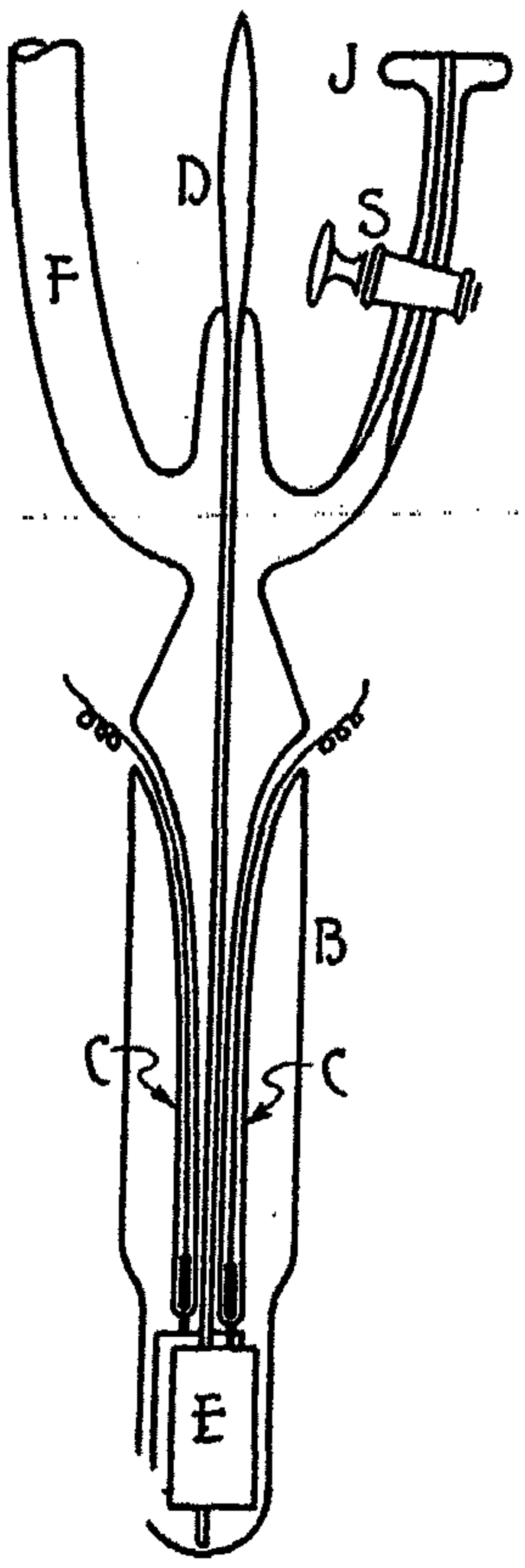

Fig. 1

Purification of materials. The phosgene was purified by fractional distillation of the technical product supplied by the Chemical Warfare Service in the manner described by Germann and Gagos[1] and had a vapor tension at zero of 557 mm.

The aluminium chloride used was distilled from a mixture of the purest obtainable aluminium chloride and powdered aluminium, under a pressure in excess of two and one half atmospheres, in a specially constructed pyrex still. The product obtained in this way is snow white, and deliquesces in an atmosphere of phosgene vapor, while the unpurified product dissolves very slowly.

Constant temperature baths. Conductivities were measured at three temperatures. A water-filled thermostat, maintaining a temperature of 25°, constant to within 0.01°, was used for the highest temperature. At zero, a large Dewar tube filled with washed cracked ice was used. For the lowest temperature, a Dewar tube filled with liquid ammonia exposed to the air, and

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[1] J. Phys. Chem., 28, 965 (1924).

whose temperature was found to remain constant to within one or two degrees, was employed.

Results. Tables I, II and III contain the data obtained for the conductivity of the solutions at 25°, 0° and −45° respectively. Six samples of aluminium chloride were used for the measurements, numbered A, B, C, D, E, and F, weighing respectively 0.7865 gm., 3.0935 gm., 12.5100 gm., 0.0144 gm., 0.1057 gm., and 1.1922 gm. The subscripts attached to each sample number in the tables, as A_1, A_2, A_3, etc., refer to the different dilutions obtained with the sample in question by adding or distilling off phosgene. The percentage of aluminium chloride in column 2 was calculated from these weights. Column 3 records the density of the solution, obtained for the solutions at 25° and at 0° from the density curves given by Germann[1], and for the solution at −45° by simple extrapolation, assuming the coefficient of thermal expansion between 0° and 25° to hold. Column 4 gives the molecular concentration of Aluminium chloride, column 5 the molecular volume, or the dilution, column 6 the specific conductivity multiplied by 10^6, and the last column the molecular conductivity multiplied by 10^3. In the calculation of the molecular conductivities, following the method adopted by Franklin[2] for the conductivity of sulfur dioxide solutions no correction was made for the conductivity of the solvent. Figure 2 contains the conductivity curves. From the smoothed curves, plotted on a large scale, the molecular conductivities have been read off at regular intervals, and set down in Table IV.

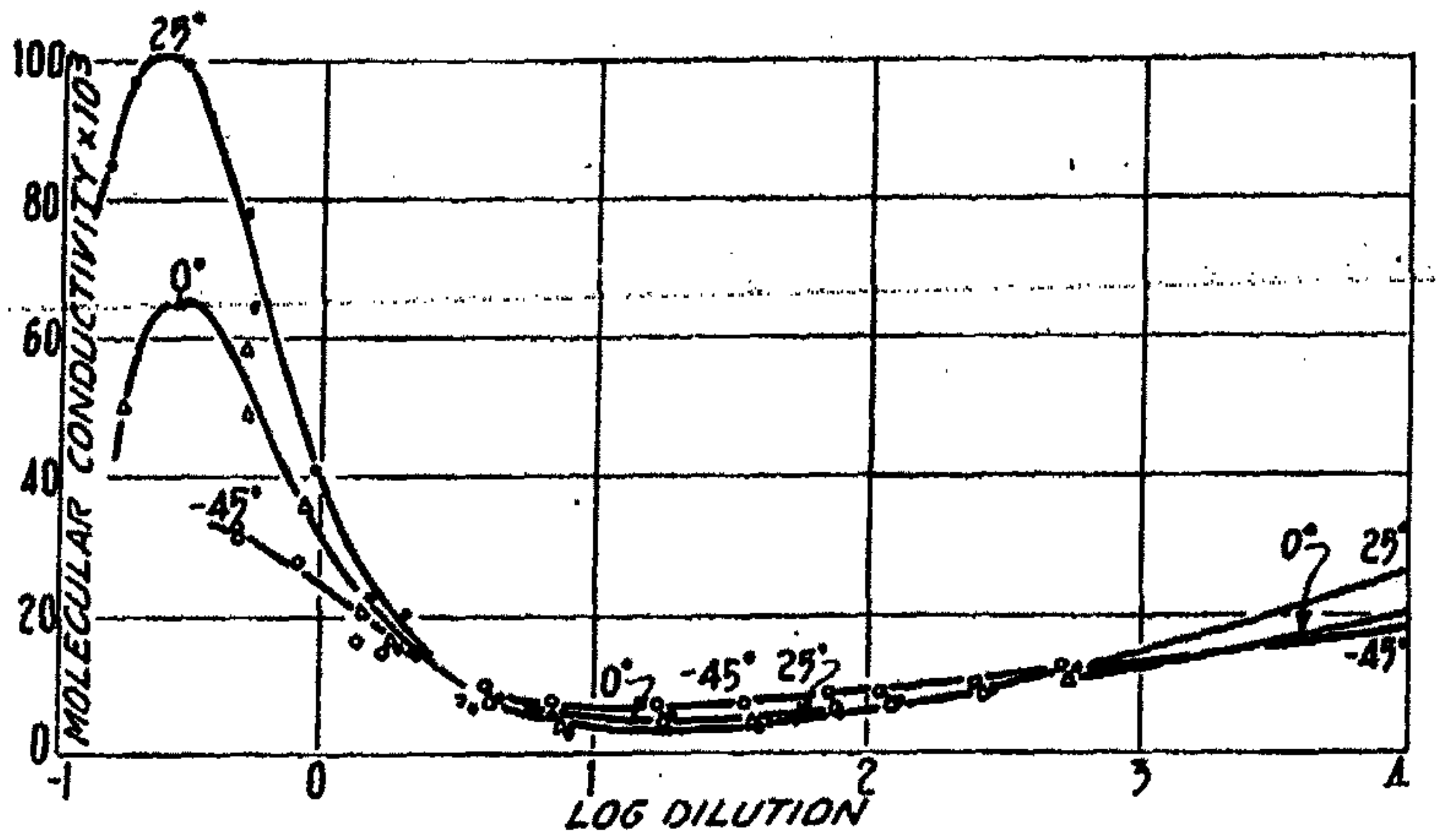

FIG. 2

Discussion of Results. The form of conductivity curve obtained for solutions of aluminium chloride in phosgene is one that has been found in more or

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[1] J. Phys. Chem. 29, 138 (1925).

[2] J. Phys. Chem., 15, 675 (1911).

less modified form in numerous other cases of solutions in weakly ionizing solvents, and a most exhaustive discussion of the phenomenon has been given by Franklin in his study of the conductivity of sulfur dioxide solutions.

According to this interpretation, we must consider the most concentrated solutions, which contain relatively little of the solvent, to approach the condition of the fused salt; that is, whatever ionization there is, must be due only in very small part to the presence of the solvent, and almost entirely to the self-ionization of the solute. At the highest concentrations, however, the mobility of the ions will be considerably diminished because of the relatively high viscosity of the solution; as the solution is diluted, the viscosity will rapidly diminish, so that the ionic mobility, and therefore the molecular conductivity, will increase. This would account for the initial rise in conductivity.

Table I

Conductivity at 25°

Sample	% $AlCl_3$	Density	Molecular concentration $AlCl_3$	Molecular volume	Specific Conductance $\times 10^6$	Molecular Conductance $\times 10^3$
		1.3685			0.007	
D_1	0.01725	1.3686	0.00177	565	0.0218	12.30
D_2	0.0357	1.3687	0.00366	273.4	0.0333	9.10
D_3	0.0763	1.3690	0.00783	127.7	0.0564	7.2
E_1	0.123	1.3692	0.01262	79.3	0.0706	5.6
E_2	0.245	1.3700	0.02515	39.75	0.1047	4.16
E_3	0.514	1.3716	0.0528	18.95	0.276	5.23
A_3	1.240	1.3759	0.1279	7.82	0.604	4.72
F_1	1.25	1.3760	0.129	7.76	0.416	3.23
A_1	1.355	1.3766	0.1398	7.16	0.717	5.13
A_2	2.18	1.3813	0.2258	4.43	1.80	7.97
F_2	2.66	1.3840	0.276	3.624	1.81	6.56
A_4	4.62	1.3947	0.483	2.07	9.8	20.3
B_1	5.00	1.3966	0.523	1.912	8.38	16.0
F_3	6.19	1.4027	0.651	1.535	14.57	22.4
B_2	10.00	1.4225	1.066	0.938	43.6	40.9
C_1	17.3	1.4602	1.893	0.528	122.0	64.4
B_3	17.8	1.4627	1.953	0.512	153.	78.3
C_2	29.5	1.5232	3.37	0.297	335.	99.5
C_3	44.6	1.5998	5.35	0.187	520.	97.3
C_4	53.0	1.6425	6.525	0.153	554.	85.0

TABLE II

Conductivity at 0°

Sample	% $AlCl_3$	Density	Molecular Concentration $AlCl_3$	Molecular Volume	Specific Conductance $\times 10^6$	Molecular Conductance $\times 10^3$
		1.4275			0.007	
D_1	0.01725	1.4276	0.001845	542.0	0.0194	10.5
D_2	0.0357	1.4277	0.00382	262.0	0.0325	8.52
D_3	0.0763	1.4279	0.00817	122.5	0.0605	7.41
E_1	0.123	1.4281	0.01317	75.9	0.0852	6.46
E_2	0.245	1.4287	0.0262	38.2	0.130	4.97
E_3	0.514	1.4301	0.0551	18.15	0.2935	5.33
A_3	1.240	1.4337	0.1333	7.50	0.735	5.51
F_1	1.250	1.4338	0.1344	7.44	0.491	3.65
A_2	2.18	1.4385	0.2350	4.26	2.09	8.91
F_2	2.66	1.4408	0.287	3.485	2.03	7.07
A_4	4.62	1.4510	0.5026	1.99	10.23	20.35
B_1	5.00	1.4530	0.5447	1.84	8.95	16.47
F_3	6.19	1.4590	0.677	1.477	14.44	21.3
B_2	10.00	1.4780	1.109	0.902	40.8	36.8
C_1	17.3	1.5140	1.963	0.510	97.1	49.5
B_3	17.8	1.5165	2.022	0.495	118.2	58.5
C_2	29.5	1.5715	3.475	0.288	228.	65.7
C_3	44.6	1.6400	5.485	0.1824	277.	50.5
C_4	53.0	1.6765	6.660	0.150	Crystals	

TABLE III

Conductivity at −45°

Sample	% $AlCl_3$	Density	Molecular Concentration $AlCl_3$	Molecular Volume	Specific Conductance $\times 10^6$	Molecular Conductance $\times 10^3$
D_1	0.01725	1.5338	0.00198	505.	0.0236	12.78
D_2	0.0357	1.5339	0.00410	244.	0.0368	9.64
D_3	0.0763	1.5340	0.00877	114.	0.0676	8.28
E_1	0.123	1.5341	0.0141	71.0	0.1172	8.90
E_2	0.245	1.5343	0.0282	35.5	0.193	7.38
E_3	0.514	1.5354	0.0591	16.9	0.373	6.77
A_3	1.240	1.5377	0.143	7.00	1.008	7.56
F_1	1.25	1.5378	0.144	6.95	0.625	4.65
A_2	2.18	1.5415	0.252	3.97	2.27	9.67
F_2	2.66	1.5430	0.307	3.26	2.20	7.67
A_4	4.62	1.5523	0.537	1.86	9.76	19.42
B_1	5.00	1.5545	0.582	1.72	8.06	14.82
F_3	6.19	1.5603	0.724	1.38	11.26	16.62
B_2	10.00	1.5779	1.18	0.848	30.4	27.4
C_1	17.3	1.6109	2.09	0.479	61.9	31.6
B_3	17.8	1.6134	2.15	0.465	65.7	32.5
C_2	29.5	1.6582	3.66	0.273	Crystals	

TABLE IV

Molecular Conductivity of $AlCl_3$ in Phosgene
at 25°, 0°, and −45°

Molecular Volume	Molecular Conductivity in Reciprocal Ohms.		
	25°	0°	−45°
0.10	0.063		
0.15	0.085	0.031	
0.20	0.099	0.058	
0.25	0.101	0.065	
0.30	0.099	0.065	
0.40	0.085	0.061	0.033
0.50	0.072	0.055	0.031
0.60	0.063	0.049	0.030
0.75	0.052	0.041	0.027
1.00	0.039	0.032	0.024
1.50	0.025	0.021	0.019
2.0	0.018	0.015	0.015
3.0	0.012	0.010	0.011
5.0	0.0070	0.0060	0.0070
10.0	0.0040	0.0040	0.0060
25.0	0.0035	0.0040	0.0065
50.0	0.0040	0.0055	0.0075
100.	0.0060	0.0070	0.0090
250.	0.0090	0.0080	0.0100
500.	0.012	0.010	0.012
1000.	0.015	0.012	0.013
10000.	0.026	0.018	0.017

As the solution is diluted, the conductivity must reach a maximum, since the two principal effects considered, diminishing self ionization and viscosity, carry the molecular conductivity in opposite directions. The dilution finally gets to a point where the self-ionization of the solute is negligible, where conductivity depends solely on the ionization produced by the ionizing solvent; the conductivity at this point may have a minimum value; this point is especially well defined in the curve at 25°.

Finally, as the dilution is still further increased, ionization of the solute proceeds according to the Ostwald dilution law, after the fashion familiar to us in water solution. As a matter of fact, phenomena similar to those recorded here have been observed in somewhat modified form in water solution by Sloan[1] for potassium iodide and potassium bromide, but ordinarily the effect, if present, is obscured by the powerful ionizing action of water.

The variation of the temperature coefficient of conductivity is similar to that found by Franklin in solutions of potassium iodide and potassium bromide

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[1] J. Am. Chem. Soc., **32**, 946 (1910).

in liquid sulfur dioxide, and the explanation offered by him seems to meet all of the requirements of this case. Assuming that, in the very concentrated solutions the self-ionization is little affected by change in temperature, but that rise in temperature rapidly diminishes viscosity, we would expect to find, as we do find, a positive temperature coefficient for this part of the curves. Schlundt and Germann[1] have found the dielectric constant of liquid phosgene to be 4.29 at 25°, with a negative temperature coefficient of 0.4% per degree. If the Nernst Thompson rule holds, we would expect the ionizing power of phosgene to diminish as the temperature rises; at the same time, rise in temperature would increase the ionic mobility; the net effect of these opposite tendencies, as recorded in the curves, is a negative temperature coefficient for intermediate dilutions, and at higher dilutions the sign is reversed, so that the temperature coefficient becomes positive.

The value given for the conductivity of the solvent, 0.007×10^{-6}, is to be regarded as the upper limit of the conductivity of phosgene, as no effort was made to prepare a product of the highest purity. The presence of a trace of moisture in the conductivity cell would give rise to the formation, by hydrolysis, of hydrogen chloride and carbon dioxide, both of which are soluble in phosgene, and may be expected to give conducting solutions. The conductivity of pure phosgene is undoubtedly very much lower than the value given.

The work recorded here was carried out in collaboration with the Chemical Warfare Service, with phosgene supplied from Edgewood Arsenal.

Stanford University,
California.

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[1] J. Phys. Chem., 29, 353 (1925).

AQUEOUS SOLUTIONS OF SODIUM SILICATES. I PREPARATION AND ELECTRICAL CONDUCTIVITY

BY R. W. HARMAN.

Introduction

No satisfactory proof of the possible number and constitution of sodium silicates, and no explanation of their behaviour in solution and the behaviour, in general, of solutions of varying ratios $Na_2O: SiO_2$ has, so far, been advanced. At the time this work was undertaken our knowledge of the alkali silicates was meagre, vague, and in large part contradictory. Till quite recent times it could be summed up by saying they formed solutions which are largely hydrolysed and in which most of the silica exists in the colloidal state; that several sodium silicates had a more or less hypothetical existence, but the only one whose composition was definitely established was Na_2SiO_3, or sodium metasilicate, crystallising in a number of various hydrates about which much conflicting data had appeared. Morey[1] then proved that Na_2SiO_3 and $Na_2Si_2O_5$ separated as crystalline salts at temperatures between 400°-1000°C from solution, and from fused melts. Later Bogue[2] showed that the degree of hydrolysis as determined by E. M. F. measurements was unexpectedly low and not in accord with earlier work.

No attempt had been made systematically to investigate the whole problem or to formulate a theory not in conflict with all the existing data.

In the present investigation the system Na_2O-SiO_2 H_2O at 25°C has been studied from the point of view of: (1) conductivity; (2) transport numbers; (3) hydrolysis; (4) sodium ion activity; (5) silicate ion; (6) lowering of vapour pressure and of freezing points; (7) heterogeneous equilibria.

Confusion has arisen through an indiscriminate use of the terms "sodium silicate" and "water-glass", such terms being useless unless an analysis of the substance is quoted, but this, unfortunately, has not always been done. Throughout the whole of this work, the different silicates and mixtures will be designated by the ratio $Na_2O: SiO_2$ in equivalent proportions, this being the simplest and most convenient system of nomenclature and one already finding general and serviceable use in industry. Thus a ratio of 1:2 contains one equivalent of Na_2O in grams to two equivalents of SiO_2.

All concentrations, except where otherwise stated, are expressed in weight normality (N_w) with regard to their sodium content, i. e. in gram-equivalents of sodium per 1000 grams of water. Thus, a 1 N_w solution of ratio 1:4 contains $\frac{1}{2}(Na_2O \cdot 4SiO_2)$ expressed in grams, in 1000 grams of water.

Preparation of Materials.

Preparation of silicates by fusion and subsequent solution of the melt presents many difficulties, especially if an exact ratio and a pure product

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[1] J. Am. Chem. Soc., 36, 215 (1914); J. Phys. Chem. 28, 1167 (1924).

[2] J. Am. Chem. Soc., 42, 2575 (1920).

are required. It was, therefore, decided to prepare the crystalline nonahydrate of sodium metasilicate, and to use this as the starting point for the preparation of the other ratios.

Preparation of $Na_2SiO_3 \cdot 9H_2O$.

Jordis[1] made many attempts to prepare the different sodium silicates and the other alkali silicates in a crystalline form, but he was successful only in obtaining crystals of sodium metasilicate with 10, 9, 7, 6, 5, and 2 molecules of water of crystallisation. It is doubtful whether all these hydrates exist, but this point receives full consideration later in a paper on heterogeneous equilibria of the system Na_2O-SiO_2-H_2O to be published shortly.

Vesterberg[2] undoubtedly obtained the pure salt, Na_2SiO_3 by crystallisation from an alcoholic solution of a strongly alkaline ratio and recrystallisation from a dilute alcoholic solution.

Brunner, Mond and Co., kindly supplied several of their commercial solutions of ratios varying from 1:2 to 1:4 but all of these, on analysis, were found to contain from 0.2% to 0.5% impurity, consisting chiefly of Al, with traces of Fe, Ca, Mg, and SO_4.

The sodium metasilicate was prepared according to Vesterberg from the purest of these commercial solutions. The first crystallisation took over a week, but subsequently by means of inoculation, crystallisation was brought about in a few minutes. The crystals were washed with 50 cc. water and 50 cc. alcohol on a Buchner funnel, drained thoroughly and finally dried between filter paper in a carbon dioxide-free atmosphere. This is essential as the metasilicate is quite rapidly decomposed by CO_2. Analysis showed that these crystals contained a small excess, 2.3% of Na_2O over that required by by the formula $Na_2SiO_3 \cdot 9H_2O$, and 0.2% Al_2O_3 as impurity, evidently due to the formation of a sodium alumino-silicate.

These crystals were then recrystallised from a saturated solution to which 20 cc. NaOH of sp. gr. 1.26 and 60 cc. alcohol were added to every 3 litres of warm water required to dissolve them. On seeding, the crystals came down in a few minutes, and were washed, drained, and dried as before. Analysis showed this recrystallised silicate to contain 0.9% excess Na_2O and 0.1% Al_2O_3.

A second such recrystallisation yielded crystals corresponding to $Na_2SiO_3 \cdot 9H_2O$ within the limits of experimental error. These rhombic crystals had a melting point of 47°C (Vesterberg, m. p. 48°; Erdenbrecher, 47°).

On dissolving the impure crystals in water dilute solutions were quite clear, but from solutions twice normal and over a residue separated which was filtered off, analysed, and found to contain a very high proportion of Al, while the filtrate was a very pure sodium silicate solution, but its molecular ratio Na_2O: SiO_2 had increased slightly. Evidently, the residue was a

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[1] Z. anorg. Chem. 56, 296; 58, 98 (1908); Chem. Zt. 38, 922 (1914).

[2] Eighth Int. Congress Appl. Chem. 2, 235 (1912).

sodium alumino-silicate, containing comparatively a small proportion of sodium, or it may possibly have been an alumino-silicate.

Electrolytic Preparation of Solution of Varying Ratios $Na_2O:SiO_2$.

The electrolytic removal of alkali from salts has been performed by Spencer and Proud[1] and by Lottermoser[2] who thereby prepared paratungstates and other complex tungstates; by Kroger[3] who obtained silicic acid from a dilute solution of a sodium silicate by means of a Hildebrand cell; and by Codd[4]. The same type of cell as used by Kroger and by Codd is described in Smith's "Electro-analysis" p. 303.

The method consists in the use of a rotating platinum anode and a mercury cathode. The difficulty lies in efficient stirring and mixing of the mercury used as cathode, otherwise the sodium amalgam formed redissolves in the silicate solution with little or no diminution in the alkalinity of the solution. Of course, some of the amalgam finds its way into the outer dish and is there decomposed by the water, but some remains in contact with the silicate solution and redissolves therein, especially in the more concentrated solutions of low ratio, e. g. in a $2N_w$ 1:1 solution. This necessarily makes the method slow; the fact, with a current density of 0.04 amps per sq.cm. in the above solution, it required 24 hours to remove 2% of the alkali.

This difficulty may be overcome in two ways, either by removing, as it is formed, the sodium amalgam from contact with the silicate solution, or by increasing the C.D. so that, the rate of formation of amalgam is greater than its rate of solution in the silicate solution. The first way is very difficult of satisfactory solution, as the amalgam being so light in comparison with the mercury, floats on its surface, and the mechanical devices tried whereby the mercury in contact with the solution is completely changed, often failed to remove it. Practically the only satisfactory method found was to siphon off the silicate solution, charge the cell with fresh mercury, and recommence electrolysis. This was effective but naturally cumbersome, and would be impracticable for use on a large scale. The second method of increasing the C.D. considerably hastens the removal of the alkali and gave good results; but it has its limitations in the fact that, above a certain limit, increase of C.D. causes separation of solid silica on the platimun anode. This limiting C. D., above which silica separates on the anode, varies not only with the dilution but also markedly with the ratio. The more concentrated the silicate solution and the greater the proportion of silica in the ratio, the lower must be the limiting C.D.

With a $2N_w$ solution of ratio 1:1 or 1:2 a C.D. of 0.044 amps per sq. cm. scarcely diminishes the alkalinity of the solution; a C.D. of 0.15 amps

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[1] Kolloid-Z. **31**, 36 (1922).
[2] Kolloid-Z. **30**, 346 (1922).
[3] Kolloid-Z. **30**, 16 (1922).
[4] Appl. Chem. Abs. **1924**, 56.

per sq.cm diminishes the alkalinity quite rapidly but yet does cause separation of solid silica.

With ratio 1:4 a $3N_w$ solution gave a very thick deposit of silica with a C.D. of 0.11 amps per sq.cm. A $2N_w$ solution with a C.D. of 0.11 also gave a thick deposit but with a C.D. of 0.044 amps per sq.cm., although silica was deposited on the anode, at the end of 4 hours the solution on analysis was found to be $0.8N_w$ and its ratio was 1:5.2. This solution was very opalescent and after two days set to a gel and later on exhibited synaeresis. A 0.5 N_w solution of ratio 1:4 with a C.D. of 0.13 amps per sq.cm. also deposited silica, but at the end of 10 hours, during which time the C.D. gradually fell, the resulting solution was found to be 0.08 N_w with a ratio of 1:40. This dilute solution showed no signs of gel formation.

Thus with ratio 1:1 a $2N_w$ solution may be electrolysed with a C.D. of 0.15 amps per sq.cm. but with ratio 1:4 a $1N_w$ solution gives a deposit with as low a C.D. as 0.044. It has been found possible by this means to prepare 2 N_w solutions of ratios 1:2, $1N_w$ of 1:3, and 1:4. Higher ratios than these set to a gel, viz., 1:5 above $0.1N_w$, but in very dilute solutions the removal of alkali can proceed until the solution is practically one of pure silicic acid.

The alkalinity of these solutions was determined by pipetting off 5 cc. of the silicate solution, diluting with 150 cc. water and then titrating with 0.1 N HCL using methyl orange as an indicator. The end-point in such a titration is quite sharp and since no silica separates in such dilute solution, the method is quite accurate for comparison purposes as required here. Before it was used in an investigation, the final solution was always analysed in duplicate and its concentration and ratio thus accurately found.

Conductivity

Kohlrausch[1] investigated at 18°C the electrical conductivity at concentrations ranging from 6N to 0.0001N of solutions of ratios 1:1 and 1:3.4, and also of a dilute solution of caustic soda to which were added increasing amounts of silicic acid until the ratio was 1:3.

He found that in dilute solution, the metasilicate was an excellent conductor, but in concentrated solution its conductivity was very low. The more acid silicate was also a good conductor in dilute solution but a very poor one in concentrated solution. Kohlrausch ascribed this high conductivity to complete hydrolytic decomposition of the salt into acid and base, a view which is no longer tenable on account of the results of hydrolysis experiments. He also concluded that combination of base and acid continued until they present in the proportion of 1:2.

Kahlenberg and Lincoln[2] determined the conductivity of solutions of ratios 1:1 1:2 and 1:5, in dilute solution only, as their method of preparation, mixing NaOH with a solution of silicic acid, made it impossible to prepare more concentrated solutions than 0.25 gm. equiv. per litre owing to gel formation.

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

[2] J. Phys. Chem. **2**, 77 (1892).

Their results are in fair agreement with Kohlrausch's and they too attributed the high conductivity to hydrolytic dissociation, concluding that there was 100% hydrolysis of Na_2SiO_3 at 0.05N, and that the increase of conductivity with further dilution was due to a decrease of the retarding influence of the colloidal silica on the ions.

Experimental

A modification of Kohlrausch's method was employed[1], consisting of the use of a double rotating commutator whereby a reflecting galvanometer could be used to indicate the balance point, which was thus found very accurately. The bridge wire, about 5 metres long, wound on a rotating drum, had 1000 divisions but the sensitivity of the galvanometer allowed a reading of 1 in 10,000. The bridge wire was calibrated several times throughout the course of the measurements. The resistances in ohms of any one solution for about 10-12 different positions of the contract on the bridge wire agreed at at least within 1 in 100, but generally the agreement for 10 readings was within 1 in 1000.

The conductivity cell, of the ordinary type with a tightly-fitting lid, was made of hard glass and was thoroughly steamed and cleaned before use. Since the object of this investigation was not extreme accuracy in dilute solution, the water used throughout the whole of this investigation was not specially prepared conductivity water, but freshly distilled from the labora-still. Its conductivity varied between 1.6 to 2.1 × 10^{-6} mhos. The cell constant and the conductivity water were determined quite frequently, on an average before every 2 or 3 silicate solutions were determined. The cell was immersed in a water thermostat electrically heated and reulated to 25°C+ 0.01, the temperature being registered by a standardised thermometer.

The stock solution, i. e. the most concentrated of any series, was kept in a silver flask, and the more dilute solutions were prepared therefrom by adding a weighed quantity of water to a certain weight of the stock solution. These solutions were allowed to stand at least 12 hours before they were used in a determination, as the conductivity changes a little with their age for the first 1-5 hours after dilution.

All weights, thermometers, measuring vessels etc. used throughout this work on silicate solutions were standardised before use.

The densities of the various solutions were determined by means of a pyknometer. About 4 density determinations were made for each ratio and the remaining values were obtained by interpolation and extrapolation from the curve so obtained.

The solutions of any one ratio could be obtained in three ways,—

(1) by dissolving crystalline $Na_2SiO_3 \cdot 9H_2O$ for ratio 1:1 and by electrolysing such a solution as previously descirbed for the higher ratios. This way gave the purest solutions.

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[1] See Fitzpatrick: Proc. Phys. Soc. London, **15**, 13 (1896); Whetham: Phil. Trans. **194A**, 321 (190).

(2) by adding caustic soda to ratio 1:4 to get the lower ratios.

(3) by using the commercial solutions supplied by Brunner, Mond and Co.

Solutions of different ratios at various concentrations obtained by any of these three ways gave identical results, both in conductivity and in the other measurements to be described.

Calculation of Equivalent Conductivity

Since the concentrations are expressed in weight normality i. e. in gram equivalents per 1000 gms. water, we get for the equivalent conductivity Δ the expression,—

$$\Delta = \frac{\lambda\,(2000 + x)}{N_W . \rho}$$

where λ = specific conductivity
x = no. gms. solid. in 1000 gms. water
N_W = weight normality
ρ = density of the solution.

Conductivity Results

TABLE I T = 25°C

Gm. equiv. Na per 1000 gms. water.	Gms. solid per 1000 gms. H_2O.	Density	Spec. Cond.	Equiv. Cond.
		Ratio 1:1		
N_W	x	ρ	$\lambda . 10^{-3}$	$\Delta = \frac{\lambda(1000 + x)}{N_W . \rho}$
2.435	148.90	1.145	108.3	44.6
1.133	69.31	1.068	85.0	75.9
0.516	31.54	1.034	48.8	95.0
0.204	12.50	1.013	23.0	112.7
0.096	5.868	1.006	12.6	130.8
0.050	3.057	1.003	7.182	143.6
0.020	1.222	1.001	3.054	152.7
0.010	0.611	1.000	1.552	155.2
0.005	0.305	1.000	0.792	158.4
		Ratio 2:1		
2.0	92.15	1.097	115.2	57.32
1.0	46.07	1.050	85.89	85.57
0.796	36.67	1.043	71.96	89.84
0.398	18.34	1.021	47.97	120.1
0.159	7.335	1.009	22.08	138.7
0.0796	3.667	1.005	13.83	173.8
0.0398	1.834	1.002	7.151	179.7
0.0159	0.7335	1.001	3.052	192.0
0.00796	0.0366	1.000	1.543	193.8

Ratio 1:1.5

N_W	x	ρ	$\lambda, 10^{-3}$	$\Delta = \frac{\lambda\,(2000 + x)}{N_W.\,\rho}$
2.0	152.45	1.140	62.05	32.09
1.0	76.22	1.070	49.94	50.23
0.5	38.11	1.035	33.38	66.76
0.2	15.24	1.017	17.24	86.20
0.1	7.622	1.008	9.920	99.20
0.05	3.811	1.004	5.352	107.04
0.02	1.524	1.002	2.284	114.20
0.01	0.762	1.001	1.181	118.10
0.005	0.381	1.000	0.6007	120.14
Ratio 1:2				
2.450	233.68	1.180	50.80	21.50
1.110	100.43	1.085	37.16	34.26
0.500	45.65	1.042	24.44	49.05
0.204	18.425	1.017	12.75	62.59
0.100	9.130	1.009	7.27	72.70
0.05	4.565	1.004	3.90	78.00
0.02	1.826	1.002	1.68	84.00
0.01	0.913	1.001	0.947	89.50
0.005	0.450	1.000	0.466	93.20
Ratio 1:3				
2.0	242.90	1.190	39.60	20.46
1.0	121.45	1.136	31.83	31.42
0.5	60.77	1.050	22.48	45.41
0.2	24.29	1.022	11.44	57.33
0.1	12.145	1.010	6.634	66.48
0.05	6.077	1.007	3.785	75.63
0.02	2.429	1.003	1.636	81.75
0.01	1.214	1.001	0.8516	85.16
0.005	0.607	1.000	0.4490	89.80
Ratio 1:4				
2.0	300.184	1.260	31.36	16.17
1.0	150.092	1.175	23.75	23.24
0.5	75.046	1.043	16.08	33.14
0.2	30.018	1.021	9.563	48.25
0.1	15.009	1.011	5.757	57.80
0.05	7.504	1.005	3.284	65.80
0.02	3.002	1.002	1.500	75.06
0.01	1.501	1.001	0.8154	81.54
0.005	0.7504	1.000	0.4302	86.04

These results are shown graphically in Figs. 1 and 2. In Fig. 1 the equivalent conductivity has been plotted against the concentration, while Fig. 2 shows the equivalent conductivity plotted against the logarithm of the concentration.

In Table II the results are collected together, and those of NaOH at 25°C are also given, for purposes of comparison. A few of these results have been found by interpolation from the curves in Fig. 1 so that the conductances for all the ratios could be compared at the same concentration.

Table II

EQUIVALENT CONDUCTIVITY T = 25°C

N	NaOH	2:1	1:1	1:1	1:1.5	1:2	1:3	1:4
2.0	142.0	157.32	57.25	57.50	32.09	25.80	20.46	16.17
1.0	172.5	85.57	81.25	81.20	50.23	36.10	31.42	23.24
0.5	200.0	107.80	96.80	96.5	66.76	49.05	45.41	33.14
0.2	209.0	136.90	112.70	113.0	86.20	62.59	57.33	48.25
0.1	214.5	157.5	130.80	130.0	99.20	72.70	66.48	57.80
0.05	220.0	175.5	143.80	142.6	107.04	78.00	75.63	65.80
0.02	225.5	190.1	152.7	151.8	114.20	84.00	81.75	75.06
0.01	227.5	193.0	155.0	156.0	118.10	89.50	85.16	81.50
0.005	228.0	194.2	158.0	159.0	120.14	93.20	89.90	86.04
0.0			160.0		121.00	95.00	91.00	88.00

Discussion of Results

From the curves, Fig. 1, of equivalent conductivity against concentration, it is seen that,—

(1) the values obtained for ratio 1:1, are practically identical with those of Kohlrausch at all concentrations.

(2) ratio 1:1, i. e. sodium metasilicate Na_2SiO_3, has a very high conductivity in dilute solution;

(3) ratio 2:1 gives practically the same values as 1:1 at concentrations 1-2 N_w. This is very remarkable.

(4) all the other ratios are quite fair conductors in dilute solution, but show an abnormally low conductivity in concentrated solution, especially the higher ratios 1:3 and 1:4.

This high conductivity of Na_2SiO_3 is undoubtedly due to the presence of the very mobile hydroxyl ion formed by hydrolysis, but no exact quantitative conclusions can be accurately drawn from these conductivity data as to the extent of hydrolysis. In ratios 2:1, 1:1 and 1:1.5 the low conductivity in concentrated solutions is mainly due to a decrease in hydrolytic dissociation, as a decrease in the concentration of the hydroxyl ion would cause a large decrease in the conductivity.

In ratios 1:2, 1:3 and 1:4 where the hydroxyl ion concentration is very low, even in dilute solution, the fair conductivity of dilute solutions points to a high degree of ionisation and a fairly mobile silicate ion, while in concentrated solution there may be either very little ionisation or there may be complex or colloid formation. In the latter case the osmotic activity would be abnormally low.

Equivalent Conductivity at Infinite Dilution

The value of the equivalent conductivity at infinite dilution is most difficult to determine. Several extrapolation methods are discussed by Kraus in his recent book on "Electrically Conducting Systems" by means of which Λ_∞ for binary salts may be determined with some accuracy, but no such methods have been worked out for ternary salts, and even then it would be hypothetical to assert that some or all of these ratios correspond to ternary salts. Na_2SiO_3 undoubtedly is, but owing to partial hydrolysis the problem becomes complicated. In such cases, only an approximate value may be deduced for Λ_∞ by extrapolation from the curve where the equivalent conductivity is plotted against the logarithm or the cube root of the concentration. Fig. 2 shows the plot of equivalent conductivity against the log of the concentration for ratios 1:1, 1:1.5, 1:2, 1:3, and 1:4. It can be seen that the curves conform to the type for which the extrapolation is considered valid, i. e. they eventually become asymptotic to a line parallel to the concentration axis. No accurate measurements have been made at very low concentrations but they have been made at sufficiently low concentration to warrant this extrapolation, and the values of Λ_∞ so obtained should be accurate to within 2 or 3 units.

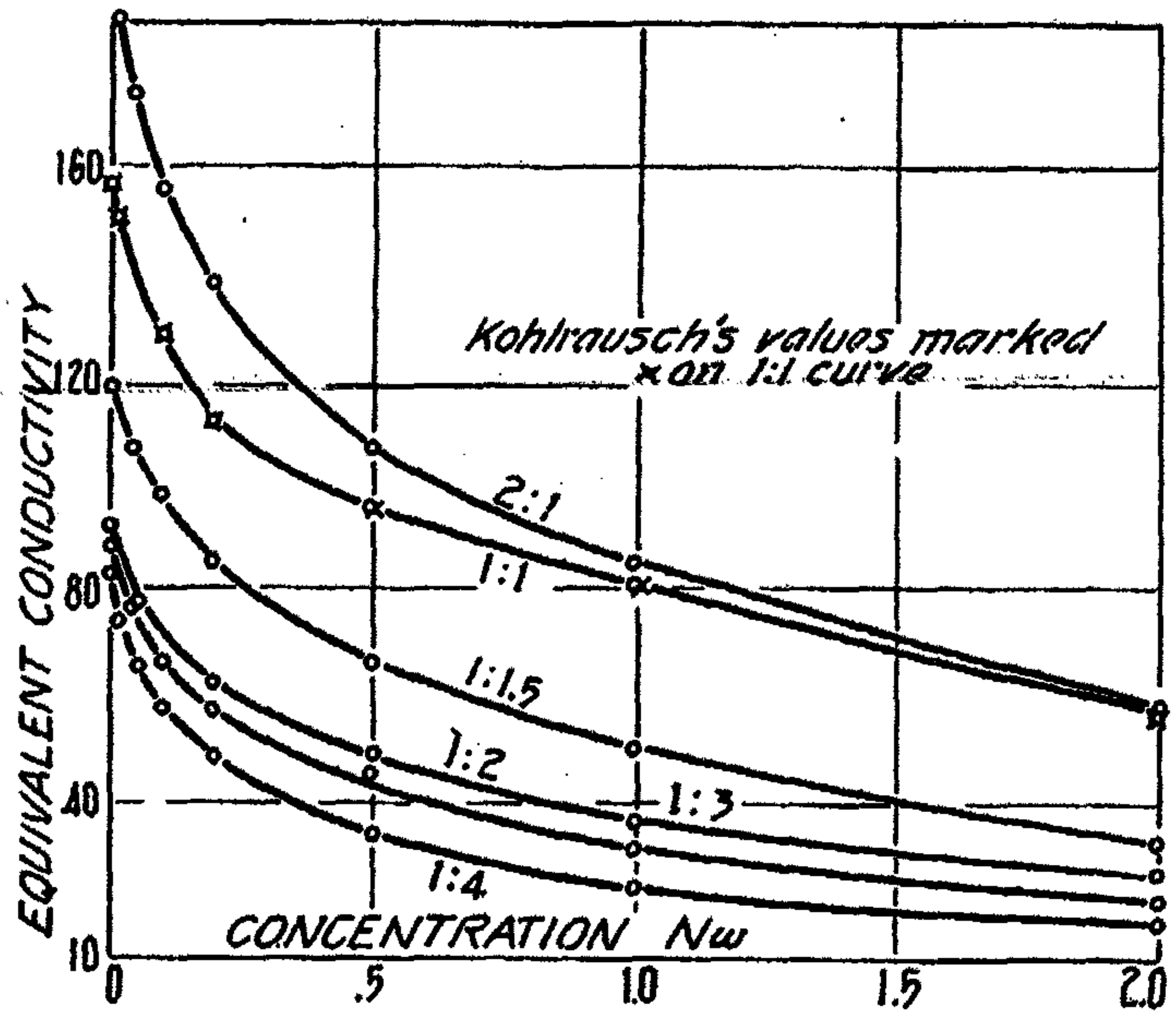

FIG. 1

The values of Ho have also been obtained from the expression[1],—

$$1/\Delta = 1/\Delta_\infty + K\,(C\Delta)^{n-1}$$

by plotting values of $1/\Delta$ against those of $(C\Delta)^{n-1}$, then taking a value of n such as would make the graph nearly a straight line, and also two other neighbouring values of n on opposite sides of this one. These three graphs were produced so as to intercept the $1/\Delta$ axis, and the most probable value of the intercept chosen to represent the value of $1/\Delta_\infty$.

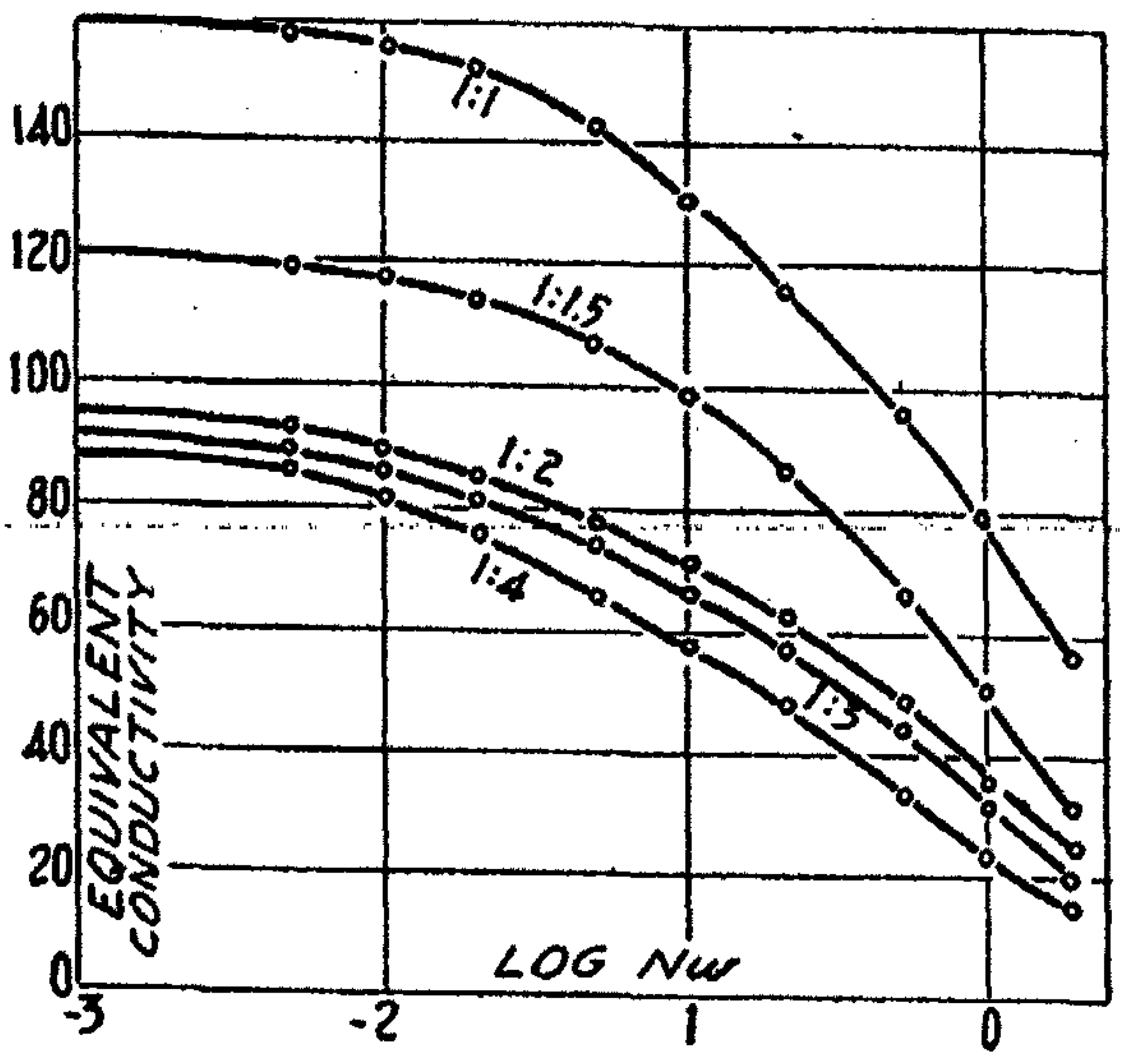

Fig. 2

The values of Δ_∞ as found by extrapolation from the log curves in Fig. 2 and by Noyes' method agreed closely. The final values assigned to Δ_∞ are shown below,—

Ratio	Δ_∞
1:1	160
1:1.5	121
1:2	95
1:3	91
1:4	88

Mobility of the Silicate Ion

If we know the concentration of the various ions in the solution and their mobilities at this concentration then the specific conductivity at that concentration may be calculated from the expression,—

$$C_{NaSil.} \times \Delta = \lambda = C_{Na}U_{Na} + C_{OH}\cdot V_{OH} + C_{Sil.ion} + V_{Sil.ion}.$$

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[1] See A. A. Noyes: Carnegie Inst. Pub. 1908, 63.

where C denotes the concentration and U or V the mobilities of the ions. The concentration of the various ions, has been found by means of hydroyxl ion concentration, sodium ion concentration, and freezing point measurements to be published shortly; and, although, in these measurements of the concentration of the ions, the laws strictly applicable only to infinitely dilute or ideal solutions have been applied to more concentrated solutions, still the values are sufficiently accurate for the purposes of this calculation. Assigning values of 45 and 180 to the sodium and hydroxyl ions respectively, we can thus calculate the mobility of the silicate ion for each ratio, with the following result,—

Ratio	Mobility silicate ion (dilute solution)
1:1	60
1:2	35
1:3	43
1:4	41

It seems justifiable to assume the presence of only three kinds of ions viz., sodium, hydroxyl, and silicate ions formed by hydrolytic and ionic dissociation, and knowing their mobilities and the extent of hydrolysis, Δ_∞ for each ratio may be approximately found. In this way are obtained the values below, those found by extrapolation from the log curves being also given for camparison.

Ratio	Δ_∞ (mobility)	Δ_∞ (extrapolation)
1:1	165	160
1:2	95	95
1:3	90	91
1:4	88	88

In the higher ratios 1:2, 1:3 and 1:4 where the hydroxyl ion concentration is practically negligible the agreement is good. In the metasilicate, as would be expected, owing to the distrubing influence of the hydroxyl ion making the application of the mobility method doubtful, the values are not so close, but are in sufficiently close agreement to warrant the conclusion that the mobilties, as given above, are fairly accurate.

The most interesting conclusions are obtained, however, when the equivalent conductivity is plotted against the ratio. This is done in Fig. 3, where the values of NaOH are given under ratio 1:0.

Considering dilute solutions first, it is seen that,:—

(1) the equivalent conductivity of a caustic soda solution to which silica is added falls linearly and rapidly until the ratio 1:2 is reached.

(2) there is a sharp change of direction at 1:2.

(3) there is no change of direction at 1:1, i. e. Na_2SiO_3.

(4) after 1:2 the conductivity again falls regularly and linearly but not nearly so rapidly.

The very sharp change of direction at ratio 1:2 would seem to indicate the existence in solution of the definite salt $Na_2O{\cdot}2SiO_2$. There is also other conclusive evidence, such as the separation from solution of the crystalline hydrate $Na_2SiO_3{\cdot}9H_2O$, that a definite salt $Na_2O{\cdot}SiO_2$ also exists in solution. The fact that there is no change of direction in the curve at 1:1 indicates that the salt Na_2SiO_3 is largely hydrolysed and that it is the gradual disappearance of the mobile hydroxyl ion that causes the conductivity to decrease linearly as ratio 1:2 is approached.

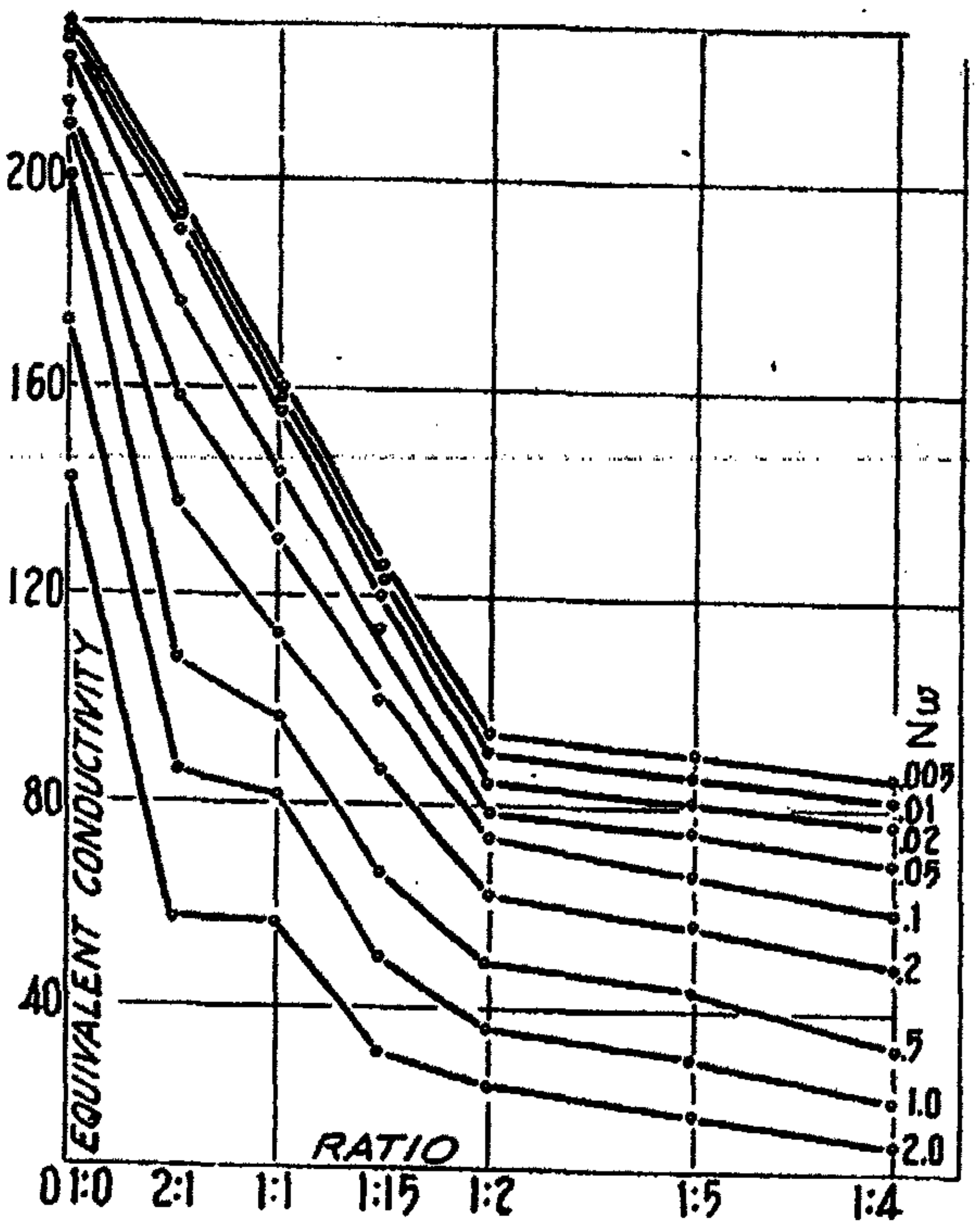

Fig. 3
Equivalent Conductivity against Ratio

The fact that beyond ratio 1:2 further addition of silica causes the conductivity to decrease regularly, but only slightly, indicates, either:

(1) that the repression of the degree of hydrolysis is only very slight, or,

(2) if the hydroxyl ion practically disappears at these ratios, then the silicate ion in ratio 1:4 either, is more mobile than that at 1:3, or its mobility is the same, but it is there in greater concentration.

Considering the concentrated solutions, we notice:—

(1) at $0.1N_w$ a change of direction begins to appear at 2:1, which becomes more pronounced the more concentrated the solution.

(2) at $0.5N_w$ a change of direction appears at 1:1 which becomes very pronounced at higher concentrations.

(3) at $1.0N_w$-$2.0N_w$ the conductances of ratios 2:1 and 1:1 are practically the same. This is very remarkable.

(4) the change of direction at 1:2 is still quite definite except for the highest concentration, but it is not so sharp as in dilute solution.

(5) beyond 1:2 the slope of the curve is the same as in the more dilute solutions.

If a change of direction of the curve indicates the existence of definite salts at that point, then there are salts of the compositions $2Na_2O{\cdot}SiO_2$, Na_2O SiO_2, and $Na_2O{\cdot}2SiO_2$. The existence of the last one appears very probable and there is good evidence that Na_2SiO_3 also exists. However, one would not be justified in concluding from these curves alone that these three salts exist here in solution; especially the salt $2Na_2O{\cdot}SiO_2$.

Ratio 2:1 may be a mixture of NaOH and Na_2SiO_3; both of these salts in solution give rise to hydroxyl ion and when mixed the total hydroxyl ion concentration will not be equal to, but less than, the sum of the separate hydroxyl ion concentrations, and so one would expect diminished conductivity on this account. This point is further discussed in a later paper on hydrolysis.

It is worth noting that the fall in conductivity from NaOH to ratio 1:2 is practically constant for all concentrations, being 120-130 units.

In concentrated solutions above ratio 1:2 we note the same behaviour as in dilute solutions, but as here the conductivity is abnormally low, and as the mobility of the silicate ion is moderately high, we can conclude that the osmotic activity of these concentrated solutions must be very low. We should, therefore, expect not only little ionisation but probably the formation of complexes or aggregates, and that these solutions would exhibit colloidal properties.

Summary

(1) Crystalline Na_2SiO_3 has been prepared, and from a solution of this salt, various other ratios Na_2O:SiO_2 have been prepared by removing the alkali electrolytically.

(2) Conductivity measurements have been made of ratios 2:1, 1:1, 1:1.5, 1:2, 1:3. and 1:4 at concentrations ranging from $2N_w$ to $0.005N_w$.

(3) Solutions of 2:1 and 1:1 are excellent conductors; 1:2, 1:3, 1:4 are good conductors in dilute solution but abnormally low in concentrated solution.

(4) Hydrolysis into NaOH and colloidal silicic acid is not sufficient to account for this conductivity and calculations have been made of the mobility of the silicate ion.

(5) On plotting equivalent conductivity against ratio, there is only one change of direction and that a very sharp one at 1:2 in dilute solution; but in concentrated solution changes of direction also occur at 2:1 and 1:1.

(6) It appears likely that salts corresponding to 1:1 and 1:2 exist in solution; and that the other ratios are mixtures of these with NaOH or "hydrated" silica as the case may be.

(7) In concentrated solutions either the extent of ionisation and hydrolysis is very low, or aggregate or colloidal formation takes place.

I wish to thank the Commissioners of the 1851 Exhibition for a Scholarship which has enabled me to carry out this investigation, and to express my gratitude to Professor Donnan, at whose suggestion this work was undertaken, for his constant kindly interest and advice.

The Ramsay Laboratories of Physical and Inorganic Chemistry
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June 22, 1925.

STUDIES OF THE OPTICAL ACTIVITY OF GELATIN SYSTEMS

BY ELMER O. KRAEMER* AND J. R. FANSELOW

In spite of very extensive studies on protein systems, it still remains uncertain to what extent such systems behave like homogeneous, monophasic systems ("true" solutions), or like heterogeneous, polyphasic systems ("colloidal" solutions). In this situation, particular attention should be given on the one hand to those properties of protein systems which are most intimately related to deep-seated chemical changes and constitution, and on the other hand to those which reflect most directly the heterogeneity (or colloidal) aspects of these systems. Upon the presumption that optical activity and Tyndall effect are examples of these two kinds of properties respectively, they are at present the objects of detailed study in these laboratories.

In view of the prominent position which gelatin has taken in former protein investigations, and the complicated and unique behavior which it displays (capacity to form gels, second "isoelectric" point, mutarotation, etc.), it seems appropriate to present in this preliminary paper some of the quite interesting results which have been obtained by a study of the optical activity of gelatin systems.

The most recent important study of the optical activity of gelatin systems was that of C. R. Smith[1], who determined the influence of temperature upon the optical activity of commercial gelatins containing the usual amounts of ash. The data in this paper, having been obtained with de-ashed gelatin over a wide range of pH values and temperature, furnish a considerable extension to the work of Smith. The authors in this work have made a study of the effect of pH between pH values of 2.30 and 12.31 at temperatures of 10°, 15°, 20°, 25°, 27½°, 30°, 35°, 40°, and 50°C upon the optical activity of aqueous gelatin systems.

Experimental

Materials: The gelatin used in this work was de-ashed in the laboratories of the Eastman Kodak Company. It had an ash content of less than 0.05% and a water content, determined by subjecting to 105°C in a vacuum oven until weight became constant, of 13.7%.

To avoid accidental differences in individual samples, the gelatin solutions for a series were made from a common stock solution. A weighed amouut ot air-dry gelatin was allowed to swell for one hour in a desired quantity of distilled water at room temperature. This was then placed in a water bath at 50°C for one hour and frequently stirred. Portions of this stock were diluted with solutions of NaOH or CH_3COOH to the desired pH and concentration of gelatin (usually 0.5%). The pH values at 23° and 40°C were determined after 10 hours by means of the hydrogen electrode. These solutions were then

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[1] Smith: J. Am. Chem. Soc., **41**, 135 (1919). For earlier work, consult Ostwald: "Licht und Farbe" (1924).

preserved for the four days required by a series of measurements in a water bath maintained between 7 and 10°C.

Measurement of Rotation: Portions of the above solutions were placed in thermostats and allowed to attain "optical equilibrium" (50 to 35°C—8 to 10 hours; 30 to 25°C—10 to 20 hours; 20 to 10°C—24 to 36 hours; below 10°C—48 hours). The rotations of these solutions at equilibrium were then determined for the 546.1 mu mu line of Hg, isolated by means of the special Wratten filter from the radiation of a quartz mercury vapor lamp. The temperatures of the solutions during measurement were controlled to 1/10°C between 15 and 40°C, and to 2/10°C at 50 and 10°C by circulating water through a well insulated, jacketed polarimeter tube.

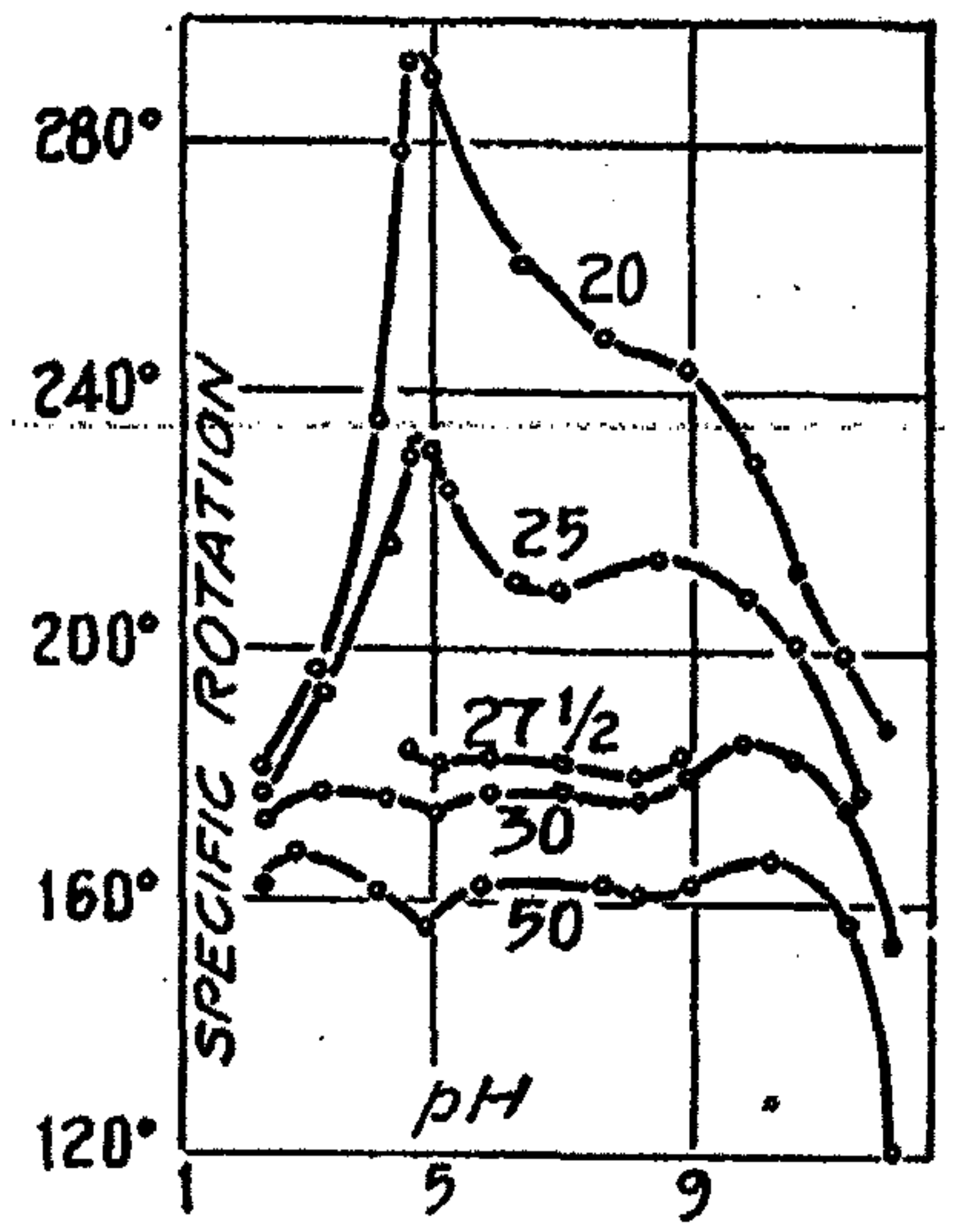

FIG. 1

Influence of temperature and pH upon the specific rotation of 0.5% gelatin systems.

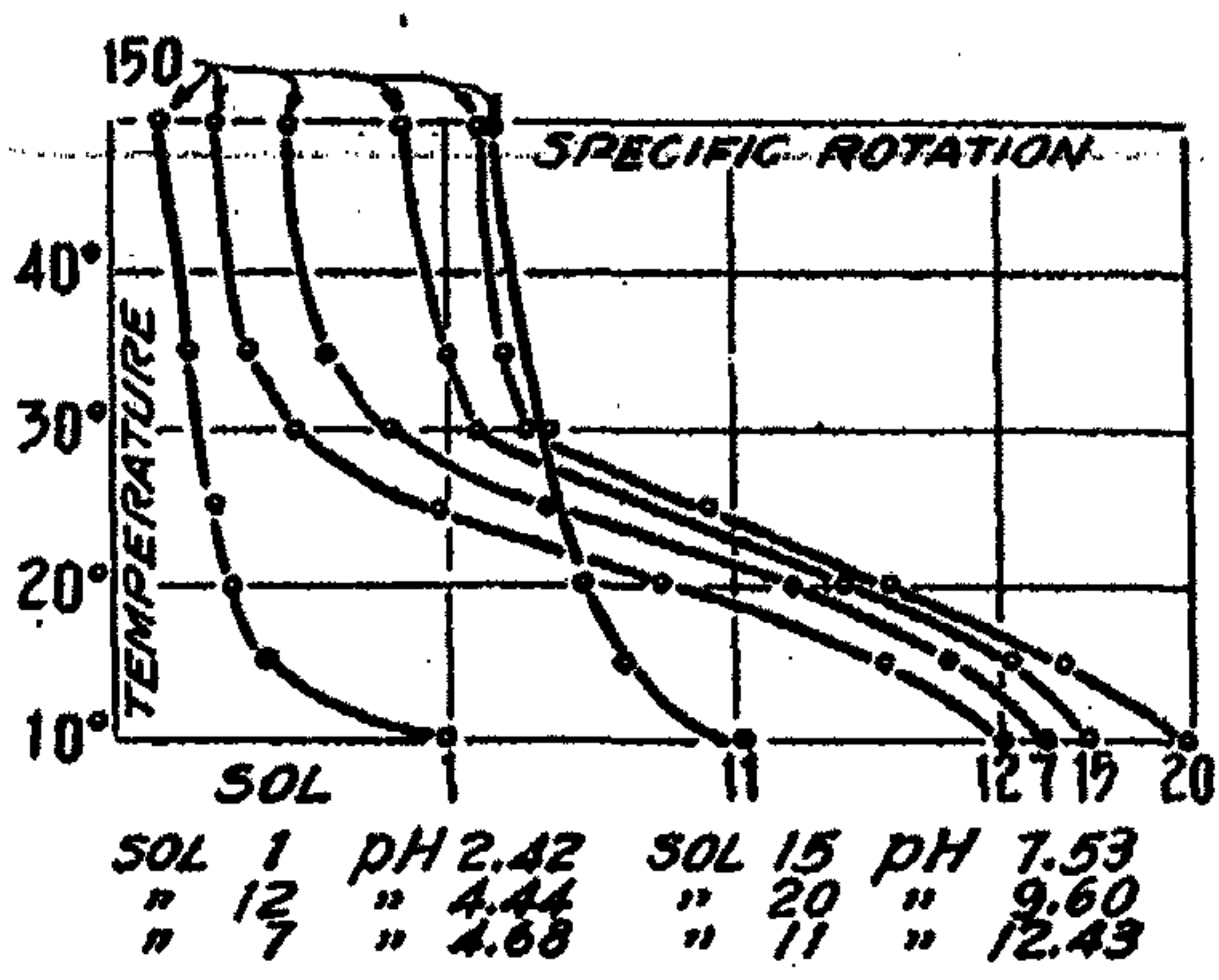

FIG. 2

Influence of temperature upon the specific rotation of 0.5% gelatin systems at constant pH.

The specific rotations of the samples were calculated by means of the usual formula: $[\alpha]_{546.1} = 100\alpha/gdl$

$[\alpha]_{546.1}$ = specific rotation for 546.1 mu mu.

α = observed rotation

g = grams of dissolved gelatin per 100 g of solution

d = density of solution

l = length in decimeters of column of solution

The data from these measurements are presented in graphic form in Figs. 1 and 2.

Tyndall Effect: To serve as an indicator of the strictly colloidal behavior of these systems, the Tyndall effect or relative light-scattering capacities were measured at room temperature (23°C) by Kraemer and Dexter. Their data are presented in Fig. 3.

Results

(1) In plotting specific rotation with pH values for the results at different temperatures, one obtains curves for temperatures above 27½°C which shows a well defined minimum at a pH 4.9, and one less pronounced at a pH between 7 and 9; these correspond to the two "isoelectric" points at pH 4.7 and 7.7-8 mentioned by other investigators. (2) It will be observed, as reported by Smith, that the apparent temperature coefficient for these temperatures is comparatively small. (3) Above 27½°C the change in rotation with pH is small for pH values between 3 and 11. (4) The general character of the curves at these temperatures closely resembles those of properties which may be described in terms of Donnan's theory of membrane equilibrium.

(5) At the lower temperatures (below 25°C) the curves assume a decidedly different character. Instead of the minimum at a pH 4.9, there is a pronounced maximum. Also, the minimum at the higher temperatures between pH 7 and 9 becomes, at the lower temperatures, a maximum or shifts to a pH ca. 6.8. This phenomenon was duplicated with gelatin solutions of 0.33 and 1.0% concentration. As the temperature is lowered to 15 and 10°C, there is a corresponding increase in specific rotation for each decrease in temperature, but the general character of the curve is not altered markedly. (6) These curves for the lower temperatures lose their resemblance to curves for properties that are described by the Donnan theory of membrane equilibrium.

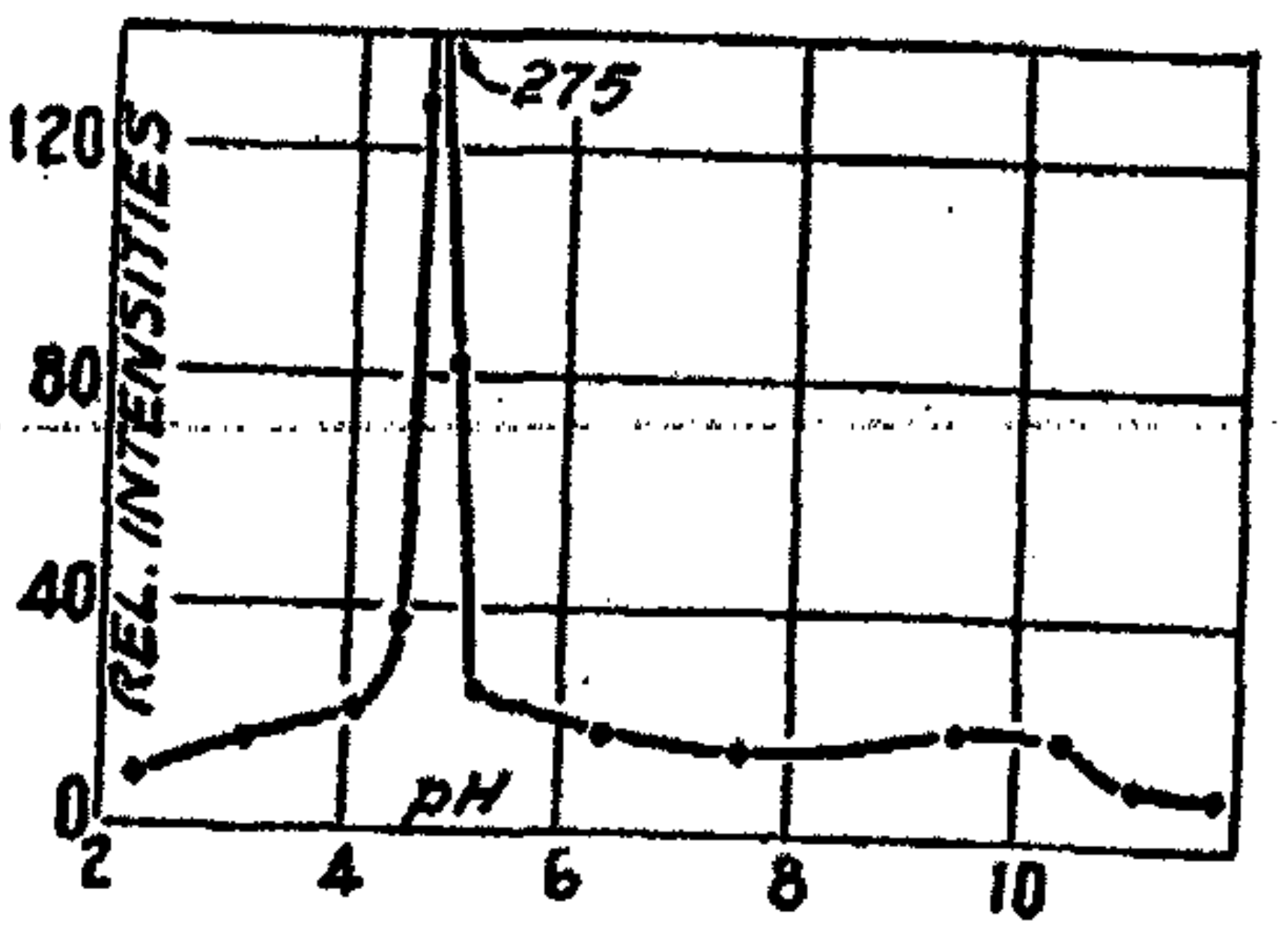

Fig. 3

Influence of pH upon the relative light-scattering capacities of 0.5% gelatin systems at 23°C.

(7) The change in character of the curves from that typical of the high temperatures to that typical of the low temperatures appears quite distinctly between 25 and 27½°C, as is shown in Fig. 1. The location of this transition region is also well shown by the curves of Fig. 2 which give the relation between specific rotation and temperature at constant pH. Between pH values of 4.44 and 9.60, the rate of increase of specific rotation with decrease in temperature takes a very decided turn between 25 and 30°C. This differs distinctly from the gel$\rightleftarrows$sol transition temperature at 38.03°C as reported by Davis and Oakes[1].

(8) The specific rotation of solutions of de-ashed gelatin for intermediate pH values, plotted against temperature (Fig. 2), conforms in a general way to those obtained by Smith for commercial gelatins, except that the rotation does not become constant, as he found, for temperatures below 17°C. Measurements below this temperature showed a large temperature coefficient down to 5°C, but below 5°C the increase in specific rotation is not marked. (9) At pH values below 3 and above 11, these curves show that the rotation is

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[1] Davis and Oakes: J. Am. Chem. Soc., 44, 464 (1922).

less sensitive to temperature changes than at pH's between these values; but between 20 and 5°C, they show a noticeable increase in apparent temperature coefficient at all pH's studied.

(10) The light-scattering capacity of these solutions, as measured by Kraemer and Dexter[1] shows a pronounced maximum in the heterogeneity of the system at a pH ca. 4.7 (Fig. 3). The Tyndall effect and optical activity are roughly parallel at pH values below 5, but show little resemblance at higher pH values.

(11) There is a qualitative parallelism between gel-forming tendency and the increase in optical activity at low temperatures. At 20°C, 0.5% solutions between pH values of 4.65 and 5.01 show a slight tendency to form gels, corresponding to the maximum in optical activity. At 15°C, this tendency extends over a wider range of pH. At 10°C, there is a noticeable gel-forming tendency for pH values between 4.3 and 6.36, with a maximum gelation at pH 5.01-5.21.

Discussion

To the authors, the most reasonable view of the situation may be expressed in the three following statements: I. There is insufficient evidence for supposing that gelatin contains two related molecular species in chemical equilibrium with each other. II. The behavior of gelatin systems is in part typical of disperse systems. The state of aggregation and the nature of the micellae are closely dependent upon the temperature, as well as upon the pH and the presence of salts. III. The so-called mutarotation of gelatin systems is an outward reflection of colloidal changes tending to gel formation.

The basis for this view is given below.

I. In the work already mentioned, Smith suggested that the mutarotation of gelatin may be due to the presence in gelatin of two molecular species in equilibrium with each other at temperatures between 15 and 35°C, as indicated in the equation

$$\text{Gel Form (or (Sol Form)}_2) \underset{15^\circ}{\overset{35^\circ}{\rightleftarrows}} 2 \text{ Sol Form}$$

The molecular rotation of the Gel Form was said to be 4.4 times that of the Sol Form. The formation of a gel was assumed to be dependent upon the formation of the Gel Form of gelatin by a bimolecular condensation of the Sol Form. Treating the data from the point of view of *homogeneous* equilibrium and the mass law, Smith calculated values for velocity "constants" and equilibrium "constants", which were in fact quite constant. In spite of the general agreement accorded Smith's explanation of the phenomena, it must be admitted that there are a number of objections which may properly be raised to the assumptions underlying the explanation.

(a) In the first place, every effort to establish the existence at any temperature of a single molecular species with constant composition in gelatin has met

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[1] Work as yet unpublished.

with failure. Thus Knaggs and Schryver[1] conclude, at the end of careful attempts in purifying gelatin to obtain a material of constant composition, that "there is no reason for regarding 'gelatin', even after submission to elaborate methods of purification, as a chemical entity". In such a system with an unknown number of undetermined molecular species, it seems scarcely possible to identify the properties of any single constituent. Nor is it feasible to assume that any particular physical or chemical behavior is the result of the existence in the system of a reversible equilibrium between two forms of a single but unknown substance.

(b) Even though there were reason for considering gelatin as a chemical entity, gelatin sols and gels do not meet the conditions which would justify the application of the principles of *homogeneous* equilibrium. With respect to the capacity for forming gels, the general properties of the gels, the vapor pressure, Tyndall effect, ultrafiltration, viscosity and the almost unrestricted motion of ions and diffusing molecules through dilute sols and gels, gelatin systems display a behavior characteristic of disperse, *heterogeneous* systems[2]. This being the case, it is incorrect to treat the mutarotation accompanying the formation of a gelatin gel as a physical reflection of a *chemical change* in a *homogeneous* system. It might be thought that the success with which certain aspects of gelatin behavior may be described by the same equations as appear in Donnan's theory of membrane equilibrium should demonstrate the legitimacy of treating gelatin systems as homogeneous. The incorrectness of this view is shown however by the fact that to a certain extent, the same equations may be applied to systems undoubtedly heterogeneous[3] (as a gold sol). Even in the application of the Donnan theory to gelatin systems, the gelatin gel replaces the membrane (a *separate phase*) of the original form of the theory.

(c) Furthermore, the successful description of the velocity of any given process by means of the equation for a bimoecular reaction is absolutely no proof that a *bimolecular* reaction is actually taking place in a homogeneous system, for, as has been shown theoretically by Smoluchowski[4], and experimentally by several workers,[5] even the process of coagulation in a clearly heterogeneous system (as a gold sol) is formally and superficially a "bimolecular" reaction.

(d) The assumption of a new molecular species, a special Gel Form, contributes nothing to an understanding of the nature of gel structure, nor does such an assumption explain how or why a gel is formed, or how the Gel Form differs from the Sol Form. Since it is not customary to explain the change of properties during the formation of a gel of soap, silica, ferric oxide, arsenates, etc., by the assumption of new molecular species and corresponding chemical changes, it is not obvious why such a questionable procedure should be used

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[1] Knaggs and Schryver: Biochem. J., 18, 1095 (1924).

[2] See for instance, Wilson: Colloid Symposium Monograph, No. 1, p. 224 (1923).

[3] Wilson: J. Am. Chem. Soc., 38, 1982 (1916).

[4] Smoluchowski: Z. physik. Chem. 92, 129 (1917).

[5] Westgren and Reitstötter: Z. physik. Chem., 92, 750 (1918); J. Phys. Chem., 26, 537 (1922); Zsigmondy; Z. physik. Chem., 92, 600 (1917).

in the case of gelatin gels. Inasmuch as gel formation, in the great majority of cases, either organic or inorganic, may be properly regarded as due to suspended or incomplete precipitation or coagulation, it is probable that the formation of a gelatin gel may be considered in the same way.

(e) The differences in the specific rotation vs. pH curves at 35° and 20°C are not readily explainable in terms of an hypothesis involving a Gel Form and Sol Form in chemical equilibrium with each other. The relatively slight differences in rotation between 20 and 50°C at extreme pH's—where the combination with acid and base reaches a maximum—and the great differences in rotation at a pH 4.7 indicate that *the difference in the two forms of gelatin,* if they exist, *is largely limited to their isoelectric or uncombined states.* And furthermore, the extreme variation in rotation with change in pH under 25°C indicates that the *seat of optical activity must be closely allied with the seat of acid-base combining capacity,* if the phenomenon be considered as taking place in a homogeneous system. As shown by the decided discontinuities in rotation at pH 4.7 at all temperatures studied, *both forms possess a like isoelectric point* and, as shown by pH measurements at 40 and 23° C, *both forms possess practically identical acid-base combining capacities.* It is difficult to reconcile this behavior with Smith's suggestions, for it is rather unlikely that a drastic chemical change should take place to modify so profoundly the seat of combining capacity, as revealed by the great variation of optical rotation with pH, *without* changing either the isoelectric point or the acid-base combining capacity. In the absence of any such change, Smith's Gel Form and Sol Form may well be the object of scepticism.

(f) It would also be without precedent to find a chemical equilibrium between two such molecular species, as Gel Form and Sol Form are supposed to be, so sensitive to the presence of specific neutral salts (as NaI) as Smith would have to assume to explain the disappearance of the mutarotation at constant pH in the presence of such salts[1].

The suggestion by Lloyd[2] that the relationship between Gel Form and Sol Form is one of keto-enol tautomerism has already been discussed by one of us[3]. In addition to the remarks made at that time, it may be pointed out that the assumption of a keto-enol change to explain gel formation is subject to the same criticisms as have been presented above (particularly paragraphs a, b, d, e and f), and also necessitates additional difficult explanations, not yet given, for the apparent absence of the same keto-enol behavior in other proteins, all of which presumably contain the keto-enol possibilities of the peptide linkage. However, in view of the fact that the peptide linkage does not appear to participate in acid-base combination in dipeptides within an intermediate range of pH ca. 2-11[4], it may be doubted whether there is any such acid-base combination in the proteins. In fact, with more detailed study

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[1] Stiasny: Kolloid-Z., 35, 353 (1924).

[2] Lloyd: Biochem. J., 14, 147 (1920).

[3] Kraemer: J. Phys. Chem., 29, 410 (1925).

[4] Harris: Proc. Roy. Soc., 95B, 445 (1924); Levene, Simms and Pfaltz: J. Biol. Chem., 61, 445 (1924).

of protein systems, it becomes more difficult to interpret their behavior in terms of the theory of ampholytes[1]. It remains to be seen whether this is due to a real limit in the applicability of the theory to these systems, or to the complexity of these bodies as ampholytes.

These remarks, showing the doubtful existence of a keto-enol isomerism in gelatin, also increase the difficulties in the way of extending the assumption as Wilson and Kern[2] have done, by assigning to the hypothetical Gel Form, and Sol Form isoelectric points at pH 4.7 and ca. 8 respectively, in order to explain the "second isoelectric point" of gelatin at pH 8. A brief discussion of this elaborated hypothesis was also given in the note mentioned above, in which it was shown that the discontinuities in the physical properties at a pH ca. 8 cannot consistently be related to or connected with the Sol Form-Gel Form of Smith, the gelatin A and B of Davis and Oakes[3] or the keto-enol tautomerism of Lloyd. The studies of optical activity have confirmed this opinion by indicating that if there are separate chemical entities to which the terms Sol Form and Gel Form may be applied, their isoelectric points fall at the same pH, i.e. 4.7, as pointed out in paragraph (e). The cause for the apparent isoelectric point at pH 8 is still to be found. It must be admitted however, that the common presumption is not so certain that protein-like constituents with isoelectric points different from pH 4.7 are removed in the ordinary purification of gelatin. The presence, in relatively small quantity, of an independent constituent with an isoelectric point at pH 8 could give rise to the behavior observed in the neighborhood of that pH. Attempts are under way to remove such a constituent from gelatin.

Therefore, on the basis of the data now available, the authors feel justified in claiming that there is no unequivocal evidence for supposing that gelatin contains two related molecular species—a Sol Form and a Gel Form—in chemical equilibrium with each other, as assumed by Smith, Lloyd or Wilson and Kern.

II. To the authors, it seems that a more adequate understanding of the phenomena, which these other workers attempt to interpret, will be attained if it is recognized that gelatin systems in many ways display the characteristics of disperse systems. Besides those mentioned in paragraph (b) above, these characteristics include the properties to which it has been possible to apply the Donnan equilibrium equations[4]. As explained in detail elsewhere[5], the formation of a gel is due to what may be called an incomplete or suspended precipitation or coagulation of a colloidal solution, and is therefore limited to disperse systems. (The sol state may however be a short-lived one between a true solution and a gel). As is well known, the coagulation which leads to

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[1] Harris: Proc. Roy. Soc., 97B, 364 (1925).

[2] Wilson and Kern: J. Am. Chem. Soc., 44, 2633 (1922); see also Thomas and Kelly: ibid, 47, 833 (1925).

[3] Davis and Oakes: J. Am. Chem. Soc., 44, 464 (1922).

[4] See for instance Wilson: "Theory of Heterogeneous Equilibria", Chapter I in "Colloidal Behavior", edited by Bogue (1924). Also Loeb: "Proteins and Theory of Colloidal Behavior", 2nd ed., (1924).

[5] Kraemer: Colloid Symposium Monograph, No. 1, p. 67 (1923).

the formation of a gelatin gel is dependent upon the temperature. Those properties of gelatin systems which show a very great apparent temperature coefficient, or change with time below 50°C, are therefore in all probability closely related to the process of gel formation. The properties change with temperature, accompanying a readjustment of the gel state or sol state, and they may reach equilibrium relatively slowly, corresponding to the slowness with which colloidal changes frequently take place. It is unfortunately not yet possible to state whether the decrease of temperature leads to gel formation because a new phase appears (due to a decrease in the solubility of material in true solution) or whether the decrease in temperature causes the coagulation of an existing disperse phase with gel formation. The latter seems more probable; gelatin systems resemble, on this basis, Odén sulfur sols[1] to the extent that they both show *reversible* coagulation with change in temperature.

III. In the absence of evidence for the various hypotheses involving chemical changes (Section I), it seems likely that the phenomenon called mutarotation is, in the case of gelatin, intimately connected with *colloidal changes tending to gel formation*[2]. This view is consistent with the close parallelism between mutarotation of gelatin and gel formation. Thus, both gel formation and mutarotation are prevented by temperatures above ca. 35°C; gel formation and mutarotation are prevented by extreme pH's, either high or low; gel formation and mutarotation are prevented by the presence of certain "liquefying" salts as NaI; the magnitude of the mutarotation is a maximum at a pH where, according to the light-scattering capacity, gelatin systems are most pronouncedly colloidal or disperse in character. The slowness with which constant rotation is attained after a temperature change is paralleled by the accompanying changes in gel strength, and is typical of corresponding changes in disperse systems in general.

Since, as was emphasized in Section II of the discussion, gel formation is a property limited to disperse systems, "mutarotation" is really a misnomer when applied to gelatin, for it is dependent upon quite a different mechanism from that of glucose solutions for instance. Changes in optical rotation as observed in gelatin systems reflect changes in the nature of the micellae of a polyphasic system. The phenomenon is probably not unique to gelatin gels; gel formation and optical activity simply have not been studied in other systems containing optically active material.

Although gelatin gels are assuredly disperse systems, their optical activity demonstrates that, with respect to the wave length of light, they are more or less homogeneous. That is, the structure is a very fine-grained one, in spite of the pronounced light-scattering capacity. The heterogeneities may even approach "supermolecular" magnitudes as Sheppard has suggested[3]. The

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[1] Svedberg: Kolloid-Z., 4, 49 (1909); Odén: Nova Acta, Upsala, 3 No. 4 (1913).

[2] Manning has reached the same conclusion on the basis of much less data, Biochem. J., 18, 1085 (1924).

[3] Sheppard: Nature, 107, 73 (1921).

apparent mutarotation of gelatin gels also necessitates a slight modification of McBain's statement[1] that only the elasticity and rigidity change during formation of a "true" gel, for gelatin gels probably should not be classed with "curds". The optical activity of a "true" gel may differ from that of the sol.

Summary

1) The optical rotation of gelatin systems (Eastman's de-ashed gelatin) was studied for pH's between 2.30 and 12.31, and for temperatures between 10° and 50°C.

2) The relative light scattering capacities (or Tyndall effects) of the same systems were determined.

3) Various hypotheses involving Gel Forms and Sol Forms or tautomeric changes which have been proposed from time to time to explain certain behavior of gelatin systems, including optical activity, lack experimental support, and are probably confusing rather than helpful.

4) Many of the phenomena which have given rise to the speculations mentioned above are due to the fact that gelatin sols and gels display the characteristics of polyphasic (or colloidal) systems.

5) The so-called mutarotation of gelatin systems reflects colloidal changes in the systems tending to gel formation. Influences which prevent gel formation also prevent mutarotation.

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Note. After this paper was written, it was noticed that Vlès and Vellinger have just published their results on the Optical Activity of Gelatin (Compt. rend. **180**, 439 (1925)), which coincides in several points with the data of this paper. However, we have allowed our paper to remain in its original form.

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[1] McBain and Laing: J. Chem. Soc., **117**, 1507 (1920).

EQUILIBRIUM IN THE SYSTEMS: ZINC CHLORIDE-PYRIDINE; AND CADMIUM CHLORIDE-PYRIDINE*

BY RALPH B. MASON AND J. H. MATHEWS**

A compound of zinc chloride with pyridine has been described previously, viz., $ZnCl_2 \cdot 2C_5H_5N$ by Lang[1] and Monari[2]. Lachowicz[3] described the compound $ZnCl_2 \cdot 2C_5H_5N \cdot 2H_2O$ and Lang the compound $ZnCl_2 2(C_5H_5N \cdot HCl)$. The compound $ZnCl_2 \cdot 2C_5H_5N$ has been used by Heap, Jones and Speakman[4] in the preparation of pure pyridine. The compound is soluble in anhydrous alcohol and pyridine. In some potential difference work (to be described in a separate paper) in anhydrous pyridine it was necessary to know the extent of the solubility of the $ZnCl_2$. With this end in view the equilibrium has been determined from 0° to 105°C.

Materials used. A sample of Baker's pure pyridine was dried for several weeks over fused potassium hydroxide and then distilled. After this treatment it was digested with potassium permanganate for ten to twelve hours, using a reflux condenser. It was then refluxed with barium dioxide and finally distilled with a fractionating column. The fraction used, boiled at 114.2-114.6° at 741 mm. Hg (corr.)

Some pure zinc chloride was fused and then dissolved in anhydrous pyridine and the compound $ZnCl_2 \cdot 2C_5H_5N$ recrystallized three times from the anhydrous pyridine by heating and then cooling in a freezing mixture. The purified salt was kept in a desiccator. However the compound is not hygroscopic and a sample that has remained in the open air of the laboratory for over a year has as bright and shiny crystals as the day it was set out.

Method. The solubility determinations were made with a modified Meyerhoffer-Saunders[5] apparatus which was immersed in an electrically controlled hermostat. The mercury thermometer was graduated to 0.1° and capable of being read to .01°; it was compared with a thermometer standardized by the United States Bureau of Standards.

Analysis of Samples

Determination of Zinc. Zinc was determined volumetrically by the ferrocyanide method. The pyridine interfered with the end-point and was therefore removed by boiling with sodium hydroxide before attempting the zinc determination. An analysis of the zinc chloride complex gave 22.28 percent zinc while the theoretical value is 22.20 percent.

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*A portion of a thesis submitted by Ralph B. Mason in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

**Contribution from the Laboratory of Physical Chemistry of the University of Wisconsin.

[1] Ber. 21, 1578 (1888).

[2] Jahresber. 1884, 629.

[3] Monatsheft, 9, 516 (1888).

[4] J. Am. Chem. Soc. 43, 1936 (1921).

[5] Walton and Judd: J. Am. Chem. Soc. 33, 1039 (1911); Z. physik. Chem. 28, 464 (1899)

Determination of Chlorine. The chlorine was determined by Volhard's method. By analyzing a sample of zinc chloride with and without pyridine, it was found that the pyridine had no effect upon the chlorine determination. A one gram sample of zinc chloride complex was dissolved in dilute nitric acid and the chlorine determined in the usual manner. The value obtained for chlorine was 23.98 percent while the theoretical value is 24.08 percent. Since the chlorine determination was easier to carry out and more accurate, the solubility of zinc chloride at different temperatures was calculated from the chlorine determinations. However zinc was determined in several samples as a check upon the chlorine determinations.

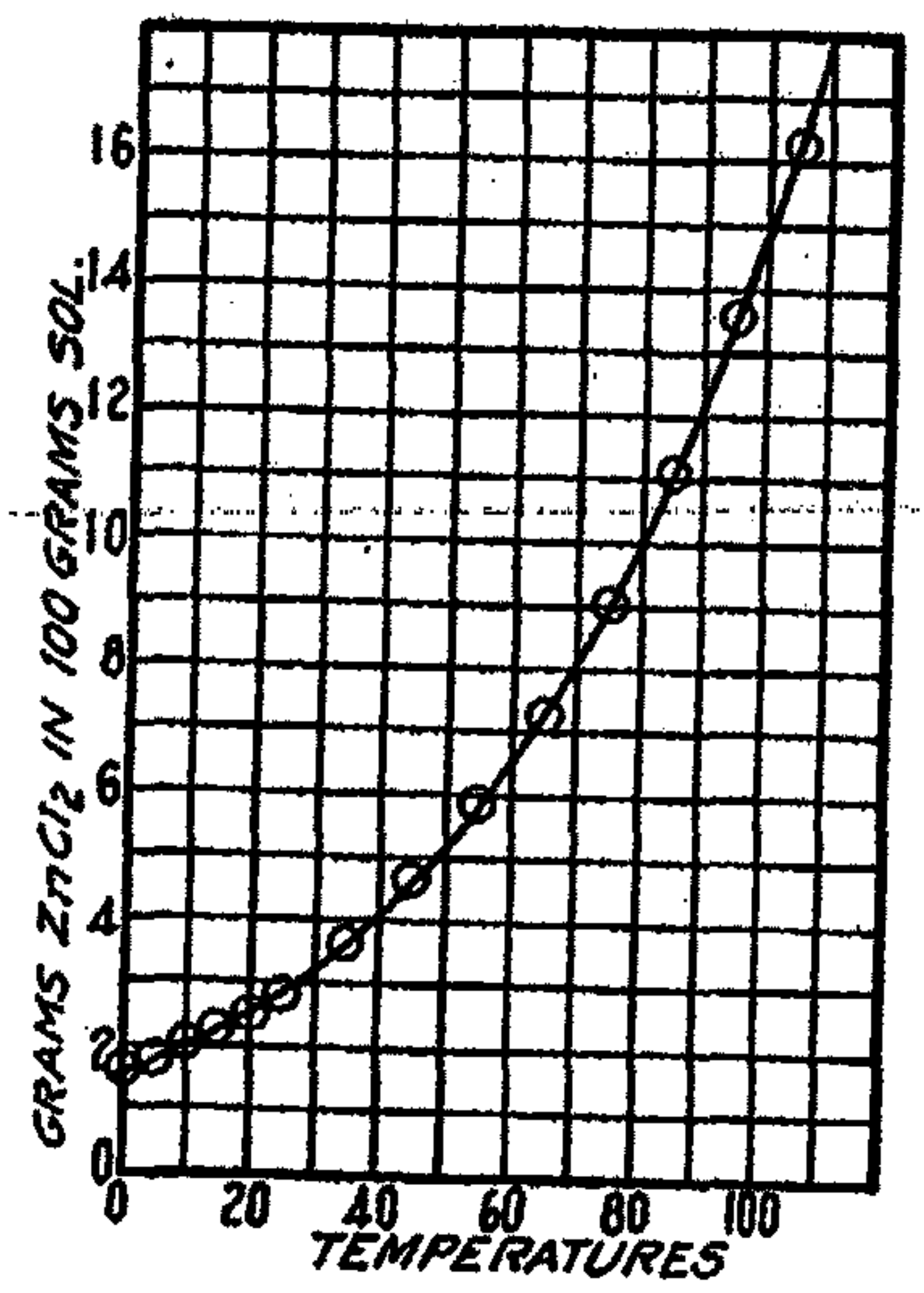

Fig. 1

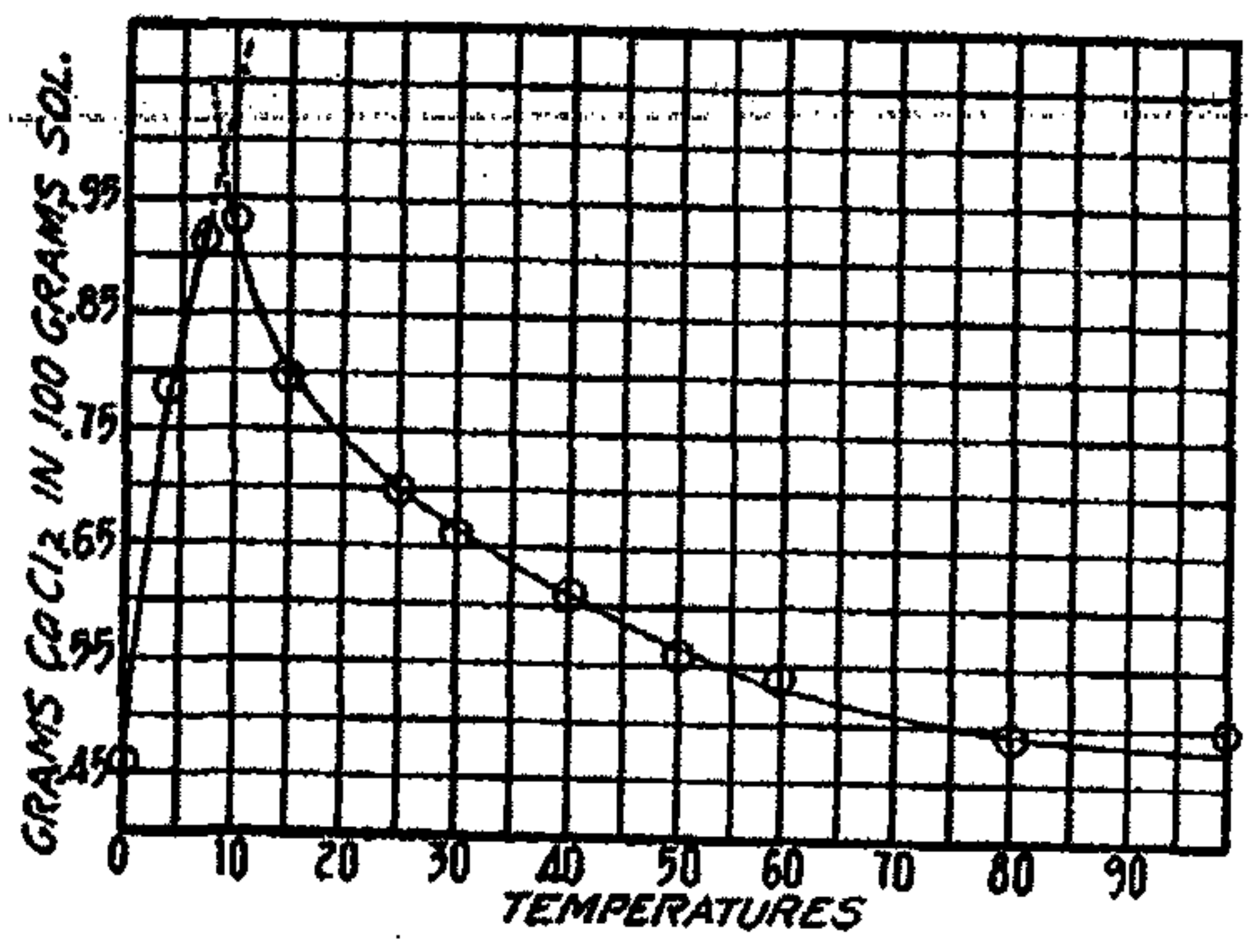

Fig. 2

Numerical Data

The data obtained are given in Table I and shown graphically in Fig. 1. Temperatures are plotted as abscissas and percentages of zinc chloride in the sample as ordinates.

From the solubility determinations of $ZnCl_2$ in pyridine from 0° to 105° it is evident that there is only one compound of $ZnCl_2$ with pyridine, viz., $ZnCl_2 \cdot 2C_5H_5N$. There is a gradual increase in solubility with increase in temperature.

Equilibrium in the System: Cadmium Chloride-Pyridine. Only one compound of cadmium chloride with pyridine has been described previously, viz., $CdCl_2 \cdot 2C_5H_5N$ by Lang[1], who analysed the compound for cadmium, chlorine, and pyridine. Koenigs and Geigy[2] mention the fact that $CdCl_2$ forms crystals from pyridine solutions. Lincoln[3] says that $CdCl_2$ is insoluble in pyridine or only very slightly soluble, forming a solution which is a very poor conductor

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[1] Ber. **21**, 1584 (1888).

[2] Ber. **17**, 594 (1884).

[3] J. Phys. Chem. **3**, 461 (1899).

of the electric current. Naumann[1] reported $CdCl_2$ as insoluble in pyridine. Kragen[2] used pyridine for the quantitative precipitation of $CdCl_2 \cdot 2C_5H_5N$. He stated that the $CdCl_2 \cdot 2C_5H_5N$ loses one molecule of pyridine at 115-120°C but no more, and weighed the cadmium as $CdCl_2 \cdot C_5H_5N$. He found that at 22°C, ninety nine percent pyridine (B. P. 114-116°C) dissolved 1.347 grams $CdCl_2 \cdot 2C_5H_5N$ for each hundred grams of solution, a value which agrees with the results of this research.

TABLE I

Temperatures	Weight of Samples	cc. $AgNO_3$	Per cent $ZnCl_2$
0	4.220	9.93	1.60
	3.990	9.33	1.59
5	4.073	10.76	1.80
10	4.070	12.22	2.04
	4.230	12.46	2.00
15	3.531	11.79	2.28
20	3.646	13.67	2.55
24.12	3.628	14.87	2.79
	3.945	16.40	2.81
	3.643	14.92	2.79
35	3.492	18.72	3.65
	2.921	15.82	3.69
45	2.950	20.16	4.66
	2.908	19.86	4.65
55	2.529	21.58	5.82
	3.613	31.08	5.89
65	3.272	35.20	7.33
75	3.627	48.20	9.06
85	2.621	42.68	11.11
95	2.098	41.84	13.60
105	2.146	51.09	16.24
	2.056	48.87	16.26

1 cc. $AgNO_3$ = .00682 grams $ZnCl_2$.

Materials used. The pyridine was purified in the same manner as for the $ZnCl_2$. It boiled at 114.2-114.4° at 736 mm. Hg (corr).

Cadmium chloride of "C. P." grade was dissolved in water and precipitated as sulfide. The sulfide was dissolved in HCl and the H_2S removed by boiling. The chloride was then precipitated by HCl gas. The calculated amount of NH_4Cl to form the double salt was added and the double salt recrystallized from water. The double salt was heated in a porcelain boat in a pyrex tube while a stream of HCl gas was passing through the tube. After the

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[1] Ber. 37, 4609 (1904).

[2] Monatsheft, 37, 391 (1916).

NH_4Cl had been sublimed away the tube was heated to redness and the $CdCl_2$ distilled. The beautiful white crystalline $CdCl_2$ was preserved in a desiccator until used.

Method. The solubility apparatus used was similar to that used for $ZnCl_2$, except that it was made entirely of pyrex with no rubber stopper. The stirrer was also made of pyrex and the apparatus was made air tight by a mercury seal.

Some of the pure $CdCl_2$ was fused in a small pyrex tube in an atmosphere of N_2. After cooling it was added to the solubility apparatus and the pyridine distilled directly into the solubility chamber. The pipette was dried by passing hot dry air through it for half an hour. It was then allowed to come to the temperature of the bath before the sample was removed.

Determination of Cadmium. Some pure $CdCl_2$ was dissolved in absolute alcohol and the cadminum precipitated as $CdCl_2 \cdot 2C_5H_5N$. This compound was allowed to stand in excess anhydrous pyridine and then filtered and washed with pyridine. A sample of the $CdCl_2 \cdot 2C_5H_5N$ was weighed and dissolved in hot water. Pyridine was liberated upon boiling. Excess pure potassium hydroxide was added and then CO_2 passed until the cadmium was completely precipitated as $CdCO_3$. The $CdCO_3$ was washed upon a filter and dissolved in HCl. It was then evaporated on the water bath in a weighed porcelain crucible and changed to the sulfate by addition of conc. H_2SO_4. After heating in an air bath until no more fumes of SO_3 were given off, the crucible was weighed.

Chlorine Determination. The Volhard method was again used for the determination of chlorine. In the case of the $CdCl_2$ the pyridine seemed to interfere with the end point. When the $CdCl_2.2C_5H_5N$ is boiled with water for about ten minutes, the pyridine is given off and the determination can be carried out in the usual manner.

Numerical Data

The solubility of the $CdCl_2$ in pyridine at different temperatures was determined by analysing each sample for chlorine and then calculating the amount of $CdCl_2$ present in each one hundred grams of solution.

The data obtained are given in Table II and shown graphically in the accompanying curve. Temperatures are plotted as absicissa and percentages of cadmium chloride in the sample as ordinates.

The solubility of $CdCl_2$ in pyridine increases very rapidly from 0° to 9°. From 9° to 100° there is a very gradual decrease in solubility. This abrupt change in solubility leads one to look for a transformation of one pyridinate into another with a smaller number of molecules of pyridination. Samples of the pyridinate stable at the room temperature were analysed for chlorine by the usual gravimetric method and showed 20.74% chlorine present, a value which agrees very closely with the theoretical value of 20.76% chlorine for the compound $CdCl_2 \cdot 2C_5H_5N$.

TABLE II

Temperatures	Weight of Sample	cc. AgNO$_3$	Per cent CdCl$_2$
0	3.616	1.79	.46
	5.157	2.62	.46
4	5.113	4.30	.77
	4.987	4.33	.80
7.2	4.711	4.71	.92
	4.315	4.28	.91
10	5.045	5.18	.94
	4.876	4.87	.92
15	4.353	3.78	.80
	4.378	3.76	.79
25	4.362	3.31	.70
	5.029	3.83	.70
30	4.780	3.55	.68
	4.630	3.31	.66
40	4.803	3.18	.61
	4.553	3.02	.61
50	4.905	2.88	.54
	4.709	2.90	.57
60	4.648	2.72	.54
	4.628	2.71	.54
80	4.446	2.35	.49
	4.616	2.46	.49
100	4.082	2.25	.51
	4.899	2.66	.50

1 cc. AgNO$_3$ = .00921 grams CdCl$_2$.

$CdCl_2 \cdot 6C_5H_5N$

Some pure $CdCl_2 \cdot 2C_5H_5N$ (from alcohol) was added to an excess of pure anhydrous pyridine (B. P. 115.3° at 760 mm. Hg.) in a glass stoppered bottle. The bottle was placed in the ice box over night and the resulting crystals were dried between ice cold filter papers. The crystals were quickly transferred to weighing bottles, weighed and analysed for cadmium and chlorine. The average value obtained for cadmium was 16.76% and the average value for chlorine was 10.63%. The compound $CdCl_2 \cdot 6C_5H_5N$ theoretically contains 16.83% cadmium and 10.80% chlorine.

Below 9° there is evidently a phase which corresponds to $CdCl_2 \cdot 6C_5H_5N$. This compound has not been described previously in the literature. An analogous compound, $CdBr_2 \cdot 6C_5H_5N$, has been described by Varet[1]. The crystals of $CdCl_2 \cdot 6C_5H_5N$ are large, clear and transparent. Allowed to stand at room temperature they crumble away to a fine powder. The transition temperature is approximately 9°.

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[1] Bull. (3) 5, 843 (1891).

Summary

1. The equilibrium in the system $ZnCl_2$-Pyridine has been determined from 0° to 105°. There is only one solid phase present, namely $ZnCl_2 \cdot 2C_5H_5N$.

2. The equilibrium in the system $CdCl_2$-Pyridine has been determined from 0° to 100°. A new compound, $CdCl_2 \cdot 6C_5H_5N$, has been identified. This compound is the stable solid phase below 9° while $CdCl_2 \cdot 2C_5H_5N$ is the stable phase above 9°.

Madison, Wisconsin
May 1926.

HEAT OF FORMATION OF LEAD CARBONATE

BY A. L. MARSHALL AND B. BRUŽS*

In connection with an investigation on the velocity of decomposition of lead carbonate it was found necessary to have reliable data for the heat of formation of this compound. The data available in the literature are from measurements by Thomsen[1] and Berthelot[2] and there is a difference of 3000 cals. between the two determinations. The values given are calculated in a roundabout manner from a number of other reactions. From Thomsen's data we have calculated ΔH for the reaction

$$PbO + CO_2 = PbCO_3$$

as −22,200 cals., whereas Berthelot's data lead to a value of −19,400 cals.

In the light of these conflicting values it seemed profitable to attempt a more direct determination of the heat of this reaction.

A recent publication of M. Centnerszwer, Falk and Auerbuch[3] gives evidence for the existence of the compound $PbO.PbCO_3$ and we have determined the heat of formation of this compound from PbO and $PbCO_3$.

Experimental

The method used consisted in dissolving PbO, $PbCO_3$, and $PbO.PbCO_3$ in 10 percent nitric acid (by volume). The calorimeter used was similar to that described by U. Fischer[4]. About 800cc. of solution was used in the calorimeter. Care was taken to eliminate all effects due to the heat of solution of lead nitrate from the calculation by having the final concentration in the solution the same in all cases.

Heat of Solution of PbO. Three experiments were conducted with lead oxide. In the first two the oxide was obtained by the decomposition of a very pure sample of cerussite (crystalline $PbCO_3$). In these two experiments 10g. portions were used and between the first and second 20g. of PbO were added to the solution in order to have the same final concentration of $Pb(NO_3)_2$ as in subsequent experiments. The third experiment was conducted with PbO from Kahlbaum.

Expt.	temp. rise	amt. PbO added	heat capacity calorimeter	ΔH_1
1	0.943°	9.01 crystals	849 cals.	−19,820
2	1.137	11.73 g. powder	879	−19,000
3	0.856	9.98 g. Kahl.	1036	−19,820
			average of (1), (2)	−19,410

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*Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] "Thermochemische Untersuchungen," 3, 333, 442.

[2] "Thermochimie," 2, 345.

[3] Acta. Univ. Latviensis, 11, 289 (1924).

[4] Z. anorg. Chem., 78, 57 (1912).

Heat of Solution of $PbO.PbCO_3$. The oxycarbonate was obtained by heating cerussite at 330°C. in carbon dioxide at one atmosphere pressure to constant weight. The substance lost exactly 50 percent of its carbon dioxide. Three experiments were conducted consecutively in the same solution giving the proper final concentration of $Pb.(NO_3)_2$.

Expt.	temp. rise	amt. $PbO.PbCO_3$ added	heat capacity calorimeter	ΔH_2
10	0.555	16.04 g. crystals	1053 cals.	−8930 cals.
11	0.532	16.00 "	1047	−8550
12	0.438	14.00 "	1058	−8130
			average	−8540

It will be observed that between experiments (10) and (12) there is a difference of 800 cals. and in experiments (1) and (2) a difference of 820 cals. This corresponds to a difference in the heat of solution of lead nitrate in a 10 percent nitric acid solution and a solution containing 9 percent nitric acid and 4.3 percent lead nitrate.

Heat of Solution of Cerussite ($PbCO_3$). Six experiments were carried out using very pure crystalline cerussite. Before each determination the solution was saturated with carbon dioxide and a platinum foil cover was placed in the calorimeter to prevent loss by spattering.

The reaction goes with an absorption of heat but, in the first stage, a small temperature rise was observed. This appeared to be due to the increased solubility of the carbon dioxide evolved during the reaction and a correction had to be introduced to take account of this effect. In the last two experiments a small amount of lead carbonate was added to the solution just prior to the experiment and this practically eliminated the initial rise.

Expt.	temp. rise	amt. $PbCO_3$ added	heat capacity calorimeter	ΔH_3
4	−0.375	50.0 g. crystals	1064 cals.	2130 cals.
5	−0.325	50.05 g. "	1050	1820
6	−0.355	49.92 g. "	1054	2000
7	−0.330	50.0 g. fine powder	1057	1870
8	−0.440	46.8 g. crystals	847	2130
9	−0.390	43.61 g. powder	840	2010
			average	1990 cals.

A correction has to be introduced in the last experiments for the amount of water evaporated. This amounts to about 0.1 g. for 50 g. $PbCO_3$ corresponding to about 50 cals. absorbed and gives a corrected value $\Delta H_2 = -8690$ cals. and $\Delta H_3 = 1690$ cals.

From these data one can calculate ΔH for a number of reactions.

$$PbO + CO_2 = PbCO_3;\ \Delta H_4.$$
$$\Delta H_4 = \Delta H_1 - \Delta H_3 = -21{,}100 \text{ cals.}$$

$$PbO+\tfrac{1}{2}CO_2=\tfrac{1}{2}PbO, PbCO_3;\ \Delta H_5$$
$$\Delta H_5=\Delta H_1-\Delta H_2=-10{,}720 \text{ cals.}$$
$$\tfrac{1}{2}PbO. PbCO_3+\tfrac{1}{2}CO_2=PbCO_3;\ \Delta H_6$$
$$\Delta H_6=\Delta H_2-\Delta H_3=-10{,}380 \text{ cals.}$$
$$PbO+PbCO_3=PbO. PbCO_3;\ \Delta H_7$$
$$\Delta H_7=2\Delta H_5-\Delta H_4=-340 \text{ cals.}$$

From the table on lead carbonate it will be seen that the difference in heat content between very finely powdered cerussite and the massive crystals is within the experimental error of the method which amounts to ±100 cals. The value of ΔH obtained from the reaction

$$PbO+CO_2=PbCO_3$$

is approximately a mean between that of Thomsen and Berthelot.

We are indebted to Messrs. R. T. Major and N. F. Myers for assistance in the conduct of some of the measurements.

Summary

The heats of the following reactions have been determined:

$PbO+CO_2=PbCO_3$ $\Delta H=21{,}100$ cals.

$PbO+PbCO_3=PbO.PbCO_3$ $\Delta H=-340$ cals.

Princeton, New Jersey.

NEW BOOKS

Modern Astrophysics. *By Herbert Dingle. 22 × 14 cm; pp. xxviii+320. New York: The Macmillan Company, 1924. Price: $8.50.* "This book is intended primarily for the general public. The subject of Astrophysics is presented as a panorama, seen from a detached point of view with vision characterised by breadth rather than by acuteness. An attempt has been made also to convey indirectly to the reader something of the emotions of the practical worker—something of the strange mixture of enthusiasm and wonder, assurance and distrust, eagerness and fear; of amazement at the splendour of his achievements, and humiliation at their meanness; of delight in his knowledge, and disgust at his ignorance; of confidence for the future, and shuddering at its difficulties; in short, of the "divine despair," that agitates the breast of the modern astrophysicist when he surveys the untrodden land into which he has pierced. Astrophysics is the most imaginative of the sciences. Is it too much to hope that one day it might be the means of revealing the essentially imaginative spirit of all science?", p. v.

"There are limits to the chemical application of the spectroscope. As we shall see later, the spectrum can indicate the composition of only a small part of a heavenly body, and even there the analysis may not be complete. But the partial failure on the chemical side has been more than counterbalanced by the extraordinary wealth of physical data which the spectroscope makes available. It was soon discovered that a substance could give a variety of spectra, each chemically characteristic of its source. The variation is due entirely to physical causes, among which change of temperature is probably the most effective. Hence arose a method of estimating stellar temperatures, and later, from the distribution of light intensity along the spectrum, it was found possible to verify the results obtained. Further, exact measurements of the positions of lines in a spectrum showed that the lines could be displaced or split into components, in a perfectly definite way, by a number of agencies, such as magnetic and electric fields, mechanical pressure, velocity of the source towards or away from the observer: and each of these effects could be used as a measure of its cause. The relative intensities of particular lines in its spectrum was found to be a function of the total amount of light emitted by a star; hence stellar brightnesses became known, and, consequently, the distances of thousands of stars, irrespective of how far away they might be, provided they sent enough light to the Earth to produce a spectrum. There are suggestions—though they have not yet been verified to the satisfaction of every one—that the positions of spectrum lines may be dependent on a property of the gravitational field in which they are produced. If this is so, the spectrum may in time give a direct measure of stellar masses. Continuously, as time goes on, the spectrum is giving more and more evidence of its apparently limitless possibilities. It is as though a star throws the whole secret history of its being into its spectrum, and we have only to learn how to read it aright in order to solve the most abstruse problems of the physical Universe," p. xxiv.

"For some reason which we do not yet know, Nature has chosen to concentrate all her matter and the greater part of her energy in tiny points of her boundless space. We study these points because their characteristics are most susceptible to our methods of investigation. But is it not possible, and even probable, that the deeper secrets of Nature are to be found in the great volume of unoccupied space? Biology—which, in the multitude of its individual data and the recognition of progressive evolution, bears a strong resemblance to Astrophysics—has been forced to admit environment as a leading agent in producing its phenomena. May not the time come when Astrophysics will have to do the same? To these transcendental questions we can at present give no answer," p. xxvii.

"In a gas or vapor, the atoms are known to be far enough apart to exercise their functions unhindered. Accordingly, they yield their characteristic line spectra. Our model of the atom gives a very satisfactory explanation of the differences between flame, arc and spark spectra which we have already pointed out. In the Bunsen flame, the exciting agency is not vigorous enough to remove the electron to a very distant orbit, and we get, therefore, only the few lines corresponding to passages between the innermost orbits. The electric arc is a very much stronger stimulant, and is able to remove the electron to greater distances from the nucleus. The arc spectrum is consequently much richer in lines than the spectrum of the flame. It seems natural to attribute the production of the 'enhanced' lines to a similar effect, arising from a still stronger stimulus in the electric spark: there is now no doubt, however, that it has a more complex cause than this. We have already said that the spectra of elements containing more than one electron are due to the movements of the outermost electron in each atom. The agency responsible for the luminosity removes an electron from its orbit, but, when embodied in the flame or the arc, is not able, as a rule, to detach it permanently. The electron returns, and radiates its surplus energy as a wave of light. But now, suppose the stimulus is so great that the outermost electron is removed quite beyond the sphere of influence of the rest of the atom, and does not return at all. We are then left with what is, for all practical purposes, a new atom, in which the depleted army of electrons is no longer able to balance the nuclear charge; we, have, in fact, a positively charged atom. The now outermost electron will assume the mantle of the fugitive, and proceed to move from orbit to orbit, thus radiating waves of light and giving spectrum lines. But these new lines are not identical with the old ones. The possible orbits in the charged atom are as different from those in the neutral atom as are the orbits of one element from those of another. The modified atoms, therefore, give a spectrum of their own. It is believed that this is just what takes place in the electric spark. An atom which has permanently lost an electron is said to be 'ionised', and the enhanced lines constitute the spectrum of ionised atoms. In practice, as we have already observed, the spark spectrum is not totally dissimilar to the spectrum of the flame or the arc. There are lines which are common to all three modes of excitation. The reason is that ionisation is not a process which takes place simultaneously, at one fixed temperature, throughout the whole of a substance. Some atoms probably are ionised in a very hot flame; others remain neutral even in the spark. It appears that, at any one temperature, a certain proportion of the atoms of a substance are ionised, and this proportion grows as the temperature rises: there is a more or less definite equilibrium ratio of ionised and unionised atoms at each temperature. In the flame, the amount of ionisation is extremely small. In the arc, it is much greater, and arc spectra generally contain a considerable number of enhanced lines. The electric spark produces a still greater proportion of ionisation, so that the lines due to the ionised atom are stronger than they are in the arc and new enhanced lines are able to appear, while the lines of the neutral atom are weakened or die out altogether. One can imagine a still more extreme temperature, at which ionisation would be complete, and the spectrum would contain enhanced lines alone. This has been attained on the Earth as yet only with a few elements, but there are certain classes of stars in which it appears to be almost the general rule," p. 21.

"It has been said that the Almighty must smile upon scientific research, or He would not have filled the Universe with so many clues to its character. Those who assent to this proposition will find support for their belief in the fact that the spectra of more than 99 per cent. of the stars are absorption line spectra. Now, an absorption line spectrum is precisely the kind of spectrum from which we can learn most. In the first place, it tells us something about the internal structure of its place of origin, for we know that, to produce absorption, we must have two sources of light—a hotter and a cooler—in certain relative positions and in certain physical conditions. In the second place, an absorption line spectrum has all the essential qualities of the two kinds of spectrum of which it is built up: it has the continuous background, due to the hotter source, and also the dark lines, arising from the interposed material. Whatever there is to be learnt from either of these phenomena is available for us in respect to the vast majority of the stars we examine," p. 25.

Fowler considered at one time that the hydrogen spectrum was more complex than it had at one time been regarded and he assigned to it the Balmer series, the Pickering series, the Rydberg series, and the supposed second principal series which he had obtained. There were however two possible explanations for the observed results,—that there are four series for neutral hydrogen or two series for ionized hydrogen. How can a decision be made between these two possibilities? As so often happens in science, everything depends on a minute difference between their respective requirements. The theoretical constant for ionised helium, as we have seen, is not exactly four times the value for N for hydrogen, because of the slight modification arising from the difference between the masses of the hydrogen and helium nuclei. While N for hydrogen is 109675, the constant for ionised helium should be 4 + 109720, and this value should be put for 4N in the formulae we have just given, if the lines are generated by helium and not by hydrogen. The result of this is that there is a small difference between the wave-length calculated from the first set of formulae and those calculated from the modified set. Assuming the theory to be true, the origin of the lines will be determined by comparing the measured wave-lengths with those calculated in the two ways. Now we have already noticed a discrepancy between the predictions of Rydberg and Fowler's measurements of the observed lines. Rydberg's 4688, for example, was found actually to be 4686, and a similar discrepancy characterises the other lines which we are considering. But if we now substitute the ionised helium constant for 4N in the second set of formulae, the calculated values are almost exactly equal to the beserved ones, the differences being well within the limits of unavoidable experimental error. It has, therefore, been concluded that the Pickering, the Rydberg, and the supposed second principal series of hydrogen do not belong to hydrogen at all, but to ionised helium. To settle the question finally, Evans and others afterwards obtained the lines from helium which was shown to contain no trace of hydrogen, so that there can now be no doubt whatever that helium is their true parent," p. 53.

"The successive stages in the advance of spectral type are the replacing of unknown lines of ionised helium, of ionised helium by neutral helium, neutral helium by hydrogen and ionised metals, these by neutral metals, and neutral metals by chemical compounds," p. 71.

"Let us trace the successive stages in the history of a contracting star. At the beginning, we may note that contraction is an eminently reasonable supposition, for gravitational influences are always at work, and if they are powerful enough to hold a star together through whatever changes take place in it, we can hardly doubt that they will cause it to contract, at however slow a rate. Supposing, then, that a younger star is an extremely rarefied mass of gas, what will happen as it shrinks? This question was answered some time ago by Lane, Ritter, and others, and their conclusions have been generally accepted. So long as the density is very small, so that the laws of a perfect gas are followed (*i.e.* so long as the average distance between two neighbouring molecules is very large compared with the size of a single molecule), contraction will bring about a rise of temperature in such a way that the temperature at the centre of the mass increases at the samerate as the radius decreases. The temperature will not be so high in the outer layers as it will at the centre, because loss of heat by radiation takes place mainly at the surface, but it will rise with contraction, nevertheless, though at a slower rate. The 'effective temperature' of the star, therefore, whatever it may be, will rise with contraction in the early stages.

"But a time will come when the density is too great for the perfect gas laws to be applied. This will occur first at the centre, where the density is always greatest, and somewhat later in the outer layers. The result will be that the temperature of the star will cease to rise and will begin to fall—first at the centre, and later in the external parts. As contraction proceeds, the temperature will continue to fall until, at last, the star degenerates into a cold, dark, dense body, and swims out of our ken altogether.

"What, now, will be the value of the temperature at the critical stage when it reaches its maximum value? That will depend on the mass of the star. Other things being equal, the larger the mass, the higher will be the temperature it can attain through contraction. It follows that, since the stars have various masses, they will not all have the same history. Some will have a larger range of experience than others, and probably a longer life," p. 152.

"Saha has calculated the atmospheric temperatures of stars of different special types from the relative strengths of the spectral lines according to the equation given by his theory. His results for most types appear to be too high—higher for some than the measured photospheric temperatures. This, of course, would be expected from the neglect of subsidiary causes of ionisation: the temperature has to bear a greater responsibility than it can carry, and accordingly comes out too high. If we had an independent method of measuring the temperatures of stellar atmospheres, we should be able to estimate how much of the ionisation, in the stars of different types, is due to the subsidiary causes. At present we cannot do this with any confidence of accuracy.

"But while there are many details to be settled, we can say that we have traced the main causes of the spectral variations among stars. Laboratory experiments have shown the conditions necessary to produce the different types of spectra: the study of the Sun's chromosphere has shown how those conditions are distributed in stellar atmospheres. Together the two lines of investigation have led to the explanation of the Harvard sequence," p. 220.

'The charge of scarcity can certainly not be laid at the door of the non-galactic nebulae. These bodies exist in remarkable profusion, and must be recognised as normal products of the processes of Nature. There is reason to believe that at least a million are within reach of modern telescopes. They abound in all directions in space except in the galactic plane, where not a single one has been found. This absolute avoidance of the Galaxy is their most striking characteristic, in which they are quite unique: the plane in which all other celestial bodies are most thickly crowded is the one region which they avoid. Whatever theory may be held with regard to their function in the Universe will remain conspicuously incomplete so long as it does not offer an explanation of this remarkable distribution," p. 323.

"According to Shapley, the appearance of the Milky Way is mainly due to great star depth: there is no ring or spiral of star clouds outside the stellar system. But, at the same time, the uniform, symmetrical system, which was formerly imagined to form, with the Milky Way, the whole of the sidereal universe, is now relegated to a comparatively small region in the neighbourhood of the Sun. It is not that which provides the appearance of a Milky Way. The star depth is due to an irregular, heterogeneous, plane distribution of stars, grouped together with large variations of density, in which the stars in our own neighbourhood play a subordinate part. The larger system thus conceived is not limitless: the Sun, in fact, occupies a very eccentric position in it, and that is the reason why the Milky Way appears so much more condensed in the Scorpio-Sagittarius region—which is in the direction of the supposed centre of the system—than it does in the opposite direction. The irregularities of structure and the large rifts in the Milky Way are natural consequences of a chaotic assemblage of bodies containing more or less organised clusters, formless clouds, and isolated stars," p. 350.

"Collecting the various data bearing on the dimensions of the Universe, Shapley concludes that the whole perceptible material world forms a single system whose outline is symmetrical about the galactic plane. Apart from the globular clusters and the spiral nebulae, the cosmic bodies compose a flattened structure, whose extent may be 20 or 30 times as great in the galactic plane as in the perpendicular direction. The greatest diameter of the structure is about 100,000 parsecs. Relatively close to the structure, and, in general, approaching it from either side, are the globular clusters. The spiral nebulae also lie outside the main aggregations but they avoid the region of the globular clusters, and are moving away from, instead of towards, the galactic plane. In this comprehensive Universe the Sun occupies a position about 20,000 parsecs from the centre, and is a little north of the central plane," p. 370.

Wilder D. Bancroft

The Structure of Matter. *By J. A. Cranston. 42 × 16 cm. pp. xvi+196. New York: D. Van Nostrand Company, 1924. Price: $4.50.* The object of this book is to give "an account of the wonderful advances that have recently been made in knowledge of the structure of matter as a direct outcome of the discoveries of X-rays, radioactivity, and the electron. The intention is to expound the ideas on which the modern theories are based in the order in which they actually emerged."

The chapters are entitled: introduction; electrons; radioactivity; atomic numbers; isotopes; crystal structure; atomic theories; the valency theory of Langmuir; the present outlook. The book is a very good one—clearly written and containing a lot of interesting matter.

A photograph of the X-ray spectra of some of the elements in the third order show that "the spectrum of each element consists of two lines, one of which is much stronger than the other. The vibration frequencies V corresponding with these stronger lines are found to be directly proportional to the squares of natural numbers Q, i.e. $V = AQ^2$ where A is a constant. The elements examined by Moseley extended through the periodic table from aluminum to gold . . . . Each element is thus characterized by an integer which determines its X-ray spectrum [Q+1 equals the atomic number]. Thus an experimental proof of the fundamental nature of atomic numbers is obtained, and a means established of determining the relative value of the nuclear charge for each element. From this it follows that the absolute number of places in the periodic table from hydrogen to uranium is established, because these places are indicated by consecutive integers which express real relationships between the atoms," p. 52.

Russell and Rossi compared the "spectrum of pure thorium with that of thorium known from radio-active behaviour to contain approximately 20 per cent of ionium. These investigators were unable to detect the slightest difference between the spectra, and came to the conclusion that isotopes are spectroscopically identical. This work was confirmed by Exner and Haschek, and, further, the isotopes of lead were found to have identical spectra. "These results have profoundly influenced our views on the relation of the properties of matter to the structure of the atom. They suggest that the spectrum of an element is determined by the number of electrons external to the nucleus or, indirectly, by the number of protons in excess of the number of electrons in the nucleus, and not by the mass of the atom or by the total number of protons in the nucleus. The spectrum appears, in short, to be an extra-nuclear, not a nuclear, affair," p. 64.

"The most remarkable feature of the results shown in the Table of Isotopes, however, is that the masses of all the atoms measured, with the exception of hydrogen, are whole numbers to an accuracy of one-tenth per cent. In the case of hydrogen the mass has been compared with that of helium by the method known as 'bracketing'. Two sets of accumulators are obtained and adjusted so that they each give accurately the same potential of about 250 volts. The electric plates of the mass spectrograph can then be brought successively to two potentials, one exactly half of the other, by connecting these accumulators successively in parallel and in series. Particles differing in mass by exactly this ratio (2:1) could thus be brought to coincidence on the photographic plate. If three exposures be taken of hydrogen, using potentials of 250, 500+12, and 500−12 volts respectively, the line due to the hydrogen molecule obtained in the first exposure is found to lie half-way between the two lines due to the hydrogen atom obtained in the second and third exposure. This shows that the mass of the hydrogen molecule is exactly double that of the atom within experimental error. If, however, three exposures are obtained of mixtures of hydrogen and helium, the line obtained due to the hydrogen molecule when the potential is 250 volts does not lie symmetrically between the two helium lines obtained at potentials of 500+12 and 500−12 volts respectively. The mass of the helium atom is shown to be less than twice that of the hydrogen molecule, and to be in agreement with the atomic weight value 1.008 for hydrogen obtained with such consistency by investigators using chemical methods (o=16)," p. 74.

"The exceptional fractional value 1.008 in the case of hydrogen is explained by the theory of electromagnetism, whereby the mass of a charge spread uniformly over the surface of a sphere depends on the area, i.e. on the radius of the sphere. If the electron has a mass 1/1845 that of the hydrogen atom, it is calculated on this theory that the radius of the electron—assuming that its shape is spherical—is about $2+10^{-13}$ cm. Further, if we consider the hydrogen atom to consist merely of a proton and an electron, the mass of the proton is 1845 times that of the electron and its radius will according to theory be proportionately less, viz. about 10^{-16} cm.

"Now it is to be expected on this theory that if protons and electrons are brought together very closely their electric fields will affect each other, so that the total mass is reduced. Such a state of affairs exists in the nuclei of atoms other than those of hydrogen. The additive law of mass is not obeyed, and the mass of the nucleus is less than the sum of the masses of its constituents. In this way Aston accounts for the reduction of mass in the helium nucleus, where four protons each of mass 1.0072 and two electrons of mass 0.00054 exist so closely together that the total mass is 4.000. Aston calls this the 'packing effect', and interprets the whole-number rule as a statement that the mean packing effect of all atoms is approximately constant. He does not anticipate that the masses of the atoms are whole numbers with mathematical exactness, but believes that the packing effect will ultimately be shown to be different for some atoms.

"In the cases observed so far, the masses of atoms are whole numbers to an accuracy of about one in a thousand with the exception of hydrogen, noted above, and tin. Careful measurements of the lines obtained from tin show that, while the masses of the isotopes of tin are integral within experimental error with regard to each other, they are less than whole numbers by 2 to 3 parts in 1000 when compared with those of the isotopes of xenon. There is therefore some evidence that the protons composing the tin nuclei are packed in such a way as to cause a perceptible loss of mass," p. 75.

The author adopts the view that the real unit of matter in crystal structure is the atom itself and not the molecule, p. 89. The planes of the crystal contain atoms and not molecules. In the second place, the question arises, "Does the molecule exist in the crystal?" Each sodium atom in crystalline sodium chloride, for instance, is surrounded by six equidistant chlorine atoms, and each chlorine atom by six equidistant sodium atoms. These atoms cannot be reasonably paired off in such a way that molecules of sodium chloride can be said to exist. The crystal may be looked upon as one immensely associated molecule with the formula $(NaCl)_n$; but a much more attractive theory, which has been put forward by Kossel, Lewis, and Langmuir, and which will be considered later denies the existence of molecules in salts like sodium chloride at all. According to this theory the units in the crystal are the ions of chloride and sodium, these ions being produced as a necessary consequence of the formation of sodium chloride. In other words, the mechanism of the chemical action of sodium on chlorine is the transference of an electron from the sodium atom to the chlorine atom, so that the former becomes a positive ion and the latter a negative ion. These ions are then held in position in the crystal by electrostatic forces."

"Much has been written about the existence or non-existence of the molecule in the crystalline state. The problem cannot be regarded as settled yet, but from the evidence so far put forward, it seems possible that crystals may be divided into three types. In the first type, the units are charged particles, such as the ions of a salt. Debye and Scherrer believe that they have lithium fluoride to be ionized in the crystalline state. They assume that the diffracting power of an atom is proportional to the number of its external electrons. If the (111) planes, which consist alternately of lithium alone and fluorine alone show reflections of intensity 3 and 9 alternately, the inference wounld be that the planes contained atoms of lithium and fluorine; but these investigators found the intensities to be 2 and 10 alternately, indicating that each fluorine atom has gained an electron from a lithium atom, so that both elements exist as ions. The attractive suggestion has been made that a metal may be regarded as analogous to a salt, the positive portion being the metallic ion and the negative portion the electron itself. In a crystalline metal, the structure then consists of a lattice of electrons interpenetrating a lattice of metallic ions.

"The second type of crystal consists of neutral atoms held together by sharing electrons The diamond is an example of this type. The third type consists of neutral molecules. The majority of organic substances probably belong to this type. Sir W. H. Bragg and Shearer. have established the existence of chemical molecules in such substances as solid naphthalene and anthracene," p. 97.

"In 1916, important papers were published by Kossel in Germany and G. N. Lewis in America. These writers independently developed the idea that the electrons of the inert gases are arranged in an exceedingly stable way, and that the chemical properties of other atoms are explained by the giving or taking up of electrons so that the remainder could attain the stable arrangement existing in those of the inert gases; for example, the atomic number of neon is 10, and the inertness of this element is explained by assuming that the ten electrons in the atom are arranged in a regular way possessing great stability. The electronegative character of the preceding element, fluorine, is due to the tendency of the neutral atom possessing nine electrons to capture an additional electron, and so to become a negative fluorine ion with a configuration of ten electrons similar to that occurring in the neutral neon atom. On the other hand, the electropositive character of the succeeding element, sodium, is due to the tendency of the neutral atom with its eleven electrons to lose one, and so to become a positive sodium ion with an arrangement of ten electrons again similar to that of the neutral neon atom. (Although the ions of sodium and fluorine have configurations of electrons identical with neon and with each other, the three bodies are not completely identical because they have different nuclear charges; the nucleus, of course, remains unaltered by chemical combination.) The ready combination of sodium and fluorine is thus in accordance with the separate tendencies of the atoms, and the mechanism of the reaction is the complete transference of an electron from the sodium atom to the fluorine atom.

"In a similar way the electronegative and the electropositive characters of elements like oxygen and magnesium are explained. In the case of the combination of these two elements, two electrons are transferred from each magnesium atom to an oxygen atom, and ions of magnesium and oxygen, each doubly charged, are formed. Each ion has an arrangement of ten electrons similar to the neon atom.

"The arrangements of the electrons according to the two theories differ, for whereas Kossel imagines the electrons to rotate in concentric orbits lying in one plane, Lewis has suggested a static configuration in three dimensions to account for the fact that valency forces act in many elements in fixed directions. Lewis has criticized Bohr's theory, in which electrons can rotate without producing any effect on external charges. He is not prepared to make the sacrifice of electromagnetic theory that the suppression of radiation demands in Bohr's model. He prefers to regard a system that produces no external effect as being at rest rather than in motion," p. 111.

"The theories of Kossel and Lewis furnish us then with a simple picture of the mechanism of chemical combination in so far as this gives rise to polar compounds of the type considered. Lewis goes further and gives a valuable suggestion regarding the formation of non-polar substances, an example of which we may take in the fluorine molecule. He explains the union of two fluorine atoms and the simultaneous satisfying of their tendencies to form complete octets by suggesting that electrons may be shared in pairs by two atoms; in other words, the fourteen electrons available from the shells of the two fluorine atoms can give rise to two cubes, providing two electrons are common to both sides.

"This simple explanation of a type of combination by sharing electrons is of the utmost importance. It promises to go far towards explaining many problems regarding the valency of elements and radicles. We have here the recognition of two distinct types of valency, one of which, operating by the transference of electrons, is the common one of inorganic chemistry; the other, operating by the sharing of electrons, is exhibited by the typical non-polar organic compounds.

"The long fight almost a century ago between Berzelius with his dualistic theory and Dumas with his unitary theory of chemical compounds has now ended with the recognition that both theories were right when applied to the appropriate type of compound," p. 113.

"Langmuir does not support the idea that electrons revolve in orbits about the nuclei of atoms. The facts of stereo-chemistry show that the valency forces between atoms act in directions fixed with reference to each other. Even when the carbon atom is surrounded by fewer than four other atoms, there is evidence that these forces act in definite directions, as, for example, in charcoal obtained from the distillation of wood, during which process there is very little loss of volume. The charcoal being definitely solid must apparently be held together in its very loose structure by forces which would seem to be stronger than those produced by electrons rotating in orbits about the nuclei," p. 119.

"Innumerable further examples could be given showing how the simple theory of Lewis and Langmuir accounts for the properties of the elements and indicates the mechanism part of the theory, and the one which has given the greatest help in the study of the valencies of the elements, is that dealing with covalency. The inorganic chemist especially will welcome the theory as giving a simple and consistent explanation of the apparently random valencies of some of his elements. He has not hitherto realized the operation of a valency caused by the sharing of electrons, a valency that may almost equally well have the values 1, 2, 3, and 4 for most of the lighter elements. He has tried, without much success, to imitate the organic chemist in writing structural formulae. This has had unfortunate consequences, because he has thereby come to regard the electrovalency shown by one element as equivalent to the covalency displayed by another.

"The organic chemist, however, has been more happily served with the bond method of displaying structural formulae, because it so happens, in the vast majority of organic compounds, that the covalency displayed by each constituent element is equal to the electronegative valency of that element. He has therefore not concerned himself with the distinction between these two types of valency, and it serves his purpose adequately to use the non-committal bond. He has sometimes, however, difficulty with the element nitrogen, which he overcomes by the indiscriminate use of either three or five bonds, the latter number being suggested by the totally different type of valency, viz. the electropositive valency of this element. Five bonds would not be permitted on the octet theory as has been explained above. A covalency of four for nitrogen, i.e. the use of four bonds, is a new idea, but we have seen that the properties of some of the nitrogen compounds are better represented by formulae involving this valency," p. 166.

"Apparently there is less energy in the helium nucleus than in four free protons, so that a large amount of energy would have to be *supplied* in order to disrupt the nucleus; such is the inference from the loss of mass of four protons when bound together in the helium nucleus. Again, in the disruption of aluminium alone of the non-radioactive elements has there been found any marked gain in energy by the disruption. It is therefore quite possible that the radioactive elements are the sole representatives of types of elements, common in the early ages of the formation of the earth, which contain large stores of atomic energy due to their nuclear constitution.

"It must be remembered that such disintegration as has been effected has only been done on an excessively minute scale; for example, although each α-particle in its passage through aluminium passes through the electronic orbits of about 100,000 atoms, only about one α-particle in 500,000 liberates a H-particle. It seems almost impossible therefore to collect sufficient liberated hydrogen to be detected by ordinary chemical methods. The only known agent for effecting disintegration is the α-particle, itself the product of a natural distintegration which we are unable to control; it is therefore hardly correct to say that the disintegration of the non-radioactive elements has been effected artificially," p. 183.

Wilder D. Bancroft

Physical Chemistry, its Bearing on Biology and Medicine. *By James C. Philip. Third edition. 19 × 13 cm; pp. vii+367. London and New York: Edward Arnold and Co.; Longmans Green and Co., 1925. Price: $2.80; 8 shillings, six pence.* A new edition of Professor Philip's 'Physical Chemistry' with its sub-title 'Its bearing on Biology and Medicine' is most welcome and overdue. Here is a book, written sympathetically and accurately, which can be placed with confidence in the hands of a student early in his course. Only too frequently do students in our medical schools finish their systematic course in chemistry with a sigh of relief largely because they have failed for some reason or another to realise the importance of physical chemistry in the biological sciences. The book cannot fail to stimulate the student's interest in chemistry because it points out so clearly the physico-chemical basis on which progress in the investigation of biological and physiological problems now depends. The essential principles of physical chemistry are discussed in their most modern aspects and the applications in biology and physiology are all important and carefully chosen. The numerous references to original papers on physical chemistry, biology and physiology as well as to specialised text-books make the book of lasting value and a real guide to the student.

It is greatly to be regretted that the intensive training of medical students does not allow sufficient time for a representative course in practical physical chemistry and lecture experiments are, at the best, but a poor substitute. By pointing out to the student the importance of accurate physico-chemical measurements, Professor Philip has done and is still doing useful service in the cause of medical education. The medical curriculum with its examinations on detailed syllabuses at frequent intervals during the pre-clinical period and the inferior position in that curriculum of chemistry make it difficult for the importance of chemistry in the training of the physician to be realised by the one most concerned before it is too late. Professor Philip's book ought to be read by every medical student and not only will he be stimulated thereby but may be made discontented later with the present system of preclinical training in most medical schools. Until physiology and chemistry are infinitely more closely linked together in the medical curriculum, the progress of the former cannot be as rapid as modern methods have made possible. Fortunately, there are a few schools in which the interdependence of physiology and chemistry is realised, but progress is hindered until this is the rule rather than the exception.

To the physical chemist, Professor Philip's book cannot fail to appeal. The applications of physical chemistry in the biological sciences are so numerous that physical chemists cannot afford to be blind to the fundamental importance of investigating the reactions and conditions of life processes. One effect of studying this excellent book is to obtain some idea of the almost infinite number of problems awaiting investigation by the physical chemist with a vision.

C. S. Gibson

Space and Time. *By Carl Benedicks. 19 × 14 cm; pp. v+98. New York: E. P. Dutton and Company, 1924. Price: $2.00.* On p. 4 the author says that "for my part it has seemed essential to try to come to a clear understanding of the inner meaning of the fundamental conceptions of space and time. If the most subtle minds have for some thousands of years evolved conceptions which are now to be broken up summarily—perhaps in order to fuse them into some higher and more pregnant synthesis—then the first demand of a scientific mind will be an elucidation of the fundamental character of the old conceptions."

The author defines a solid body as an object characterized by immutability, p. 8, and thereby gets a standard of length. He considers that it is not necessary for space to have three dimensions. The three dimensions imply the freedom of movement given to Man, p. 16. "In dealing with space it is difficult to pass over the question whether its extension, which experience has taught us is very great, is also infinite. It seems to me obvious that it would be altogether outside our limitations to claim this to be the case. If thinking inhabitants were existing in a microcosmos built up of the almost innumerable atoms, each comparable to a solar system, within a tiny air-bubble in a block of glass, surely they might easily arrive at the conclusion that their universe was boundless, inasmuch as its boundaries lay altogether beyond their experience. It would certainly be conceit on the part of us earth-worms to believe ourselves to possess power to decide whether space cosmically taken, is limitless or not. Here it certainly seems justifiable to say "*ignorabumus.*"

"The conception of time has signification only for systems *in which changes occur*. The conception of time may be said to be void of meaning in a world without changes. Such a world is *timeless;* at least, we may say its time is standing still. Time could be said to have been at rest for the mammoths frozen in the ice of Siberia. But, on the other hand, it is obvious that the conception of time, equally with that of length, can, if desired be applied in cases where we have no opportunity of determining it physically," p. 30.

"It seems nugatory to worry about the question why *space,* in spite of its obvious indefiniteness, appears to have such an absolute character. There is more reason to meditate on the question why inert mass, with its property of creating directions in space, is a characteristic of matter.

"It is exclusively this property of inertia in matter which causes space to behave as an "absolute space"; should this term be found not quite satisfactory, it at least expresses the real facts," p. 39.

"At the beginning we convinced ourselves that despite all assertions to the contrary the traditional fundamental conceptions of space and time are quite clear and vigorous.

Since they enter into almost all human thought, it would be impractical to alter them, except perhaps in case of absolute necessity. No such necessity can be said to have arisen so far.

"The reason why Lorentz, Einstein, and others have wished to alter the fundamental conceptions of physics, can be said to reside in an exaggerated respect for the Maxwell-Lorentz theory of light in its present form, combined with a somewhat scant respect for the fundamental conceptions in themselves," p. 95.

The author's solution is the same as that of Ritz, to abandon the obscure conception of ether and to regard light as an emission in space.

Wilder D. Bancroft

The Effects of Ions in Colloidal Systems. *By Leonor Michaelis. 19× 13 cm; pp. 108. Baltimore: Williams and Wilkins Company, 1925. Price: $2.50.* This book is based on some lectures given in the United States in the spring of 1924. The subdivisions are entitled: some general remarks on adsorption; electric phenomena produced by the adsorption of ions; the origin of the electric double layers; the properties of charcoal; the connection between discharge, adsorption, and flocculation; the so-called Donnan equilibrium; lyotropic effects of ions; mixtures of electropytes.

The reviewer finds the theoretical views of the author a bit vague. It is hard to find out exactly what he believes on any given point. The book, however, is well worth reading for some of the facts that the author gives.

"Charcoal was considered as the prototype of an adsorbent, all other adsorbent materials being thought to differ from charcoal only quantitatively. Its very capacity of adsorption was attributed to the presence of an enormous system of superficies, not only in consequence of the finely granulated consistence but also because of the considerable unevenness or roughness of the particles and cavities of the superficies or, as it is usually called, the development of *interior superficies*. But the particular qualities of charcoal do not depend on the largeness of the specific superficies alone. This idea is entirely wrong and has brought about several distorted views. The adsorption faculty of good charcoal is not only quantitatively but also qualitatively wholly different from any other adsorbing substance. There are only very few substances endowed with similar qualities and even that only in quite a small degree. Firstly: in distinction from most powderlike, however finely granulated substances, charcoal possesses a prominent faculty of adsorbing from aqueous solutions numerous non-ionized, electro-indifferent substances. Here the rule generally holds that substances are the better adsorbed the more they diminish the surface tension against air, in aqueous solution. As this capillary activity, according to a rule of J. Traube, increases rapidly with the length of the carbon chain, also the adsorbability by charcoal increases rapidly with the length of the carbon chain, according to a rule of Freundlich. However, this parallelism is not always evident when comparing substances belonging to different homologous series. Not even does the rule hold that such substances are adsorbed which decrease the surface tension against air. For instance, sugar is adsorbed by charcoal in a measurable quantity, though it increases the surface tension against air. Experience has shown that *any* substance dissolved in an excess of water is adsorbed by charcoal, and a so-called negative adsorption never occurs in dilute solutions, in contradiction to some earlier assertions, and this holds for electrolytes, too. There are only two substances known hitherto which are not at all adsorbed by charcoal: the sulfates of alkali metal ions, according to the investigations of Rona and myself, and glycocoll, according to Abderhalden and Fodor. Different kinds of charcoal are different in respect to their adsorptive capacity, but I formerly thought the special capacity in adsorbing capillary active non-electrolytes to be characteristic for all kinds of charcoal, though they may differ in other respects. But I have newly encountered a kind of charcoal prepared from pure gelatine which lacks even this faculty, e. g., of adsorbing octyl alcohol," p. 51.

"For a long time experiences with electrical conductivity and other qualities have led us to the idea that ions in aqueous solution combine with water molecules at a rate depending chiefly on the specific chemical nature of the ion, but secondarily also on the concentration of these ions and the presence of other ions dissolved at the same time. For instance, among the univalent alkali ions the hydration decreases with increasing atomic weight or atomic radius; the hydration diminishes according to the series: Li, Na, K, Rb, Cs. As for the nature of this combination with water molecules, different opinions arose at different times. Formerly physical chemists inclined to the idea that each ion, a sufficient quantity of water being given, is combined with a quite definite number of water molecules, just as the molecules or the ions of a crystal are combined with a definite quantity of water of crystallization, and numerous attempts were made to determine the number of water molecules held by each kind of ion. However, different methods gave different results, only the relative position of the ions within the series was found to be nearly the same, whatever method might be applied. Thus by and by the opinion changed, and I think we should prefer the idea that hydration of ions does not mean combination with a definite number of water molecules, but a general attraction of all water molecules surrounding the ion. This representation has developed out of the atomic model of Rutherford and Bohr, and by the suggestion of Fajans and of Debye to consider the water molecules as an electrical dipole, with one end negative and the other positive. The attractive force of ions directed at water molecules surrounding them is interpreted as an electrostatic effect. A positive ion attracts water molecules in such a manner that the negative end of the water molecules approach the ion; and the water molecules polarized in this manner have a directing or polarizing influence on the more distant water molecules, decreasing with the distance. So an apparent effect at a distance on a colloid particle, by an ion, may take place, in which, however, the water molecules act as an intermediary; such an intermediary effect being the principle in each modern theory of "effects at a distance." The power of combining with water in ions carrying equal charges chiefly depends on the distance to which the water molecules can approach the free electrical charge of the ion. For instance, in positive ions, the free charge is situated in the atomic nucleus, and the approach of the water molecules is limited by the size of the atomic radius. Therefore, hydration of positive ions decreases with increasing atomic radius, " p. 83.

On p. 87 there must be a mistake in the account of the action of sulphates and sulphocyanates on albumin because sodium sulphocyanate is said to flocculate albumin less readily than sodium sulphate in slightly acid solutions while the reverse is actually true. It is possible that Michaelis is calling pH5 acid although it is on the alkaline side of the isoelectric point.

At low salt concentrations—up to N/100—all potassium salts affect the swelling of agar agar equally; but at higher concentrations the Hofmeister series appears and the order is citrate, ferrocyanide, sulphate, acetate, chloride, bromide, nitrate, ferricyanide, sulphocyanate, iodide, the iodide repressing the swelling the least and the citrate the most. p. 90. In dilute acid solutions the nature of the anion has no effect; but in more concentrated solutions hydrochloric acid checks the swelling less than sulphuric acid which seems to mean that there is no reversal of the effect of the anions.

On p. 98 the author states that "it is not the true concentration of hydrogen ions which we can determine by means of a gas chain, but the so-called activity of the hydrogen ions." There was a time when people tried to reconcile theory and experiment; but it was a stroke of genius on the part of Lewis to give a new name to the experimental results in order to avoid accounting for them.

On p. 100 it is shown that the apparent increase in hydrogen ion concentration when chloride is added to a hydrochloric acid solution decreases in the order: Li, Na, K, Rb. Michaelis accounts for this as follows:—

"The potential of a hydrogen electrode is the sum of two magnitudes: first, the electrolytic solution tendency of Nernst. Let us consider it as a constant. Second, the counterpressure of the dissolved hydrogen ions, which tends to push the dissolved hydrogen ions into the electrode. This counteraction is weakened by the attraction of the water molecules exerted on the hydrogen ions dissolved. When you add ions which can attract water molecules, the attraction of water molecules and hydrogen ions is diminished, and the counteraction of the dissolved hydrogen ions against the electrolytic tendency of the electrode is augmented, the solution appears to behave as one which has become more acid. From this we may infer that the apparent augmentation of acidity produced by an ion is the stronger the higher the hydration of this ion. Indeed, you see this suggestion confirmed by the experiment. The feebly hydrated rubidium acidifies the solution least, and the highly hydrated lithium acidifies most of all the alkali ions. Sometimes the effect is very considerable. Thus a 0.01 normal solution of hydrocholric acid, when a 2.7 normal solution of potassium chloride is the solvent, appears to contain a hydrogen ion concentration of about 0.017 normal, which is mere nonsense from the standpoint of the former theory of electrodes and dissociation."

Wilder D. Bancroft

Organic Derivatives of Antimony. *By Walter G. Christiansen. 23 × 16 cm; pp. 230. New York: Chemical Catalog Company, 1925. Price: $3.00.*

"The chemistry of organo-metallic compounds has been expanding very rapidly during the last few decades, owing largely to the marked physiological activity of these substances. In this great class of compounds, there are, on the one hand, some of the most powerful of the war gases and, on the other hand, some drugs which are indispensable to modern medicine. Although the organic arsenicals have been investigated much more thoroughly than the antimonials, studies in the latter field are being carried on quite actively in connection with researches on protozoal diseases, because it appears that in certain of these diseases the antimonials are much more efficacious than the arsenicals. Throughout the literature there are numerous papers in which these compounds are discussed, but there is no comprehensive compilation of these results to which one may turn. The purpose of this volume is to correlate these widely scattered data in such a way that they will be suitable both for those desiring a general knowledge of the organic derivatives of antimony and for those embarking on researches in this field. To this end the material has been so arranged that the first chapters are devoted to general discussions without the introduction of detailed directions for the production of the various compounds; the latter type of information has been grouped in the last chapters. It is hoped that by impressing the need of extensive study in this branch of chemotherapy more investigators will undertake the development of antimonials for use in pharmacology.

"Even though the antimonyl derivatives of organic compounds cannot be classed as organic antimonials in the strict sense of the words, a consideration of these substances could hardly be omitted because of their importance in the treatment of some tropical diseases and of the fact that in studying therapeutic value of the new, truly organic antimonials the object is to develop compounds which are more effective than the antimonyls. Also, the ability of organic compounds to form antimonyl derivatives is dependent upon the existence in the molecule of certain arrangements of groups."

The subject is presented under the headings: introduction and historical outline; aliphatic antimonials; aromatic stibines and their derivatives; aromatic stibinic acids and aromatic stibino compounds; antimonyl compounds; antimonials as therapeutic agents; organic compounds containing trivalent antimony; organic derivatives of pentavalent antimony; antimonyl compounds; analysis.

"Although trypanosomiasis, in its many forms, is not encountered with great frequency in temperate regions, it is widely and thickly spread in many parts of the tropics, and in addition to exacting a heavy toll of human life, it also causes great economic losses to these localities by the destruction of large numbers of cattle and horses. The control and elimination of disease caused by trypanosomes is, therefore, one of the great problems confronting the medical sciences. Progress in this direction is gradually being made, but as yet no substance or group of substances has been discovered whereby an absolute cure for these infections can be attained. In some instances the patients appear to have been permanently cured, but in a large number the disease reappears after treatment. By the application of certain methods of medication persons afflicted with these infections can be maintained in such a condition that they are able to carry on their ordinary duties of life even though they have not been definitely freed from the disease. An example of this is to be found in one of the tropical countries where at one time it was customary to segregate those people who were found to be victims of trypanosomiasis and treat them medically so that, while not permanently cured, many were outwardly fit and able to follow their normal mode of living.

"Much of the success that has been attained in recent years in the treatment of trypanosomiasis with antimonials may be attributed to the discovery by Plimmer and Thomsen that the injection of tartar emetic or the analogous sodium salt into mice and rats which were highly infected with trypanosomiasis caused the parasites to disappear with great rapidity from the peripheral blod. This important work was undertaken at the suggestion of Cushny; Mesnil and Nicolle had previously suggested the use of animony derivatives in trypanosomiasis. Immediately thereafter chemists undertook the production of may new antimonials of both the antimonyl and C-Sb type which have been subjected to therapeutic studies in relation to protozoal infections. Trypanosomiasis is caused by a number of different species of parasites which are apparently very similar morphologically, but which respond somewhat differently to different antimonials. Thus a compound which is decidedly effective in combating one type of trypanosome may be quite inferior to some other antimonial when applied to a second type. Investigators have devoted themselves to a study of the antimonials particularly because these substances are frequently much more active than the arsenicals in combating certain tropical diseases; in fact, whereas leishmaniasis is hardly affected by arsenicals, very encouraging and successful results have been reported as a result of the use of antimonials. As usual, the results of different investigators do not always agree as to the exact order of efficacy of the various substances which have been examined, but this is to be expected when one considers that the study is still in its infancy and that the field under investigation is very broad," p. 15.

"Methods of preparing potassium antimonyl tartrate for injection differ widely. There are many physicians who believe that solutions of this drug may deteriorate rapidly on keeping. To prevent this they have single doses of the powdered drug put up in papers or tablets. They then dissolve the required dose at the bedside, boil the solution, and inject it while still warm. Other physicians recommend sterilization of the solution by the fractional method or by Berkfeld filtration because they think that the high temperatures of the autoclave may cause the drug either to lose potency or to become more toxic. Borja and Amaral sterilized the powdered drug with chloroform and subsequently dissolved it in sterile salt-solution. This is a convenient method for use in the field. Still other physicians see no objection to autoclaving the drug. They prepare a strong solution of the drug in distilled water, sterilize it in the autoclave, put it up in small bottles like a vaccine, and keep it on hand for indefinite periods. Such solutions are autoclaved again before use, and are generally diluted with salt-solution to the required strength before being injected. Another method is to prepare a stock solution of suitable strength for injection in normal saline, to sterilize it in the autoclave, and to keep it indefinitely in flasks. Stock solutions of potassium antimonyl tartrate must be made from a pure product, must be sterilized, and must be protected from contamination because fungi may, otherwise, grow in them," p. 109.

"The great importance of antimonials in the treatment of human disease is that they have a curative effect in the dangerous and distressing diseases above mentioned. In the treatment of these diseases, except trypanosomiasis, they have no rival and their action is well-nigh specific. Moreover, it has been shown experimentally that some of the antimonyl tartrates will protect animals from trypanosome infection for a short period after the injection, although not for any great length of time. This fact has been put in practical use when cattle were to be driven across an area infested with tse-tse flies where animal trypanosomiasis was rife. Again, antimonials may be effective in cases of sleeping sickness resistant to arsenicals, e. g., in the form of the disease caused by T. rhodesiense, or against races of trypanosomes which have acquired tolerance to arsenicals," p. 110.

Wilder D. Bancroft

Analytical Microscopy, its Aim and Methods. *By T. E. Wallis. 12 × 18½ cm; pp. vi + 149. New York: Longmans, Green and Co., 1923. Price $2.00.* A great body of prejudice exists regarding the proper applications of the microscope in analytical studies; most workers, chemists especially, appear to believe that microscopic analysis is in order only when the material in question is of biological origin. Plant and animal tissues are admittedly characterized more by their morphology than by their chemical properties, but there is an unfortunate tendency to overlook the fact that physical properties observable by the microscope may serve just as conclusively to identify materials of inorganic origin. There is hardly an heterogeneous system conceivable which has not been or may not be studied to advantage with the microscope. Truly enough, such study involves the use of the instrument as something more than a magnifier, and requires more specialized training than falls to the lot of most biologists or chemists. But if chemists are willing to learn to determine pH, or n_d, or $\alpha^{20°}_{Na}$ why should they not learn to determine extinction angles, or crystal symmetry, or particle size?

Mr. Wallis' book deals mainly with the identification or estimation of foods, drugs, fibers, and sediments, chiefly from the biological standpoint. He includes methods for preliminary treatment of the sample, such as sifting, sedimentation, elutriation, extraction, clearing, staining, macerating and mounting, interspersed with a great variety of illustrations and special modifications. The diversity of materials dealt with is strikingly exemplified: insects as poultry foods, micro-organisms in water, starches, scales of food fishes, osazones of various sugars, sulphur ointment, mange parasites, and so on. Excellent drawings, *not*, as is so frequently the case, borrowed from other works on technical microscopy, are a valuable feature of the book. Brief mention is made of chemicals having a definite microscopical structure such as "precipitated and sublimed sulphur, kieselguhr, talc or French chalk, and precipitated chalk", and even briefer reference to microsublimation and to microscopic qualitative analysis. Fortunately for mineralogists, metallurgists, analytical and research chemists, the microscopic identification of chemical substances is of rather greater scope than Mr. Wallis implies.

Quantitative microscopy is dealt with in all too short a space, for it is on this topic that the author is peculiarly fitted to present the results of his own experience and investigations. There is a real need for an extensive treatment of quantitative miscroscopic methods, and for a survey of their accuracy, range of application and theoretical foundations. One could wish that Mr. Wallis had included more on the quantitative (not necessarily strictly analytical) determinations which can be made with the aid of miscroscope, such as hardness, specific gravity, transformation points, molecular weights, size-frequency distribution and index of refraction.

A good discussion of micrometry and of the use of the drawing camera for miscrocopic measurements or drawing to scale or to a definite magnification are important features of the book, as is a complete exposition of Mr. Wallis' method of analysis by counting. Lycopodium spores, which are definite in weight, are mixed with the sample in known proportions and used as a reference substance in the counting of characteristic particles of the substance to be determined. This eliminates the usual cell or special micrometer, the problem of measuring the quantity of sample under examination is very greatly simplified, and the method as a whole constitutes a highly valuable contribution to analytical microscopy, both as regards its immediate applications and because its principle is applicable to a wide range of determinations; (for instance, the direct bacterial count of milk.)

Fortunately, a bibliography (mostly of books in English) is provided, and these can be expected to supplement the present volume should the reader desire to specialize in any of the fields suggested. Otherwise he might have a rather unbalanced impression of the scope of the subject, such as would be gained from perusing an analyst's private notebook. Rich in curious items of information and valuable as a record of the experiences of a practiced worker, it would hardly serve as a systematic and really adequate treatise on so inclusive a field, although the fascinating glimpses of the problems which present themselves would justify its being read by even the layman. *C. W. Mason*

PLASTICITY*

BY EUGENE C. BINGHAM

The term *plastic* is much more familiar in our language than many scientific terms, such for example as the term *viscous*. It seems to have long been recognized that plasticity is exclusively a property of solids and that it is complex in character; i. e. a substance is plastic which not only can be readily molded or deformed under pressure or more exactly under shearing stress, but also will hold its shape when the shearing stress is removed. Clay has been conceived to be the plastic substance *par excellence* because it is easily shaped in the hands of the potter and once given an exact shape retains it. Butter would seem to offer an equally good example. This behavior is in sharp contrast to that of pitch which flies to pieces when one tries to deform it quickly and when given an exact shape will not hold it permanently unless constrained.

Our discussion of plasticity therefore concerns itself with the flow of solids, which is certainly broad enough to suit the most catholic taste, for the Greek philosopher Heraklitus was literally correct when he said that "*Everything flows*". It is therefore necessary to limit our discussion by excluding the flow of those things which we are accustomed to refer to as fluids, the pure liquids and gases. But the circle of our lives is not concerned principally with the fluids even air and water but with plastic materials. Our very bodies, the foods we eat, and the materials which we fashion in our industries are largely plastic solids. It may not be obvious at once that all of these are plastic or that a knowledge of the laws of plastic flow will enable man to fashion and use matter more intelligently. Most products are soft at some stage of manufacture or use or have a definite tensile strength and if this strength is exceeded the materials will bend or break. Why say that a knowledge of the laws of plastic flow will enable us to manufacture better articles and more economically? The statement may be true but it is unscientific. Let us put it this way. Investigation leads us to the belief that plasticity is made up of two fundamental properties which have been named *yield value* and *mobility*, the former being dependent upon the shearing stress required to start the deformation and the mobility being proportional to the rate of deformation after the yield value has been exceeded. Although the conception of plasticity is as old as language itself, it must be kept in mind that plasticity has never been measured until recently, due to the property being complex. If time proves the above reasoning to be correct, we have now available two *fundamental* properties of matter which can be measured. Given two new fundamental properties of matter, what need is there to ask whether a consideration of these properties may be of importance to science or industry?

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* Introduction to Plasticity Symposium, Lafayette College, Oct. 17 (1924).

One might amuse one's self by making a list of those fields of industry or science in which plastic flow plays a part and it might prove suggestive. It would include a consideration of suspensions and emulsions with smokes, films and foams, etc., constituting practically all that we denominate under the head of Colloid Chemistry. Under what we may call *non-polar colloids*, it would include paint, lime and plaster, fondant, clay, enamels, dyes, carbon black, asphalt and other bituminous products, metals and alloys, slags, cements, and rocks deep in the earth's crust. Under *polar colloids* it might include starch, cellulose, nitrocellulose, cellulose esters, viscose, plastics and condensation products, soaps, fats and greases, rubber, gelatine and glue, leather, gluten and flour, chocolate, chewing gum, blood and albumen. For good measure we may add that lubricating oils, glass, varnish, dental impression compounds are not yet excluded, since they are not always viscous liquids.

From one point of view this classification by industries is unsatisfactory since it might lead to emphasis being placed on dissimilarities. On the contrary it is hoped that this Symposium will bring about exactly the opposite result and prove that the problems of widely diverse industries and workers are essentially the same. By establishing a clearing house of the information which we already have, it may be found possible to devise better plans for further attack and to conserve effort.

More useful than the classification by industries is the one according to properties. There are many properties of materials which depend upon plasticity and they have never been sharply defined and measured due to the lack of any method for measuring plasticity itself. It may be stated with some emphasis that this state of things is not due to the properties in question being unimportant. The terms *hardness*, *tensile strength*, *ductility*, *toughness*, *malleability* and *elasticity* are of the utmost importance in the whole field of metallurgy. Plastic flow plays a rôle in connection with each of these properties. *Consistency* is a term used in connection with clay, lime, greases, cement, etc. To be sure we speak of a substance having the consistency of butter as if consistency was a well-defined quantity, but the consistency of butter varies enormously with the temperature. When a vegetable oil is hydrogenated to resemble lard is it the yield value that is important or the mobility or must both properties accord with those as found in lard? What is meant by painting consistency and trowel consistency?

Length and shortness are another pair of important properties in plastic flow which we recognize in connection with glue, rubber, paint, steel, as well as the dough of the baker. It seems probable that substances with a high yield value and high mobility are always short, while substances with a very low yield value and very low mobility are long. It is possible therefore that the measurement of plasticity of a substance will enable one to determine the length or shortness of a material.

The flow of plastic substances has proved most tantalizing for whereas the flow seemed to be very characteristic, the viscosity as measured by the standard methods was found to vary widely with the shearing stress. Such inexplicable behavior made the viscosity valueless; but by using the plasticity, the anomaly is explained and progress seems possible.

Mixtures do not generally have a definite melting point but a melting range through which the material is plastic. There may be a eutectic temperature and a temperature of complete fusion. When the melt is very viscous as is the case in many industrially important substances such as asphalt, pitch, paraffin, fats, the standard methods for obtaining melting points are highly inaccurate due to overheating or undercooling, even when the methods give reproducible results. Experiments indicate that this difficulty can be obviated by keeping the material at a constant temperature for a long time and determining its plasticity. The temperature at which the yield value just became zero would be the temperature of complete fusion. At present the method is a tedious one but it can doubtless be improved.

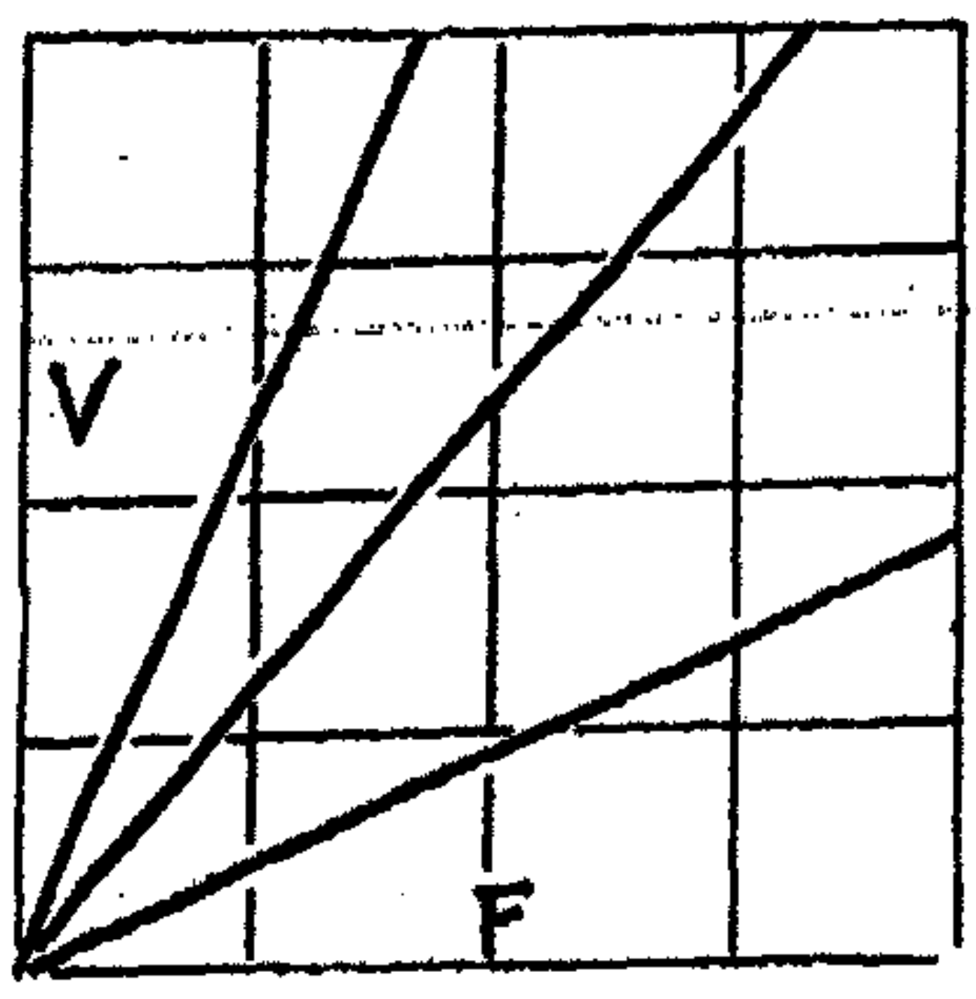

Fig. 1

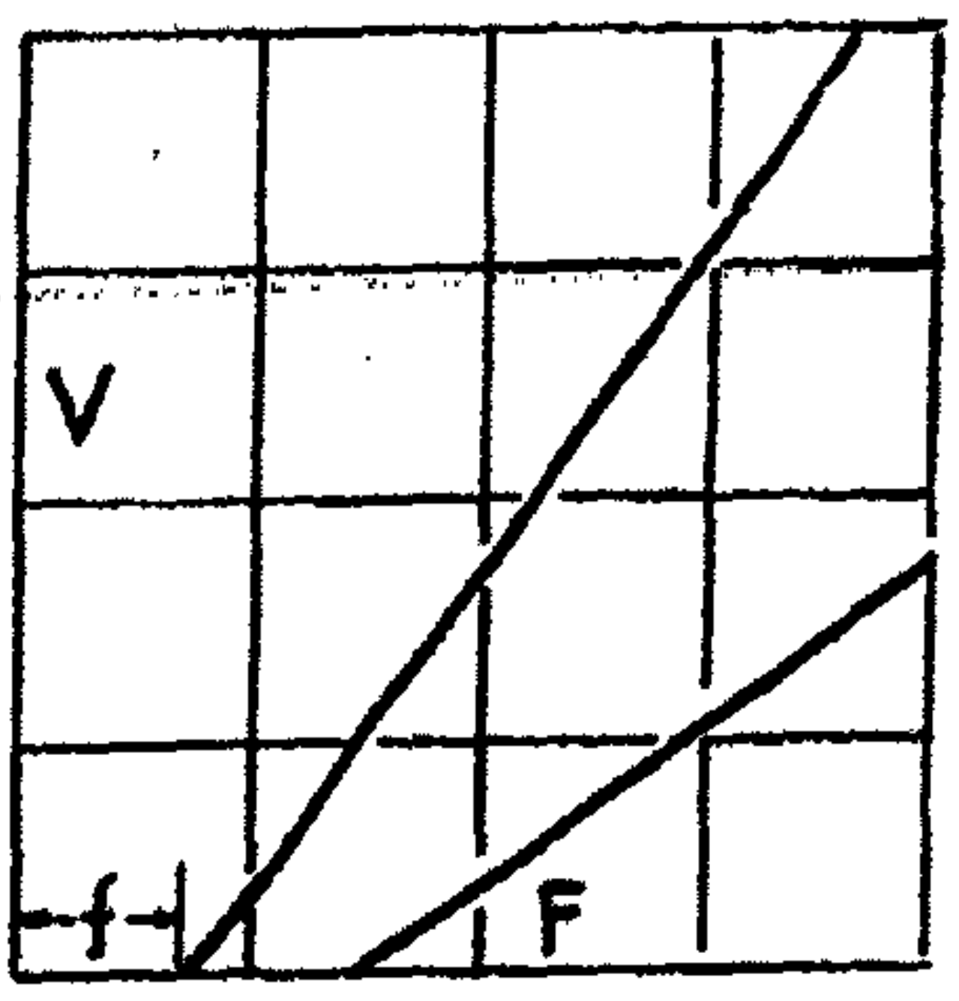

Fig. 2

Solubility in colloids is not true solubility and cannot be measured by the standard methods. It is connected with the plasticity but it is perhaps too soon to say just how. When a given concentration of two substances A and B are peptized in the same solvent, it is probable that the less soluble one is the one which displays the greater yield value. If this proves to be the case, it will become possible to measure solubility in colloids with precision just as we do in classical chemistry.

Finally as a basis for our discussion of plasticity, we may consider methods of measurement with the mathematical theory of plastic flow in different kinds of material. We have no reason to assume that the flow in a polar colloid follows the same laws as in colloids of the non-polar type. Similarly flow along the slip planes of a pure crystal offers new and interesting conditions. We must consider also the effects of temperature, concentration, H-ion concentration, deflocculating agents etc.

We are quite well agreed on the fundamental Law of Poiseuille for viscous fluids, derived from the simple expression

$$v = \Phi F r$$

where v is the velocity given to a surface by a shearing stress F, the surface being at a distance r from another surface considered at rest, the space between being filled with the viscous fluid. The constant Φ represents the fluidity. This formula gives a family of linear curves which all start from the origin as shown in Fig. 1.

For plastic substances the formula

$$v = \mu (F-f) r$$

has been proposed where μ is the mobility and F the yield value. It gives the curves shown in Fig. 2 and accords with our knowledge that soft solids hold their shape unchanged under small shearing stresses. Just as correction terms for kinetic energy etc., were required to be worked out for the Law of Poiseuille so we may assume that correction terms may have to be developed in connection with the above formula for plastic flow. It has been suggested that corrections for seepage and slippage may be required.

In polar colloids there is a breaking down of the filaments or structure during the process of flow which does not seem to resemble what takes place in the flow of a suspension. The curve obtained is also very different, as shown in Fig. 3. The yield value seems to depend upon the magnitude of the shearing stress, the substance appearing to be very viscous at very low shearing stresses but quite fluid at high shearing stresses. Moreover the yield value appears to depend upon the radius of the capillary used in measuring the flow. This seems to make necessary the addition of some new variable which is dependent upon the strength of the filaments.

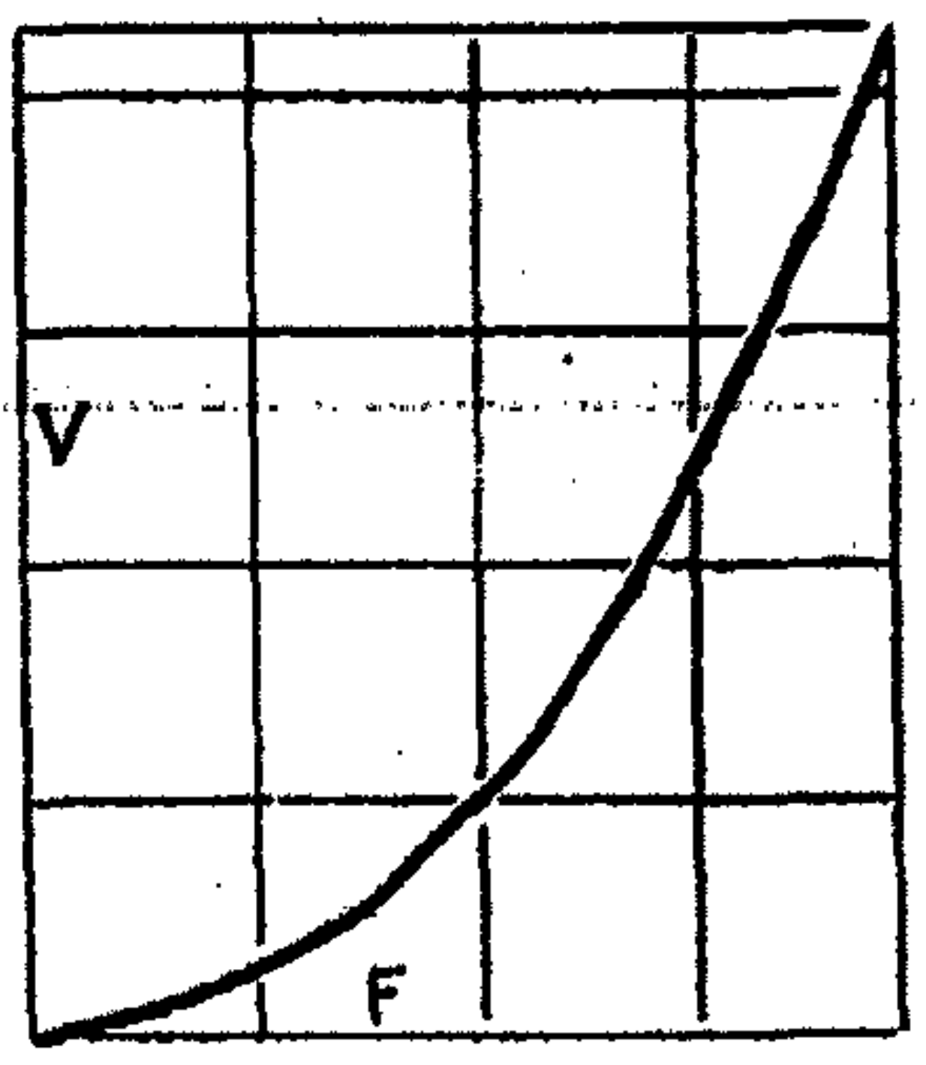

Fig. 3

Finally it is noted that elastic deformation follows a law analogous to the above,

$$s = e F r$$

where s is the distance sheared by the shearing stress F. It is particularly emphasized that elasticity is not dependent on the time factor as is true of viscous and plastic flow since $v = s/t$. Elasticity is a property which is entirely independent of plasticity and it may therefore be separately determined. This conception was not gained by the early elasticians and resulted in much confusion which still persists. It is for example quite possible to conceive of a fluid which possesses high elasticity of shape. Glass is perhaps the best example.

In the consideration of these matters here outlined the time at our disposal and much more may be profitably employed.

EMULSION FILMS[1]

BY HARRY N. HOLMES

It is a simple matter to emulsify two "immiscible" liquids by mechanical agitation but it is not so easy to prevent later coalescence of the dispersed drops. Increase in viscosity of either liquid but more particularly of the continuous phase naturally makes coalescence slower.

Quincke[2], Hillyer[3], and Donnan and Potts[4] held that lowering of interfacial tension between the two liquids was a very important factor in stabilizing emulsions. No two pure liquids yield stable emulsions except, possibly, when the volume concentration of the dispersed phase is around one percent. A third substance, usually but not always colloidal, must be present to act as an emulsifying agent. It may function by lowering interfacial tension, by affecting viscosity or by forming films around the drops. Soaps and proteins are notable among the many emulsifying agents.

The most commonly accepted theory today is the adsorption film theory advocated by Bancroft.[5]. It is held by many that, since any substance that lowers surface tension must concentrate at surfaces (Gibbs theory), colloidal films at interfaces between two liquids could thus be accounted for. Bancroft considers it sufficient to state that many substances may be adsorbed at the liquid-liquid interface and may there form coherent emulsifying films.

The existence of such films has been demonstrated by comparison of the concentration of the emulsifying agent in the impoverished liquid below (or above) the cream with that of the original continuous phase. Briggs[6] observed a removal of soap by the cream from an emulsion. Holmes and Cameron[7] found that the cream in an emulsion of glycerol in acetone removed distinct amounts of cellulose nitrate (the emulsifying agent) from the acetone layer. Recently Holmes and Williams[8] proved clearly that the cream in an emulsion of wet ether in ethereal water removed iodine (the emulsifying agent) from the continuous phase. Ramsden[9] produced visible films upon shaking oils with certain water solutions such as saponin and the proteins. Holmes and Cameron[10] saw tough elastic films of cellulose nitrate around drops of water in a mixture of amyl acetate and benzene (using cellulose nitrate as the emulsifying agent). I have observed instant formation of

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[1] Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1924).

[2] Quincke: Wied. Ann. 35. 589, (1888).

[3] Hillyer: J. Am. Chem. Soc., 25, 513 (1903).

[4] Donnan and Potts: Kolloid-Z. 4, 208 (1910).

[5] Bancroft: J. Phys. Chem. 17, 514 (1913); 19, 275 (1915).

[6] Briggs: J. Phys. Chem. 19, 210 (1915).

[7] Holmes and Cameron: J. Am. Chem. Soc., 44, 66 (1922).

[8] Holmes and Williams: Paper read at Northwestern University, Second National Colloid Symposium, June, (1924). "Second Colloid Symposium Monograph," 135 (1925); J. Am. Chem. Soc. 47, 323 (1925).

[9] Ramsden: Proc. Roy. Soc. 72A, 156 (1903).

[10] Holmes and Cameron: Loc. cit.

a visible film around a large drop of water placed in a benzene solution of gum dammar.

M. H. Fischer[1] holds that emulsifying agents function because they are solvated; that when we use more water, for example, than an alkaline soap can "bind" the emulsion is poor. It seems probable that an adsorption film of soap is formed and that an equilibrium is reached between film formation and peptization of film by water. With too much water peptization is increased at the expense of film formation. Bancroft stated that the less well peptized by one of the liquids the better the film.

Briggs[2] insists that if the emulsifying agent is peptized too well by the continuous phase the adsorption film will not be formed; consequently addition of a mild flocculating agent may be helpful in some instances. Thus a one percent solution of hydrous ferric oxide was found to be a poor emulsifying agent while addition of one gram of pure sodium chloride to 40 cc. of this solution made possible a coarse dispersion of 10 cc. of benzene in the solution. A higher concentration of salt increased the stability of the emulsion. Sodium sulfate, however, was too strong a coagulant, precipitating the ferric hydroxide in coarse flocks.

Ramsden's comment that the "persistence of many emulsions is determined largely, among other factors, by the presence of solid or highly viscous matter at the interfaces of the two liquids" agrees with R. E. Wilson's belief that emulsion films are really plastic solids. The efficiency of saponin as an emulsifying agent would seem to support this belief. Saponin lowers the surface tension of water only moderately and yet it forms excellent froth films and emulsion films as well.

Pickering[3] prepared very good emulsions of oil-in-water by the use of finely divided basic ferrous sulfate, freshly precipatated, as emulsifying agent. This is startling because any films surrounding the oil drops were composed of small discrete solid particles.

It is well known that a water-soluble emulsifying agent opposes the action of an oil-soluble agent. In the right proportion of the two no emulsion results. Newman, however, prepared a 96 percent emulsion of water-in-oil using magnesium oleate in the oil and sodium oleate in the water. He took pains to use much less sodium oleate than the amount needed to nullify the effect of the magnesium oleate. Consequently he had a double interfacial film, one face being sodium oleate and the other magnesium oleate. Such composite films merit further study.

The question of a wedge shape of soap molecules in determining curvature of the film and hence the type of emulsion has been discussed by Harkins[4] and by Hildebrand[5] but it is difficult to apply their theories to the Pickering

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[1] Fischer and Hooker: "Fats and Fatty Degeneration," (1917).

[2] Briggs: J. Ind. Eng. Chem. 13, 1008 (1921).

[3] Pickering: J. Chem. Soc. 91, 2001 (1907).

[4] Harkins, Davies and Clark: J. Am. Chem. Soc., 39, 354, 541 (1917).

[5] Hildebrand, Draper and Finkle: "Colloid Symposium Monograph," 196 (1923).

type of film. Perhaps in the case of fine powders or precipitates the films of oil *between* solid particles lying in oil are thicker (or thinner, as the case may be) than are the films of water between solid particles lying in the water.

Polar Films

The conception of definite orientation of molecules at surfaces of liquids was first offered by W. B. Hardy in 1912. Langmuir[1] later suggested that in a layer of fatty acid floating on water the -COOH groups strike into the water. Harkins, Davies and Clark believed that at the interface between water and a liquid hydrocarbon molecules of an added polar substance (such as R.COOH) would tend to orient themselves so as to throw the -COOH (or other polar group) into the water and the non-polar hydrocarbon radical into the non-polar benzene. Harkins and his associates were convinced that the best emulsifying agents were made up of long polar molecules.

Hildebrand prepared an emulsion of benzene in water using oleic acid as the emulsifying agent as did Whitby. No particular experimental study, however, was made of emulsifying agents in *true solution* in the liquids emulsified. In fact the general impression has been that emulsifying agents must be in colloidal dispersion with the exception of the fine-grained precipitates used by Pickering. Briggs stated that "in every case investigation has shown that the apparently soluble emulsifier is in colloidal suspension in the outside phase of the emulsion."

Holmes and H. A. Williams[2] investigated the clasess of polar emulsifying agents not commonly supposed to be colloidally aggregated in the liquids used.

The Alcohols.—Benzene was emulsified in water by the use of methyl or ethyl alcohol as emulsifying agent. Propyl alcohol was inferior and the butyl alcohols poor. In fact the higher alcohols were useless as emulsifying agents. Glycol, glycerol and the sugers had no noticeable value yet allyl alcohol showed a pronounced effect, not equal, however, to that of ethyl alcohol. Phenol and resorcinol showed distinct power to emulsify benzene in water but the naphthols did not. Nor did benzyl alcohol.

They found it advisable to clean the bottles with unusual care. After dissolving 2 cc. of methyl alcohol in 10 cc. of water they could add in small portions, with vigorous hand shaking, 10 cc. of benzene and secure a very good emulsion, stable for a week or more. Apparently the CH_3-group of the alcohol is attracted and pulled into the non-polar benzene while the -OH group is pulled into the polar water. Of course alcohol dissolves in both liquids but at the interface a monomolecular layer of alcohol must be held by the opposing attractions in such a way as to form a real film. In the lower alcohols the balance between the CH_3– or C_2H_5– and -OH radicals must be such as to give the optimum effect.

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[1] Langmuir: Chem. Met. Eng. **15**, 468 (1916), J. Am. Chem. Soc. **39**, 1848 (1917).

[2] Holmes and Williams: Paper read at Northwestern University, Second National Colloid Symposium, June, 1924; Second Colloid Symposium Monograph, 138 (1925).

The Acids.—Since it was already known that fatty acids could act as emulsifying agents it remained only to learn just where in the fatty acid series this property begins. Stearic, palmitic, oleic, linoleic and linolenic acids were found to be very efficient but acids below caprylic in the series were of no use. The sulfonic acids, such as β-naphthalene sulfonic, showed distinct but not unusual emulsifying power. It is interesting here to note that the sodium salt of the latter acid is far superior to the free acid.

Since oleic acid, for example, is insoluble in water it is evident that an interfacial film must form as a result of the $-COOH$ groups sticking into the polar water. The hydrocarbon chain is attracted by the non-polar benzene.

The Esters, Aldehydes, Ketones and Nitriles.—Neutral fats showed noticeable ability to act as emulsifying agents for the benzene-water system but they were quite inferior to rancid fats. Of course the $-COOH$ group of an ester with a hydrocarbon radical introduced must be less polar than the $-COOH$ group of a free fatty acid.

The aldehydes showed very little value as aids to emulsification but benzonitrile compared rather well with some of the best polar agents. Nitro and amino compounds had little if any effect nor did the ketones.

Interfacial Tension.—Oleic acid does not lower the surface tension (against air) of benzene but it does sharply lower the interfacial tension of benzene-water. The formation of a film in this instance would follow the Gibbs theory.

It is unsafe to assume that any substance soluble in both benzene and water and causing at least a distinct lowering of interfacial tension will act as a good emulsifying agent. Acetone is soluble in both of these liquids and shows no emulsifying power. Nor does methyl-ethyl ketone. We need the pull from both liquids to hold, more or less firmly, an interfacial film of a polar substance. Acetone is not very polar while methyl alcohol is.

Molecular Association.—It has been objected that "polar" emulsifying agents might not really be in true solution but might be highly polymerized in one of the liquids. It is quite true that ethyl alcohol, for instance, is somewhat associated in such non-polar solvents as benzene but the freezing point lowering in solutions of the concentration used indicated molecular weights of less than 200 hence the aggregates contain only four or five molecules, very far from colloidal dimensions. In water the alcohol is not associated at all. Even the higher fatty acids in benzene show a rather small degree of association. It is difficult to explain film formation as due to such small aggregates when sugar with a molecular weight of 343 in water has almost no emulsifying power.

Furthermore if the effect in film formation is due to aggregation of alcohol in the benzene, water should be the dispersed phase according to the well-known rule. In reality it is the benzene that is dispersed in drops.

The fact that addition of alcohol makes it possible to emulsify Nujol in water although alcohol is not soluble in Nujol and is in true solution in water apparently forces us to the polar explanation.

Further Observations.—Gum dammar shows remarkable power to emulsify water-in-oil and yet it does not lower the surface tension of benzene and similar liquids against air. In fact freezing point measurements show it to be in true solution in benzene. Probably dammar is sufficiently polar to function as an emulsifying agent.

Gum dammar[1] has important commercial possibilities as an emulsifying agent for the water-in-oil type of emulsions. It resembles lanolin in this respect but lanolin is very sticky and has an unpleasant odor. By adding a benzene solution of dammar to printers ink or lithograph ink a relatively large amount of water can be incorporated without decreasing the viscosity of the ink. More drying oils are used in the best inks than is necessary to make the pigment stick to the paper. This excess is used to secure a "body" suitable for working on the press. Emulsification of water in the ink maintains this desired body at lower coast. The water evaporates through the oil films on the paper. Dammar permits emulsification of water, alcohol or glycerol in petrolatum. Since these liquids may carry iodine or other medicinals there is at hand a superior method of making certain medicated salves and ointments. Color screens superior to the starch grain type can readily be prepared using dammar as an emulsifying agent. In using dammar it is usually better to mix by rubbing rather than by shaking.

The proteins and soaps are polar and in addition their molecules form large colloidal aggregates hence the greater strength of their films in emulsions. There is really a great difference in the emulsifying powers of the soaps and of the lower alcohols but the important point is that certain substances in true solution do form distinct emulsion films.

Viscosity of Emulsions

It has long been known that the viscosity of an emulsion increases with the volume concentration of the dispersed phase. When drops of uniform size occupy 74 percent of the total volume the drops touch each other. Naturally there must be a great increase of viscosity at this point. With increasing volume of the dispersed phase the drops must flatten and squeeze the continuous phase into thin films. The classic experiment of Pickering in preparing a 99 percent oil-in-water emulsion is often cited. This emulsion stood up like a blanc-mange.

One may readily determine the type of a rich emulsion by observing viscosity changes as more oil is beaten in or as more water is incorporated. Obviously if water is the continuous phase addition of more water must lower viscosity. If oil is the dispersed phase addition of more oil must increase viscosity.

The network or honeycomb structure of emulsion films has a profound influence on viscosity of the system. In fact Holmes and Cameron[2] in making "chromatic" emulsions were able, by addition of benzene to the contin-

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[1] United States Pat. 1, 429, 430, Sept. 19, 1922.

[2] Holmes and Cameron: J. Am. Chem. Soc. 44, 71 (1922).

uous phase of amyl acetate, to force formation of emulsion films of cellulose nitrate so substantial that the cream would stand up on a plate and quiver like a good fruit jelly. Homogenization, as Wiegner[1] pointed out, greatly increases viscosity by increasing the area of interface. A 10 percent fat ice-cream that has been homogenized in the making tastes as "smooth" as a non-homogenized 15 percent fat ice-cream.

Since the nature of emulsion film has much to do with viscosity it is evident that mathematical deductions on the basis of concentration of dispersed phase must be modified to suit the emulsifying agent. Viscosity may even change with age as in the case of gelatin films which develop structure on standing. In the preparation of emulsions viscosity may help or hinder. The pharmacist pours some oil on gum acacia (powdered), grinds to a viscous mud and then works in water and oil alternately. Unless he gets a viscous nucleus to start with he has poor success. And in preparing mayonnaise it is easier to incorporate oil after a viscous mass has been secured than it is right at the start. When neither liquid is very viscous shaking or beating methods are superior to rubbing. Holmes and Child[2] found that a 0.4 percent solution of gelatin in water was more favorable in the emulsification of kerosene than a higher viscosity. They used the shaking method and found that more viscous gelatin-water simply did not splash so well with the kerosene. Once such an emulsion was well made a higher viscosity, if it could then be secured, must retard coalescence of drops. The problem is to make the emulsion in the first place as well as to keep it. With other methods of agitation a different concentration of gelatin might be desirable.

Where the continuous phase is a plastic solid, as in butter and in margarine, the emulsion is plastic. There is much yet to be learned about viscous and plastic emulsions.

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[1] Wiegner: Kolloid-Z. **15**, 1105 (1914).

[2] Holmes and Child: J. Am. Chem. Soc. **42**, 2049 (1020).

PLASTICITY OF SINGLE CRYSTALS[1]

BY WHEELER P. DAVEY

Plasticity, as applied to single crystals has to do with the slipping of planes of atoms upon adjacent planes. It is related to ductility, for in order to be ductile, a substance must be plastic in addition to having sufficient strength to keep it from breaking from the strain of pulling it through a die. The following discussion is strictly limited to the plasticity of single crystals, thus avoiding those complications incident to grain size which make the properties of polycrystalline materials so often different from those of the corresponding single crystals.

The results of experiment may be generalized by the statement that the plastic, ductile, and malleable metals such as copper, silver, gold aluminum, etc., have face-centered cubic structures, and that the metals which are relatively non-plastic, such as chromium and tungsten, have body-centered cubic structures. This rule is not, however, of universal application, for iron is reasonably plastic and has a body-centered cubic structure. The reason for this exception is not known,—it may be caused by some peculiar configuration of the valence electrons of iron. Single crystals of metals, such as zinc, which are ductile in the cold only in certain directions through the crystal, have a "hexagonal close-packed" structure.

The work of Mark, Polyani and Schmid[2] and others makes it appear that, other experimental conditions being strictly the same, mechanical working of the metal causes slip along those planes in the crystal which have the maximum atomic population. It is a characteristic of the geometry of crystal structure that the planes of maximum atomic population are those which are furthest apart from each other. This means not only that the atoms in an individual plane are packed so closely together that they can hold to each other quite strongly, so that these individual planes of atoms are quite strong, but also that, because of the distance from any one of these planes to its nearest similar plane, the interlocking of atoms from plane to plane is relatively weak, so that each plane can glide over its neighbor.

In the face-centered cube, the 111 (octahedral) planes are those of greatest atomic population. There are four families of 111 planes symmetrically placed about 70.5 degrees from each other. Each atom is symmetrically placed with respect to six other atoms in adjacent 111 planes, for there are three atoms which form an equilateral triangle in the plane immediately above, and three which form an equilateral triangle in the plane immediately below. This means that each atom is directly below the center of a triangle of atoms of the 111 plane next above it and is directly above the center of a

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[1] Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1924).

[2] Z. Physik, 12, 58 (1922).

triangle of atoms of the 111 plane next below it. This close packing prevents loss of cohesion during slip. The 100 planes have nearly as large an atomic population and are, therefore, almost as far apart from each other as the 111 planes. There are three families of 100 (cube face) planes mutually 90 degrees to each other. Each atom in the 100 plane is equally spaced from four atoms in the adjacent plane below. The face-centered cube is, therefore, well supplied with both primary and secondary slip planes, and since both of these families of planes have high orders of symmetry, a face-centered cube can hardly escape being plastic in almost any orientation.

If the axial ratio of a hexagonal close-packed crystal is greater than 1.735 the 00.1 planes are the planes of greatest atomic population and should, therefore, be the planes of primary slip. This is the case with zinc, whose axial ratio is 1.86. Each atom in an 00.1 plane is equally spaced from three atoms in the two adjacent planes much as in the case of the face-centered cube. But the 00.1 planes are the basal planes of the hexagonal prisms. There is, therefore, only one direction through a zinc crystal which is the optimum direction for mechanical working. The planes of next highest atomic population in zinc are the 10.0 planes. These are the faces of the hexagonal prisms. There are three families of 10.0 planes, all parallel to the z-axis and all 120 degrees from each other. The atomic arrangement is not as favorable to slip without loss of cohesion as in the case of the 00.1 planes, for a given atom is equally spaced between four atoms in the adjacent on one side of it, and between only two atoms in the adjacent plane on the other side of it. There will be, therefore, greater loss in cohesion during slip along the 10.0 planes of zinc. We should expect that, contrary to the common opinion, slip along the 10.0 planes of zinc will show different characteristics from slip along the 00.1 planes. Instead of nearly every plane sliding over its neighbors we should expect the 10.0 planes to slip in blocks. If a single crystal of zinc is stretched beyond its elastic limit we should expect the etch figures to show block-slip along the 10.0 planes to a very much greater extent than along the 00.1 planes. In a private communication some time ago to Dr. S. L. Hoyt of this laboratory, O. E. Romig reported that he has found this to be actually the case. It is a pleasure to acknowledge Mr. Romig's permission to mention his experimental results which coincide so well with the theoretical deductions.

If the axial ratio of a hexagonal close-packed crystal is less than 1.735 (as is the case with magnesium) the atomic population of the 10.0 planes will be higher than that of the 00.1 planes. Primary slip will, therefore, occur along the 10.0 planes. Since there are three families of 10.0 planes polycrystalline magnesium should be a little more plastic than zinc. Because of the unfavorable arrangement of atoms in the 10.0 planes of the hexagonal close-packed lattice, and since it has only three families of planes for primary slip and one for secondary slip, magnesium should be much less plastic than face-centered cubic metals like copper or aluminum, which have a favorable arrangement of atoms, and four families of planes for primary slip, and three for secondary slip. These conclusions are in accord with the results of practical experience.

In this connection cobalt is of peculiar interest. Pure cobalt is of only moderate ductility, and therefore of only moderate plasticity, while cobalt containing traces of impurities is fairly ductile. Hull[1] showed that pure cobalt may contain some face-centered cubic crystals, but that it usually crystallizes in a hexagonal close-packed lattice. Traces of impurities always make cobalt take the face-centered cubic structure, thus giving a rational explanation of the ductility of impure cobalt.

A consideration of the body-centered cubic lattice shows it to be an inherently non-plastic structure. The planes of highest atomic population, and, therefore, those which are furthest apart, are the 110 planes. The atomic arrangement is such that each atom in a 110 plane is equally spaced from two atoms in the adjacent plane above it and from two other atoms in the adjacent plane below it. This means that slip along the 110 planes is necessarily accompanied by very great loss in cohesion. The crystal will tend to crack during mechanical working. The planes of next highest atomic population are the 100 planes. The atomic arrangement is here more favorable to slip, for each atom is equally spaced between four atoms on each side of it, but it is of little use to have planes of secondary slip with good cohesion if cracking occurs along the planes of primary slip. The outstanding exception to all this is iron. Iron is body-centered cubic, and yet it is reasonably ductile. But this is not the only way in which iron is an exceptional metal. Its magnetic properties are such as to give rise to the term "ferro-magnetic." It is the only known metal which, when sufficiently heated, changes from a body-centered to a face-centered cubic lattice. It is quite likely that the exceptional behavior of iron during mechanical working is tied up in some way with the underlying causes of its other exceptional properties.

Substances which crystallize with a simple cubic structure have practically no plasticity. An example of this sort of structure is ordinary NaCl. The rhombohedron of calcite has the same sort of structure except that the "cube" is deformed in the direction of its body-diagonal. In the simple cubic crystal the 100 plane (cube face) is the plane of highest atomic population, and is therefore the plane of primary slip. In these planes, each atom can only hold to one atom in the plane above it and one in the plane below it. The 110 plane (the dodecahedral plane) is the plane of second highest atomic population. Here too, each atom can only hold to one atom above and one below. The simple cubic structure, therefore, tends to crack apart upon the application of very small forces,—it is the least plastic of all the structures we have considered. It is said that the only way a sodium chloride crystal can be deformed at room temperature is to bend it while it is immersed in fresh water. Then if the bending is done so slowly that the rate of propaga-

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[1] Phys. Rev. (2) 17, 571 (1921).

tion of the cracks is less than the rate of solution in the water, the crystals may be successfully bent.

It would seem from the above that the plasticity of single crystals is intimately connected with the marshalling of their atoms in space, and that, in general, the relative plasticities of two crystals may be predicted from a consideration of their crystal structure.

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THE PLASTICITY OF CLAY[1]

BY WILDER D. BANCROFT AND L. E. JENKS

A plastic substance is one that can be moulded under a finite pressure. This connotes that any break due to the deformation is self-healing. A mobile liquid is not plastic because it will not retain its shape. With increasing viscosity, a liquid or a suspension passes through the point of zero fluidity and there is a change, as Bingham has shown, from viscous to plastic flow. Molasses candy is plastic until it crystallizes. Glass becomes plastic when heated to a suitable temperature. These are cases of plastic liquids. Crystalline solids may become plastic under suitable conditions. Metals are squirted into rods or pipes because they are plastic under high pressures. The flow of a glacier is due, at least in part, to the plasticity developed in ice under high pressures.

Between the extreme cases of a solid such as a metal and a liquid such as glass or molasses candy, we have the intermediate case of putty, which is a mixture of whiting and oil, a solid with a liquid film round it. If a liquid is adsorbed strongly by a solid, thin films of the liquid will hold the solid particles together, while still permitting them to move relatively to one another. The tendency of the liquid surfaces to coalesce causes any break to heal at once. A liquid film will therefore act as a bond for solids and may make the mass plastic. One kind of oil is used as a binder in roads and another to make putty out of calcium carbonate. Everybody knows that dry sand cannot be moulded whereas wet sand can.

The clay workers use the word plasticity in a special sense to denote that a clay is plastic and that it will burn to a coherent mass. From this point of view a metal is not plastic, because it melts when heated; and wet sand is not plastic, because it falls to pieces when dried. Clay particles must therefore have on the surfaces some form of gelatinous material which burns to a solid bond. Since clay is essentially a hydrous aluminum silicate, so-called, the gelatinous material must be essentially hydrous alumina, hydrous silica, or some intermediate composition. The difficulty is that neither hydrous alumina, hydrous silica, nor any mixture of them will take up water again to form a satisfactory gelatinous mass after having been dried out pretty thoroughly in a hot sun. If we designate our gelatinous material as a so-called hydrous aluminum silicate with hydrous alumina and hydrous silica as the two possible end terms, there must be present some other substance or substances which keep the so-called aluminum silicate from losing its plasticity when dried in the sun. The two possible things to consider are electrolytes and organic matter to which we will give the general name of humus.

The problem that Mr. Jenks set himself was to find out whether any electrolyte would make and keep a non-plastic clay plastic when added in

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[1] Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1924).

moderate amounts. Before starting on this it was necessary to have some test for plasticity. A modification of Sokolow's method was used. A weighed amount of clay was moulded to a ball with the optimum quantity of water, dried at 110° and placed in a beaker of water. The longer the time before the clay ball disintegrates, the more plastic the clay. Of course this process does not measure plasticity but it apparently measures something which runs parallel with plasticity because it was possible, in this way, to arrange a number of clays in the exact order in which the clay workers arrange them.

As a non-plastic clay, we used kaolin furnished by the Norton Company. It was found that addition of about a quarter of one percent of a lithium salt, usually lithium chloride, together with a little sodium chloride, gave kaolin a very high plasticity as measured by this method, higher than that of the most plastic ball clay tested. No burning experiments were made, so that we do not know what effect lithium salts have on the burning properties.

It was hoped at first that the problem of the plasticity of clay had been solved; but this proved not to be the case. Experiments by Dr. Papish showed no connection between the lithium contents of the different clays and the plasticities. Special experiments showed that lithium chloride kept alumina gelatinous rather than silica, which is a further proof that this is not Nature's way of making a plastic clay, because the lateritic or alumina-rich clays are not plastic as a rule.

It seems certain therefore that we cannot account for the plasticity of ordinary clays without taking humus into account and it is probable that the plasticity of clay will be due to the combined effect of humus and some electrolyte. While our experiments have not yet brought us to the desired goal, it is quite certain that we are on the right track and it is something to have increased the low-temperature plasticity of kaolin so much by such relatively small additions.

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THE OSTWALD VISCOMETER AS A CONSISTOMETER*

BY WINSLOW H. HERSCHEL AND R. BULKLEY

1. Introduction

The Ostwald viscometer, shown in Fig. 1, is the standard instrument of the rubber experimental stations in the Dutch East Indies for determining the consistency (usually called "viscosity") of benzene solutions of crude rubber.[1] As ordinarily used the flow takes place solely under hydrostatic head.

In connection with investigational work of the Crude Rubber Evaluation Committee of the American Chemical Society, it was found that one percent benzene solutions of unmilled, crude rubber are not viscous but plastic[2] so that their consistency must be determined by some type of instrument in which it is possible to make measurements at various average rates of flow. The Ostwald viscometer, as ordinarily used, is not suitable for this purpose unless provided with more than one lower bulb, so that it may be filled to different heights as in the modified form of instrument used by de Jong[3]. It is however possible as will be shown, to use the usual form of Ostwald viscometer with an external source of pressure, as is done with the Bingham viscometer.[4]

At the Bureau of Standards the Bingham viscometer is used for the primary determination of viscosity. However, since the Ostwald viscometer is in general use throughout the rubber industry, and its simpler construction facilitates cleaning, it seemed desirable to investigate the suitability of this latter instrument as a consistometer, i. e., an instrument which may be used to distinguish between a viscous and a plastic material, and to measure the consistency of either. The two instruments of Fig. 1, used in this investigation, were obtained through the kindness of Dr. E. A. van Valkenburg[5] as typical of those used in testing benzene solutions of crude rubber.

2. Methods of determining Mean Effective Heads

With the Bingham viscometer, in which the effect of the hydrostatic head is very small, the times of flow in both directions are used in determining the mean effective, usually called the average pressure. With the Ostwald viscometer where the hydrostatic head is considerable, the assumptions involved

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*Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1924), and published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[1] A. van Rossem: Kolloid-chem. Beihefte, 10, 83 (1918–19)

[2] Winslow H. Herschel: Ind. Eng. Chem., 16, 927 (1924)

[3] H. O. Bungenberg de Jong: Rec. Trav. chim. 42, 1 (1923)

[4] E. C. Bingham: Bureau of Standards Scientific Paper No. 298, p. 64 (1917)

[5] Chief Chemist, Ajax Rubber Co., Trenton, Member Crude Rubber Evaluation Committee.

in this method appear of doubtful validity. The following methods of determining the average head were considered.

1. Applebey[1] determined the variation of pressure and of time with the fall in level of the liquid in the viscometer, and from these data determined the variation of pressure with time, and thus the average pressure during the run.

2. Washburn and Williams[2] took for the average pressure, the pressure at mean time. This method, according to Applebey, is approximately correct. Methods 1 and 2 were rejected as inapplicable to Ostwald instruments with short times of flow.

3. With cylindrical or spherical bulbs, under certain conditions, the average head h may be calculated by equations or more conveniently by Fig. 2. By average head is meant that head which, if maintained constant, would cause the time of flow to be the same as with the variable head actually existing. The lower curve applies to an Ostwald viscometer with two equal cylindrical bulbs, and also to an instrument of the pipette type with one cylindrical bulb. The upper curve may be calculated from formula of Barr[3] for a pipette with spherical bulb, and it applies equally well to an Ostwald viscometer with two equal spherical bulbs, provided the menisci at the start of run are at the top of the upper bulb and at the bottom of the lower. Fig. 2 shows that there is less error in assuming that the average head is equal to the arithmetical mean with spherical than with cylindrical bulbs.

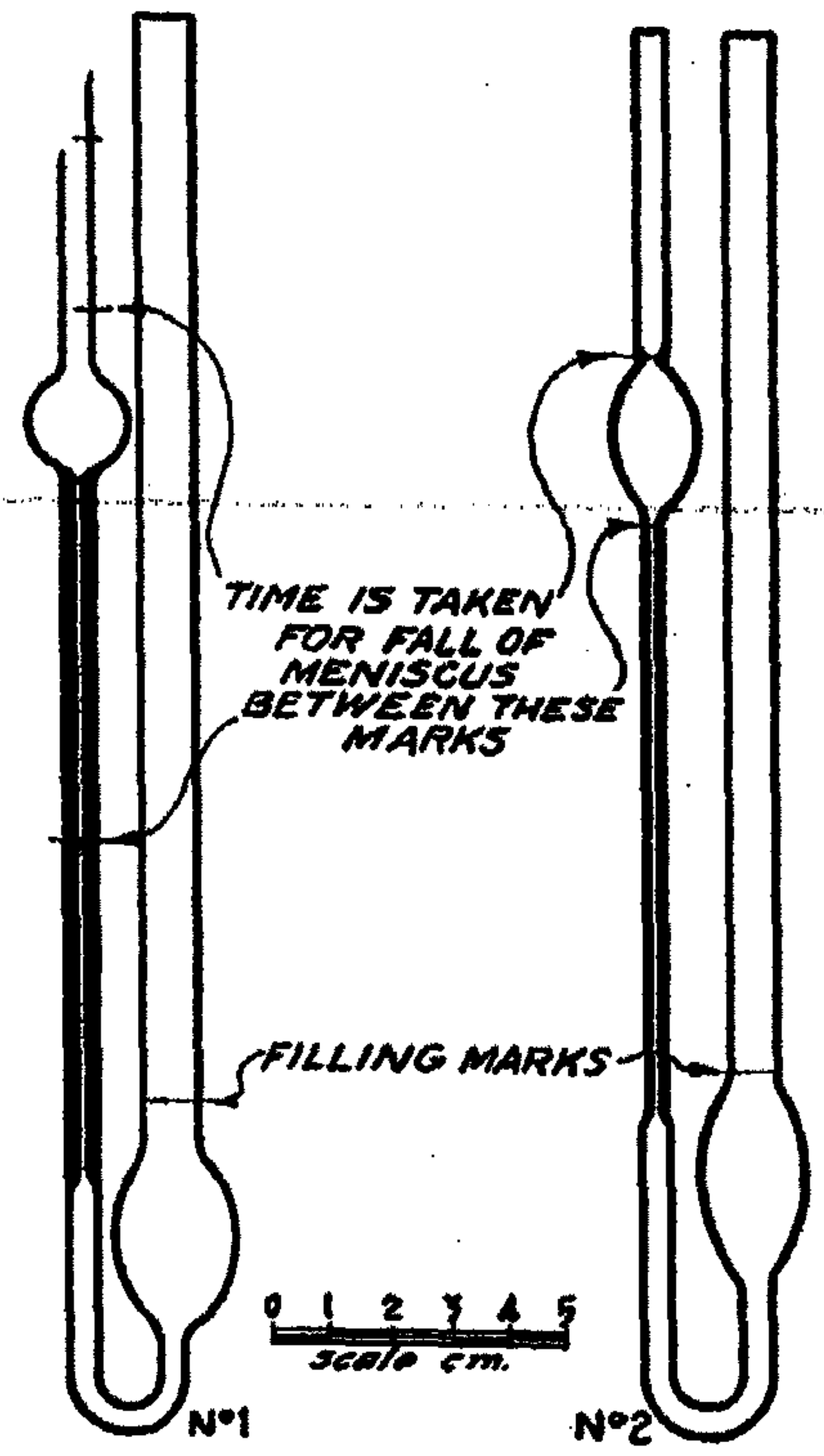

FIG. 1
Ostwald Viscometers

If h_1 is the initial and h_2 is the final head, Barr's equation may be written in the more convenient form,

$$h = \frac{h_1 - h_2}{3\,\frac{h_1 + h_2}{h_1 - h_2} + 6\,\frac{h_1 h_2}{(h_1 - h_2)^2 \log_e \frac{h_2}{h_1}}} \qquad (1)$$

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[1] M. P. Applebey: J. Chem. Soc. 97, 2000 (1910).

[2] E. W. Washburn and G. Y. Williams: J. Am. Chem. Soc., 35, 737 (1913).

[3] G. Barr, J. Soc. Chem. Ind., 43 29T (1924).

which may be compared with the corresponding formula for cylindrical bulbs,

$$h = \frac{h_1 - h_2}{\log_e \frac{h_1}{h_2}} \qquad (2)$$

The attempt was made to apply equation (2) to the instruments of Fig. 1, but it was found that at low pressures more concordant results could be obtained by the simpler equation

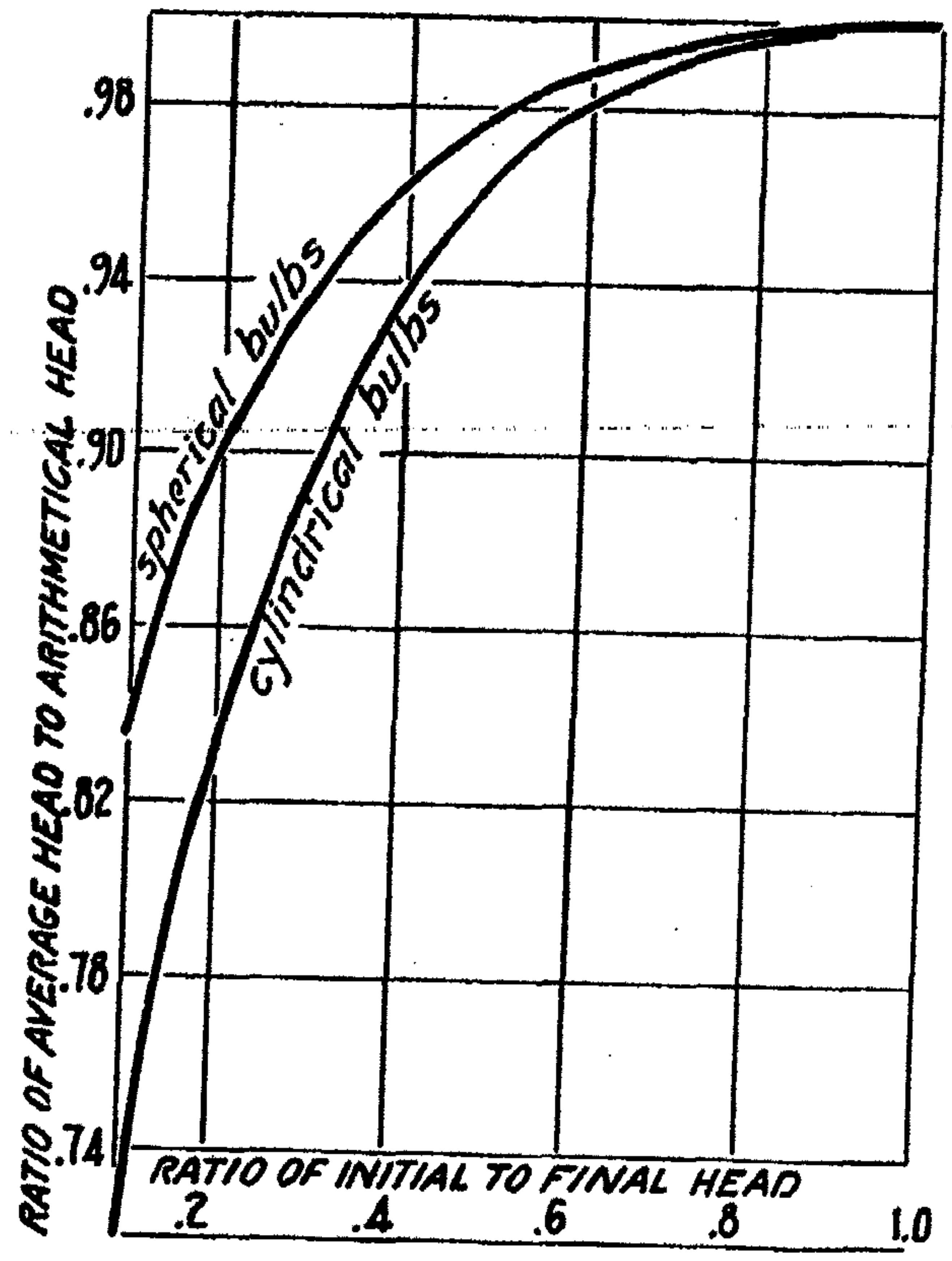

Fig. 2
Relation of Mean Effective Head to Arithmetical Mean Head

$$p = p_m + h_o \rho \qquad (3)$$

where ρ = density of liquid in grams per cc

p_m = external pressure, calculated from manometer reading, in grams per cm^2

h_o = average hydrostatic head in cm

Equation (3) is known to be only approximate when p_m is small. According to Bingham, equation (2) should be used when p_m is less than 30ρ multiplied by the height of bulb.

In the instruments of Fig. 1, the bulbs are unequal and the meniscus is near the center of the lower bulb at the start of a run. Thus since neither equation (1) nor (2) is strictly applicable, it appeared preferable to use the simpler though approximate equation (3).

4. For any given instrument, h_o will be constant, at sufficiently high pressures, no matter what the shape of the bulbs. It can not in general be measured directly on the instrument, but must be considered as an instrumental length which must be determined by flow tests. After h_o has been determined, equation (3) may be used to determine p in the calculation of viscosity.

3. Calibration of Ostwald Viscometers

With efflux viscometers where the driving force is entirely due to hydrostatic head, the relation between viscosity and time of flow is given by the equation

$$\mu = \rho\,(At - \frac{B}{t}) \qquad (4)$$

where μ = viscosity in poises
ρ = density in grams per cc
t = time of flow, in seconds
A and B = instrumental constants which may be obtained by Higgins' graphical method.[1]

Equation (4) is applicable to the Ostwald viscometer as ordinarily used (without external pressure). When there is an external pressure p_m in addition to the hydrostatic pressure $h_o\rho$

$$\mu = C\,(p_m + h_o\rho)\,t - \frac{B\rho}{t} \qquad (5)$$

as with the Bingham viscometer, provided p_m is not too small in comparison with $h_c\rho$.

Since the time of flow may be very short for a calibrating liquid like benzene or water, it is desirable to use as low a pressure as possible in order to reduce the timing error. On the other hand, when very viscous liquids are under test it is an advantage to use a high pressure in order to reduce the time of flow. Thus it is desirable to calibrate instruments by both equations (4) and (5) since a wide range of pressures is of advantage with viscous as well as with plastic materials.

Although these equations do not apply for plastic materials, as will be seen later, the constant C is convenient for use in calculating the diameter of the capillary.

The neglect of a kinetic energy correction because there is submerged discharge does not appear to be justified, and the practice of Bingham in applying it has accordingly been followed.

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[1] W. F. Higgins: J. Soc. Chem. Ind., 32, 568 (1913).

Since the kinetic energy correction is small in comparison with the previous term in equation (4), for the Bingham viscometer it is customary to calculate the value of B from the equation

$$B = \frac{m\,Q}{8\pi l} \qquad (6)$$

where Q = volume of upper bulb, in cc.
l = length of capillary in cm
m = coefficient for which, on the basis of available data, the value of 1.12 is usually assumed.

It is believed that, for the Ostwald viscometer, the values of B obtained by Higgins' method, are to be preferred to those obtained by equation (6).

The absolute viscosities of the calibrating liquids were obtained by the Bingham viscometer. In using these liquids to calibrate the Ostwald viscometer, a series of about 6 runs was made with each liquid with varying values of p_m and a value of h_o was found by trial which would make C as nearly constant as possible. The average value of h_o obtained with all liquids was used in the final calculation of the average value of C as given in Table I.

TABLE I

Dimensions and Instrumental Constants of Ostwald Viscometers

	No. 1	No. 2
Length of capillary, cm	12.3	10.3
Capacity of upper bulb, cc	2.75	2.4
Time of flow for benzene, 30°C, sec. without external pressure	17.4	12.3
Time of flow for water, 30°C, sec., without external pressure	21.0	14.9
Constant, A, in equation (4)	0.000407	0.000583
Value of B:		
By equation (6), for comparison only	0.0100	0.104
By Higgins' method, and used in calculating C	0.0137	0.100
Number of calibrating liquids	6	5
Maximum variation in C with any one liquid, %	0.58	0.40
Maximum variation in C with all liquids, %	1.29	1.16
Averate hydrostatic head, h_o cm	13.07	11.50
Final average value of C	0.0000309	0.0000499
Minimum external pressure used in calculating h_o grams per cm^2	5.3	11.0

The minimum pressure which could be used without materially changing the value of h_o was not determined, but it was found that the calculated value of h_o was higher when no external pressure was applied; 1.5 percent higher for instrument No. 1, and 1.9 percent for instrument No. 2. When there is no external pressure it is simpler to use equation (4).

4. Method of Analysis of Plasticity Tests

In testing a rubber or other colloidal solution it is necessary by means of observations made at several sufficiently high pressures, to determine whether or not the value of μ calculated from equation (4) or (5) is constant. If it is constant the material is viscous; if not, the material is plastic. A viscous liquid may also be distinguished from a plastic material by plotting the rate of flow, q, in cc per second, against the pressure, p. If the kinetic energy correction is negligible, the graph will be a straight line passing through the origin if the material is viscous.

If variations in the calculated values of μ are too great to be ascribed to the experimental error, or if the graph obtained as above described is curved, or, when straight, intersects the pressure axis to the right of the origin, the material is plastic and equations (4) and (5) do not apply.

The simplest method of expressing the consistency of a plastic material, is in terms of its mobility and yield shear value[1].

It is ordinarily sufficiently accurate in testing plastic materials, to neglect the kinetic energy correction and any possible difference between the measured and the effective length of capillary, but there are unsolved difficulties especially with very stiff pastes.

The intercept of the experimentally determined graph on the pressure axis gives a value p′ known as the yield value. Then the yield shear value, which is the stress at the walls of the capillary, in dynes per square centimeter, is equal to

$$f = \frac{p'dg}{4l} \tag{7}$$

where l is the length and d the diameter of capillary in centimeters. It is difficult to measure d with sufficient accuracy, but its value may be obtained from the relation

$$C = \frac{\pi g d^4}{128 l Q} \tag{8}$$

where Q is the volume of the upper bulb, in cubic centimeters, g = acceleration of gravity = 981 cm per sec^2 and C is obtained by flow tests as previously described. It was calculated from equation (8) that d = 0.081 for instrument No. 1 and 0.084 cm for instrument No. 2.

The reciprocal of the viscosity in poises is known as the fluidity. The corresponding property of a plastic material is known as the mobility and is given by the equation,

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[1] For other methods see E. Buckingham: Am. Soc. Test. Mat. 21, 1154 (1921), and F. P. Hall: Bureau of Standards Technologic Paper No. 234, 351, (1923).

$$M = \frac{128\,q\,l}{\pi\,g\,d^4(p - p')} = \frac{q}{CQ\,(p - p')} \qquad (9)$$

where $\frac{q}{p - p'}$ is obtained graphically from the straight portion of the experimentally determined graph.

5. Conclusion

1. The Ostwald viscometer may be used at varying rates of flow by applying external pressure, and hence may be employed to measure the consistency of apparently liquid materials which are known, or may prove to be plastic.

2. To measure plasticity, a sufficient number of readings must be taken at various rates of flow to determine with sufficient accuracy the relation between the rate of flow and the pressure which produces it.

PLASTICITY IN RELATION TO GELATIN*

BY S. E. SHEPPARD**

Introduction

In view of the very close relation between gelatin and glue it is evident that a considerable degree of overlap is possible where the plasticity of the two materials is discussed separately. Since this paper is to be followed by one on the plasticity of glue by Dr. Bogue, I have omitted discussion of hydrolytic effects and limited the matter to results obtained with straight gelatin solutions.

Sols and Gels

In this and another paper (cellulose) I have introduced a certain amount of matter dealing formally with *elasticity*, because in treating the mechanical properties of the colloid gels we encounter both plastic and elastic phenomena. I do not propose to traverse at any length the vexed ground of definitions of solids and liquids, of elasticity, plasticity and viscosity. This has been discussed very ably in a recent paper by Professor Bingham[1]. It is in general agreed that in "perfect elasticity" the strain (deformation) is proportional to the stress (Hooke's law), and disappears immediately (simultaneously) with the removal of the stress. Bingham points out that two cases are possible on working at shearing force of constant value (1.). No further deformation as the stress continues to be applied up to the point of rupture (perfect elasticity). (11.) No further deformation so long as the shearing stress does not exceed a certain value (yield point). The substance follows Hooke's law up to the yield point, and then suddenly breaks down and shows true plastic flow. He points out further that actual solids never show "perfect elasticity"; these two types are only approximately realized and Hooke's law is never exactly obeyed even at very low stresses so that there is a certain amount of yielding long before the elastic limit.

Practically, under given conditions we can measure (a) primary or elastic strain [Bingham's instantaneous elasticity] i. e., the instantaneous elastic deformation which disappears simultaneously with the suppression of the stress (b) the secondary strain or subpermanent deformation, a reversible deformation which is a function of time (c) the viscous flow which is irreversible with time, and produced at a constant rate.

Mardles[2] speaks of (c) "viscous or plastic" flow as if these were equivalent. In view of the definite differentiation of "plastic" from "viscous" flow, this appears unsatisfactory, and *it is in the region (b) that the most pronounced*

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* Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1924).

**Communication No. 227 from the Research Laboratory of the Eastman Kodak Company.

[1] J. Franklin Inst., 194, 99 (1924).

[2] cf. E. W. J. Mardles: Trans. Faraday Soc., 19, 118 (1923).

plastic effects of solids are shown. (Pseudo-plastic flow, Bingham et al). The imperfection of elasticity, or elastic deficiency, is therefore closely related to plasticity, and elastic measurements give valuable indications of the plasticity of materials, once the limit of elasticity is passed. This limit is not absolute but depends upon the rate at which stress is applied, as well as on the previous loading of the material.

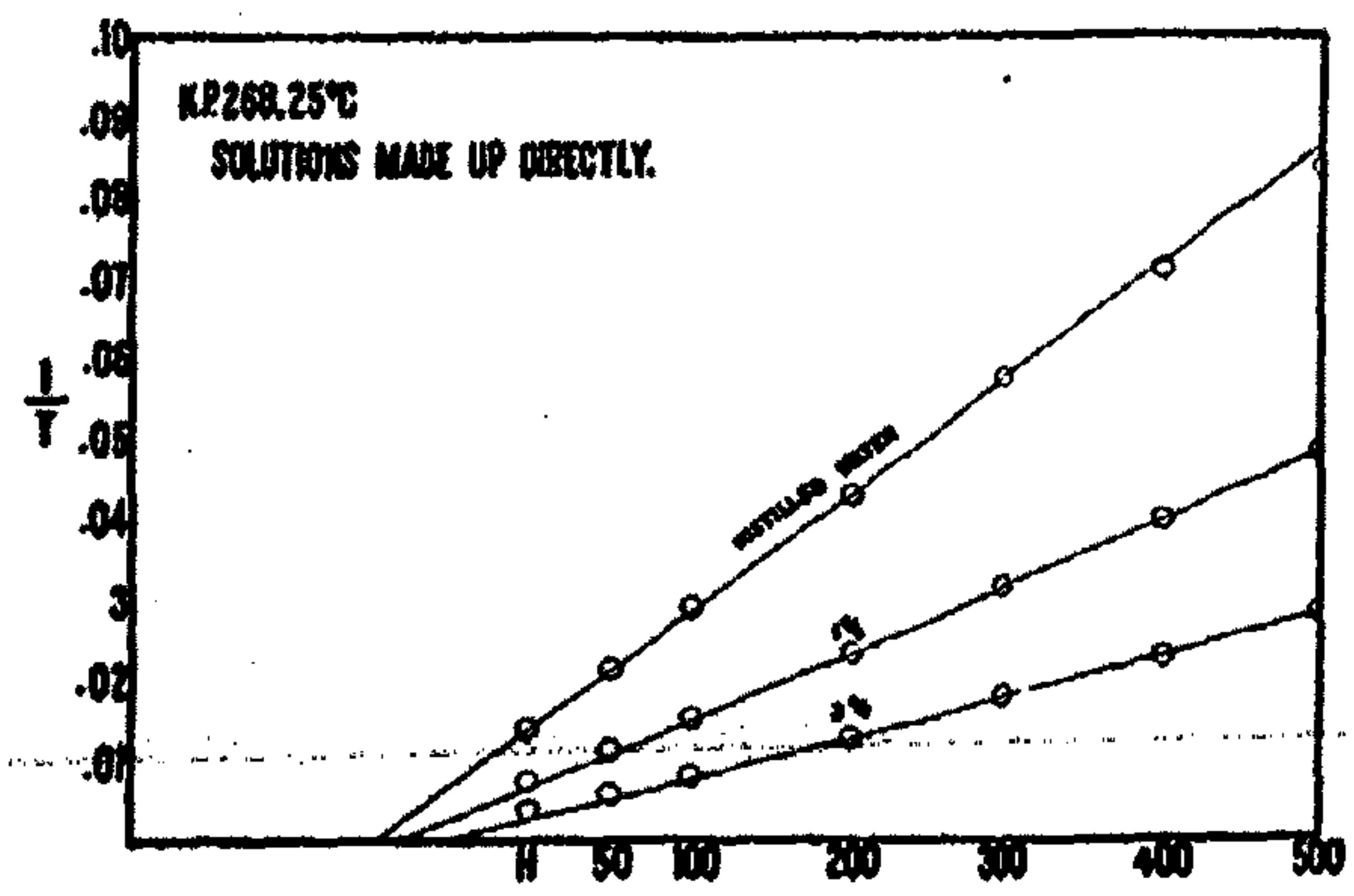

FIG. 1

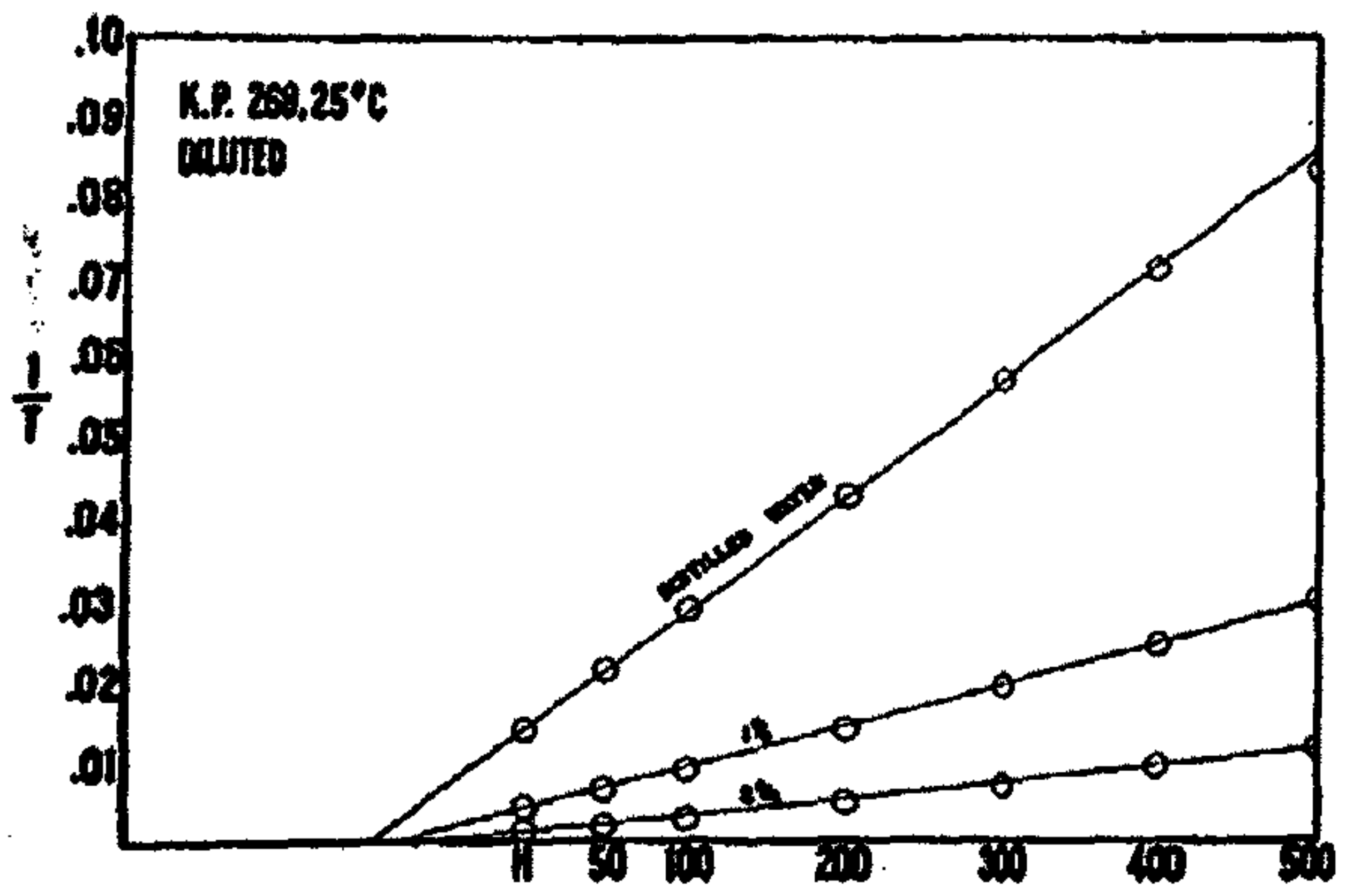

FIG. 2

Fluidity and Plasticity of Gelatin Sols

A good deal of time has been wasted in the past in the endeavor to make relatively precise viscosity measurements of gelatin sols. It was observed that the "viscosities", whether measured by capillary pipettes or other methods, generally showed (a) great variations depending upon the method of preparation and pretreatment (b) showed marked progressive (or regressive) variations with time. For a while these were cheerfully chronicled as outstanding characteristics of those mysterious colloids—everything not understood being magnificent in colloid chemistry. Thanks largely to Oakes and Davis, Bogue and others, the following facts may be regarded as established:

a. the "viscosity" of gelatin sols below a certain temperature tends to increase steadily with time, due to gelation,
b. the "viscosity" of gelatin sols above a certain temperature may fall off with time till a fairly constant value is reached,
c. at still higher temperatures (above 70° C.) the "viscosity" falls steadily, due to hydrolysis,
d. with change of pH, the rate of change with time is least (Bogue) at the isoelectric point 4.7 - 4.8.

The "viscosity" figures here were usually determined from times of flow at one rate of shear. Comparison of such figures is only permissible if the flow is solely that of a viscous fluid, and examination of gelatin sols has shown that this is not necessarily the case. Experiments by R. H. Bogue indicated that only above 34° C. was this the case. In a series of experiments made in this laboratory for gelatin solutions from 1 to 8 percent it was found that for each concentration above a certain temperature the flow: shearing stress curve was a straight line cutting the axis of shearing stresses at the same point as that for water. Results shown in graphs illustrate this, as also the following table:

Gelatin No. 268

Temp.	Made	Intercept (Yield value)				
		Water	1.0%	2%	4%	8%
30° C.	dil.	0	13	15	25	100
	dir.	0	0	13	15	70
28° C.	dil.	0	28	35	45	100
	dir.	0	4	6	17	
25° C.	dil.	0	34	40	100	
	dir.	0	15	23	100	
			Deashed			
28° C.	dil.	0	10	15	60	310
25° C.	dil.	0	40	200		

In obtaining the intercepts or "yield values" the value of H, the mean hydrostatic head, when no over pressure was applied, was taken as the value at the half period of flow. This is not accurate, but the error does not affect the order of the results or the inferences as to change of yield point with temperature and concentration. So far as this goes, it shows that the temperature at which *plasticity* appears in gelatin sols depends both on the concentration and on the way the solution is prepared. There does not appear to be a definite transition temperature between "sol" and "gel" states. At low temperature, very dilute "sols", if investigated with apparatus of sufficient delicacy, give evidence of a kind of elasticity. This is shown by the work of Rohloff and Shinjo[1]. ("On the boundary between the solid and liquid conditions of gelatin solutions"). They found that at a temperature of 8° C. gelatin sols down to 0.18 p. c. showed a measureable elastic resistance to shear, although

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[1] Physik. Z. 8, 442.

behaving quite like a fluid, as regards pouring, etc. The growth of the elastic resistance with time (in days) is shown in the figure and is most marked for the more concentrated solutions. The existence of an elastic factor in gelatin sols has been noted by other observers, e. g., (See Fig. 3 on page 1228) H. Freundlich and Seifriz[1], and A. Szegvari[2] has attempted to develop a theory of the "inner friction" of colloidal solutions from a relatively simple superposition of an elastic constant on the supposed "true" viscosity coefficient. But it does not appear probable that this relation will be adequate for the greater number of emulsion colloids; the phenomena are more complex.

Sol-Gel Transition

It has been suggested that in the sols and gels of gelatin respectively two distinct forms of the substance exist. C. R. Smith[3] made a study of the optical rotation, and found that above 33° C. a constant rotation was obtained in a short time, whereas at lower temperatures much longer times were necessary. From 35° C. and upward constant rotation values independent of concentration were obtained. Also below 15° C. a constant value was ob-

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[1] Z. physik. Chem., 104, 233 (1923); also Freundlich and Schalek: 104, 233 (1923).

[2] In recent papers by H. Freundlich and collaborators (cf. Z. physik. Chem. 108, 153 (1923) and by A. Szegvari (108, 175) the flow of colloidal solutions under varying shearing stress is discussed. In particular the theory is dealt with by the last named. No mention is made of the work of Bingham, Buckingham and others in this country. Szegvari develops a theory of "plastic" flow on the simple assumption of a superposition of elastic resistance on viscous flow, the theoretical viscosity being supposed independent of the shearing stress. With these assumptions he obtains (a) for the Couette (MacMichael, etc.) viscosimeter the expression

$$w = \Delta/G + \eta$$

w = resistance (apparent viscosity)
Δ = elastic constant
G = velocity gradient
η = theoretical viscosity

taking ϕ = angle of deflection
ω = velocity of rotation

this becomes $\phi/\omega = \Delta/\omega + \eta$

or $\phi = \Delta + \eta\omega$

which gives a function identical with Bingham's for simple plastic flow. Similarly for (b) a capillary, in this case he adds a constant to the velocity-gradient to take care of the assumed reduction of diameter of free flow by the elastic elements. This gives

$$w = \frac{\Delta}{G+k} + \eta$$

hence, if v = volume of flow per unit time
p = pressure

$$1/v = \frac{\Delta}{\frac{p}{\eta}+k} + \eta = \frac{\Delta\eta+\eta^2}{p+k\eta}$$

or $$v = \frac{p+k}{\Delta\eta+\eta^2} = \frac{p+B}{A} = \frac{p}{A} + c$$

giving again a curve of similar type for the flow: pressure curve. There does not appear to be any advance in this upon Bingham's primary conclusion, and furthermore no notice is taken of the failure of this relation at low rates of shear.

[3] J. Am. Chem. Soc., 41, 135 (1919).

tained. Between these values, the rotation was found to take intermediate values according to the temperature. Smith considered this indicated the existence of two distinct forms of gelatin, one, the *sol* form stable at 35° C. and above, the other the *gel* form stable at 15° C. and below. At temperatures between an equilibrium between the two forms existed. The existence of TWO critical temperatures of this type, or a *temperature range* instead of a transition temperature for thermodynamically distinct forms of a substance did not appear probable. Oakes and Davis[1] from an investigation of the change of "apparent viscosity" with time at different temperatures concluded that at a temperature of 38.03° C. gelatin sol and gel were in equilibrium, that is, that this is a true transition temperature, but generally masked by phenomena of retarded transition—analogous to supersaturation. Comparative invariance of "apparent viscosity" for a 2 percent gelatin at 38° C. was observed also in this laboratory but later work of Loeb[2] and Bogue[3] showed that this temperature is a function of the hydrion concentration. In general the variation is, least at pH = 4.7, the isoelectric point, but, as shown by Bogue, other factors influence it, and there is not sufficient evidence for a definite transition temperature. This leaves then the former view that the sol or gel transition is continuous as most probable, and it is likely that, as in soaps, the particles of the sol and the gel are identical. The continuity

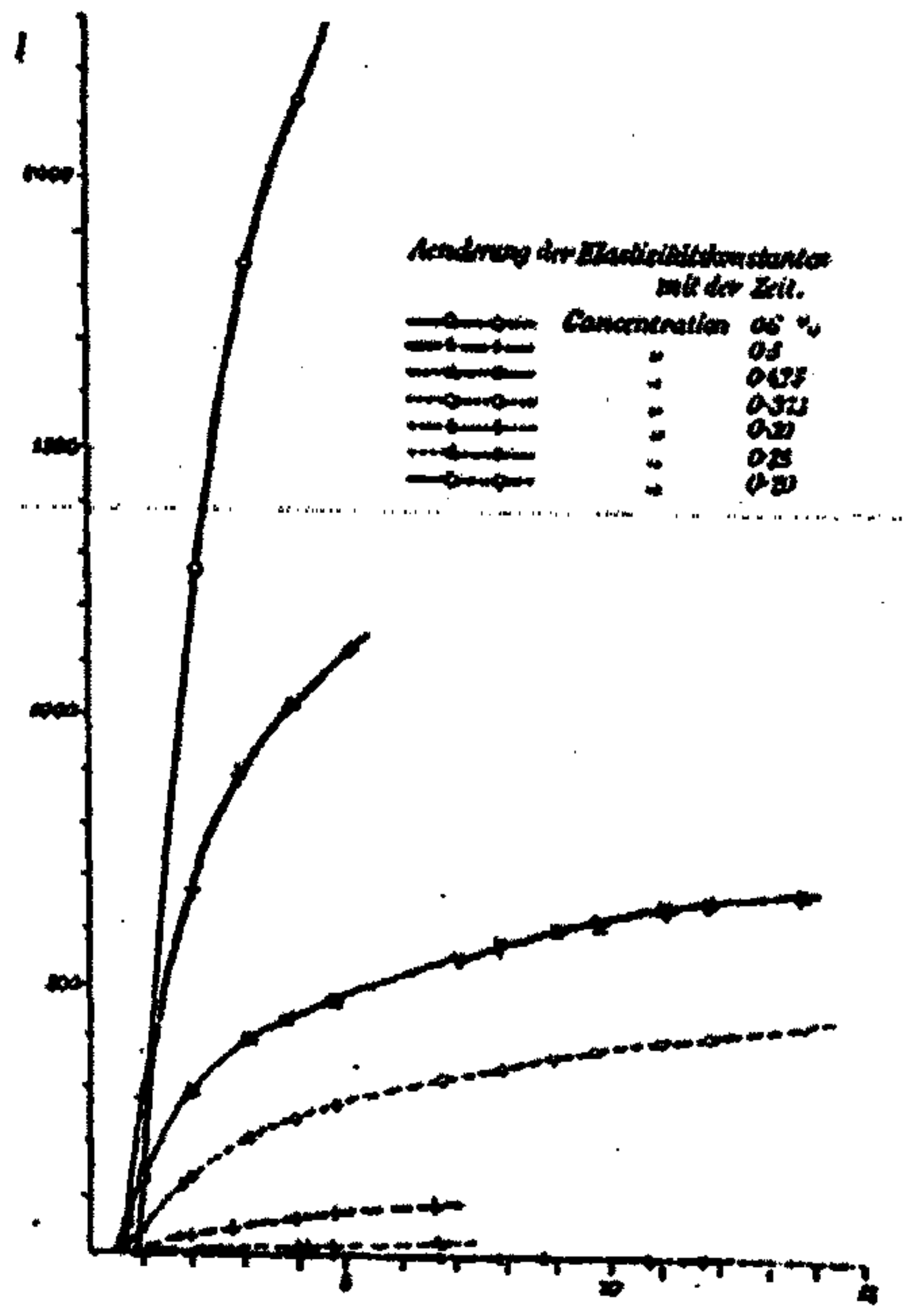

FIG. 3
(Rohloff and Shinjo)

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[1] J. Am. Chem. Soc., 44, 464 (1922).

[2] J. Gen. Physiol. 4, 107 (1921).

[3] J. Am. Chem. Soc. 44, 1343 (1922).

of this change, and the existence of a region in which *plasticity* is preeminently developed is then illustrated in comparing, by the same, if arbitrary, method, a series of so-called *melting* and *setting* points at different concentrations of gelatin. The general form of these curves is shown in Fig. 4.

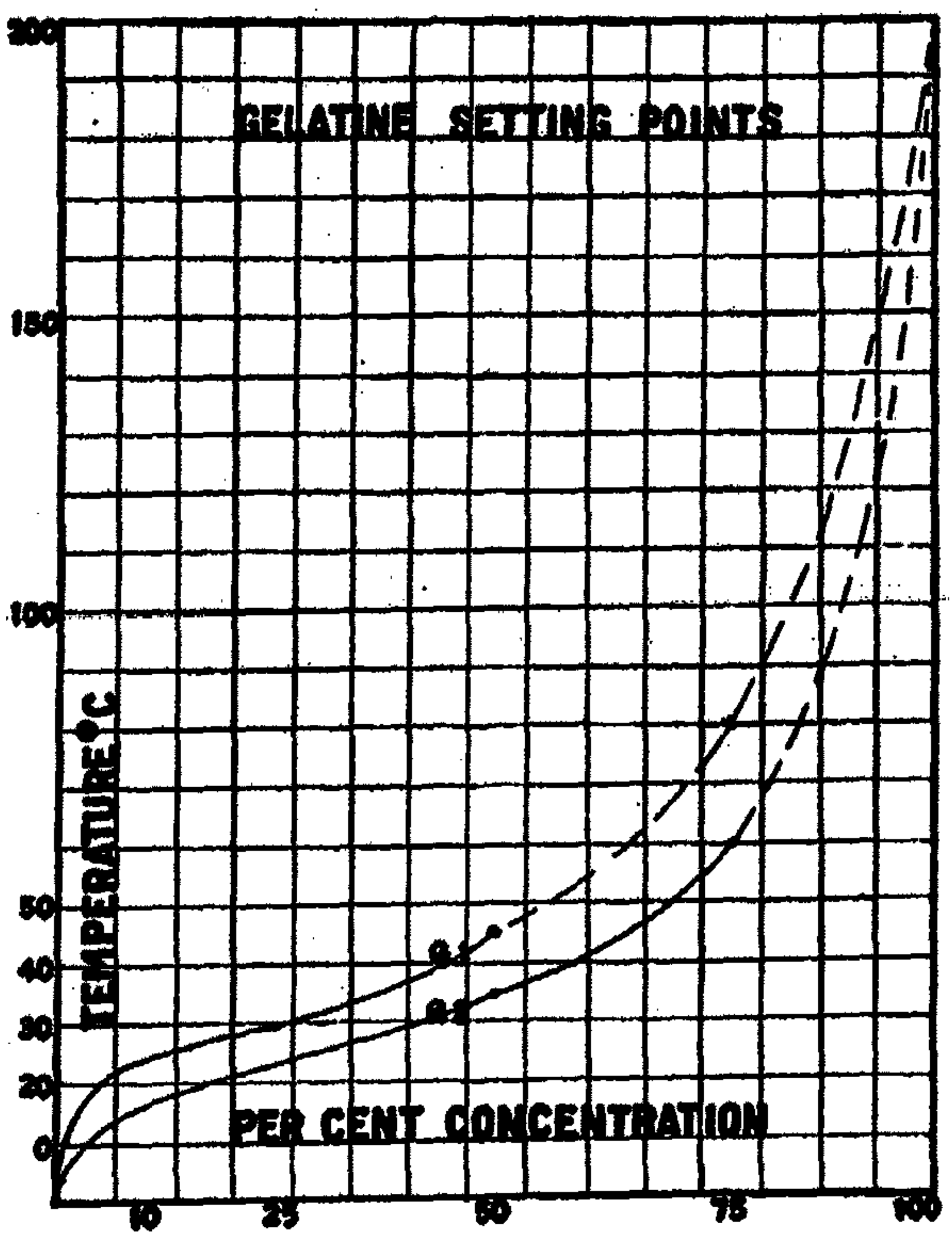

Fig. 4

G1 Melting Points
G2 Setting Points

The enclosed region is one of imperfect temperature equilibrium but also a region in which *plasticity* is well developed. Above the upper curve, the *sols* examined would show little plasticity, but behave as viscous liquids, below the lower curve we have elastic gels.

Plasticity of Jellies

Gelatin jellies subjected to increasing stresses below a certain temperature show a high degree of elasticity[1]. This is illustrated in Figs. 5 and 6 where the elastic resistance to torsion and to stretch is shown graphically. When an increasing load is applied fairly rapidly, the jelly follows Hooke's law practically up to the breaking point. The volume of jelly remains con-

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[1] Cf. S. E. Sheppard and S. S. Sweet: J. Am. Chem. Soc., 43, 540 (1921).

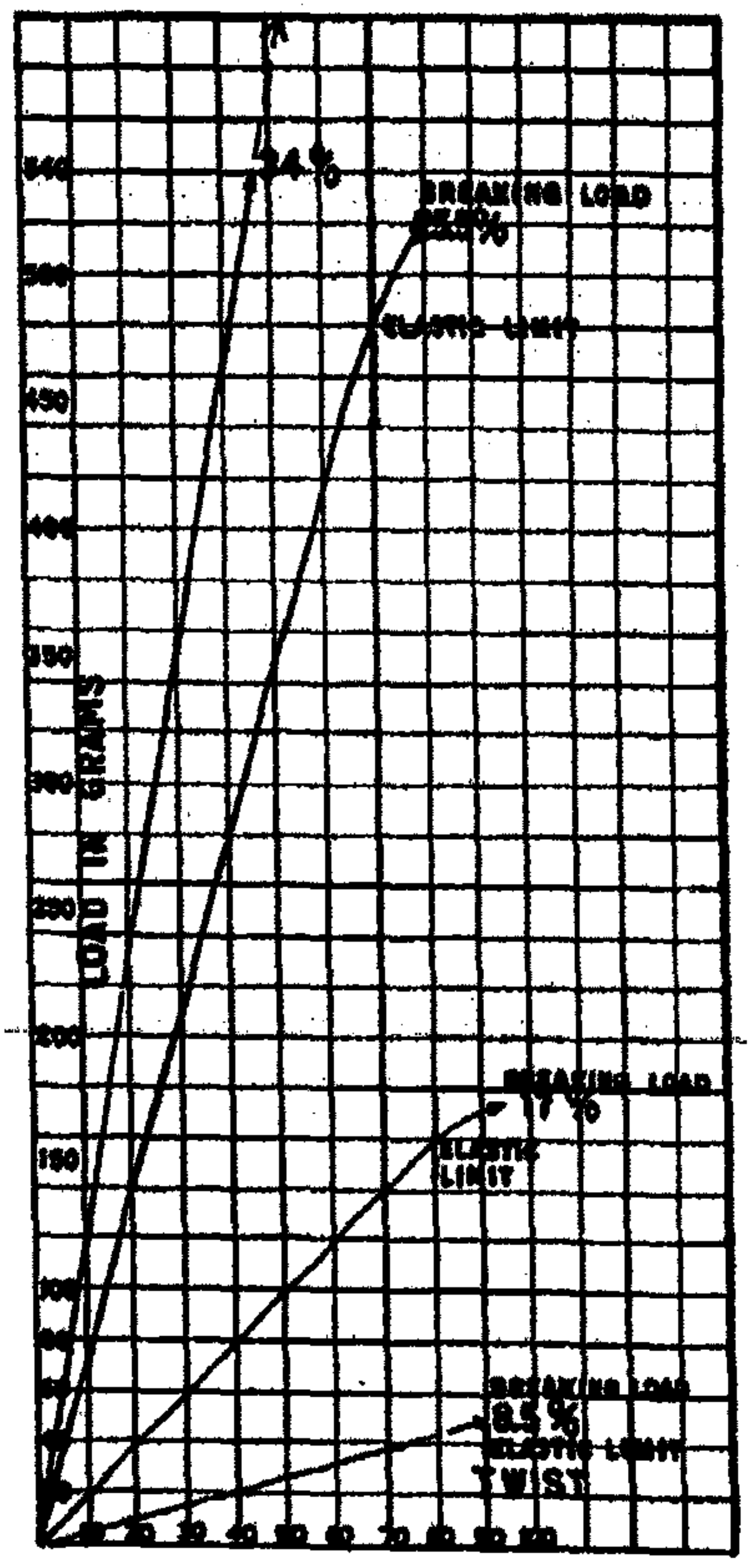

Fig. 5
Behavior of Gelatin Jellies under Torsion

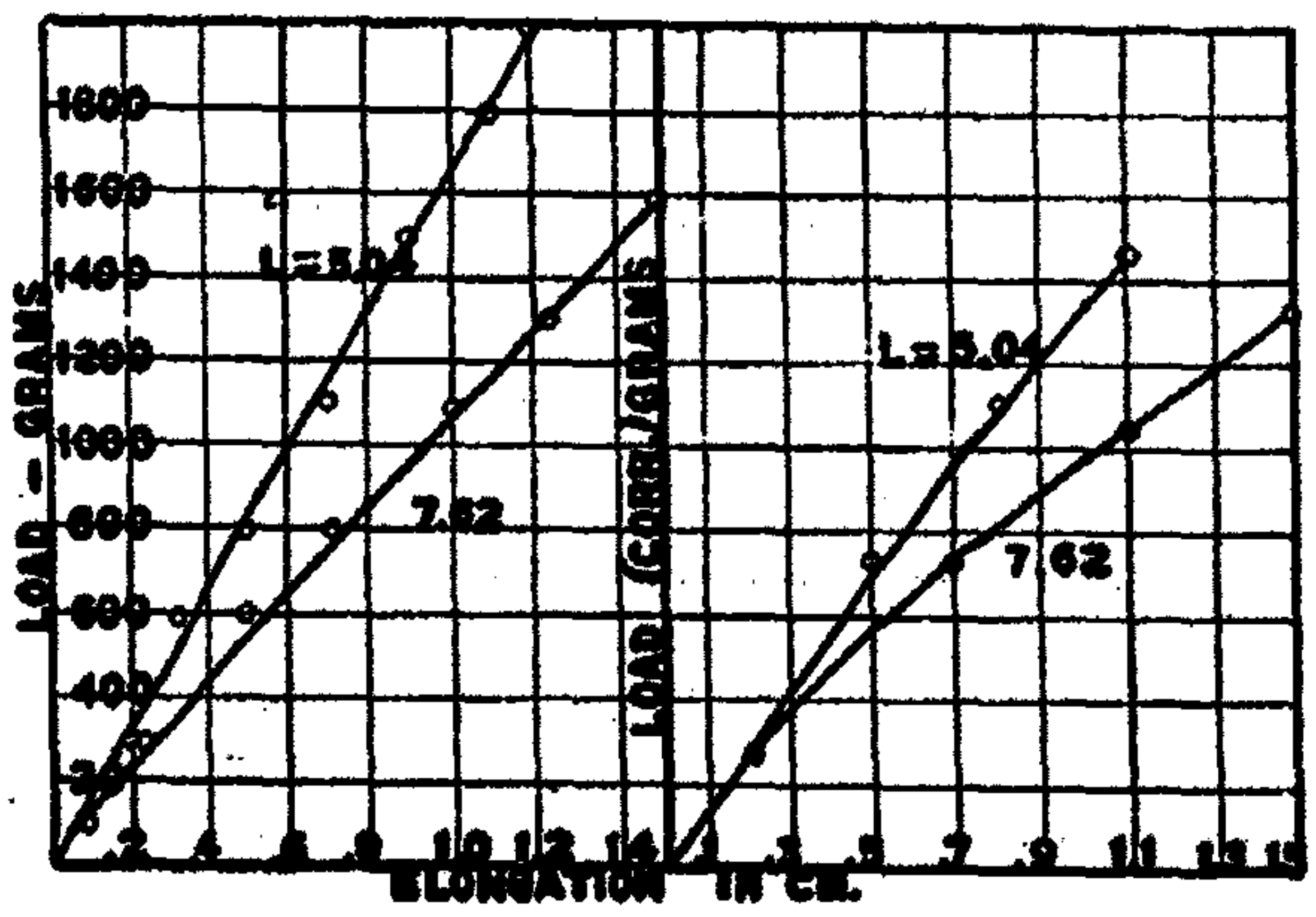

Fig. 6
Behavior of Gelatin Jellies under Stretch

stant under stress, indicating that the modulus of rigidity N, and the modulus of elasticity (for extension or compression) E are simply related by the expression

$$N = \frac{E}{2(1 + \mu)} = \frac{E}{2(1 + 0.5)} \text{ or } E = 3N,$$

since for elastic systems whose the volume is unchanged Poisson's ratio $\mu = 1/2$. This is probably connected with the highly elastic behavior of gelatin jellies. None the less, if such jellies are subjected to steady loads for long periods in the neighborhood of the elastic limit, evidence of plastic flow is found. Hatschek[1] has observed that the rates of mechanical and optical relaxation are different. Rankine[2] strained gelatin jellies, at a temperature of 16.5° F. under constant load of 500 gms. He removed the load so that the deformation remained constant, and found that the load fell to a certain value when there was an abrupt break in the curve, coming higher the greater the concentration.

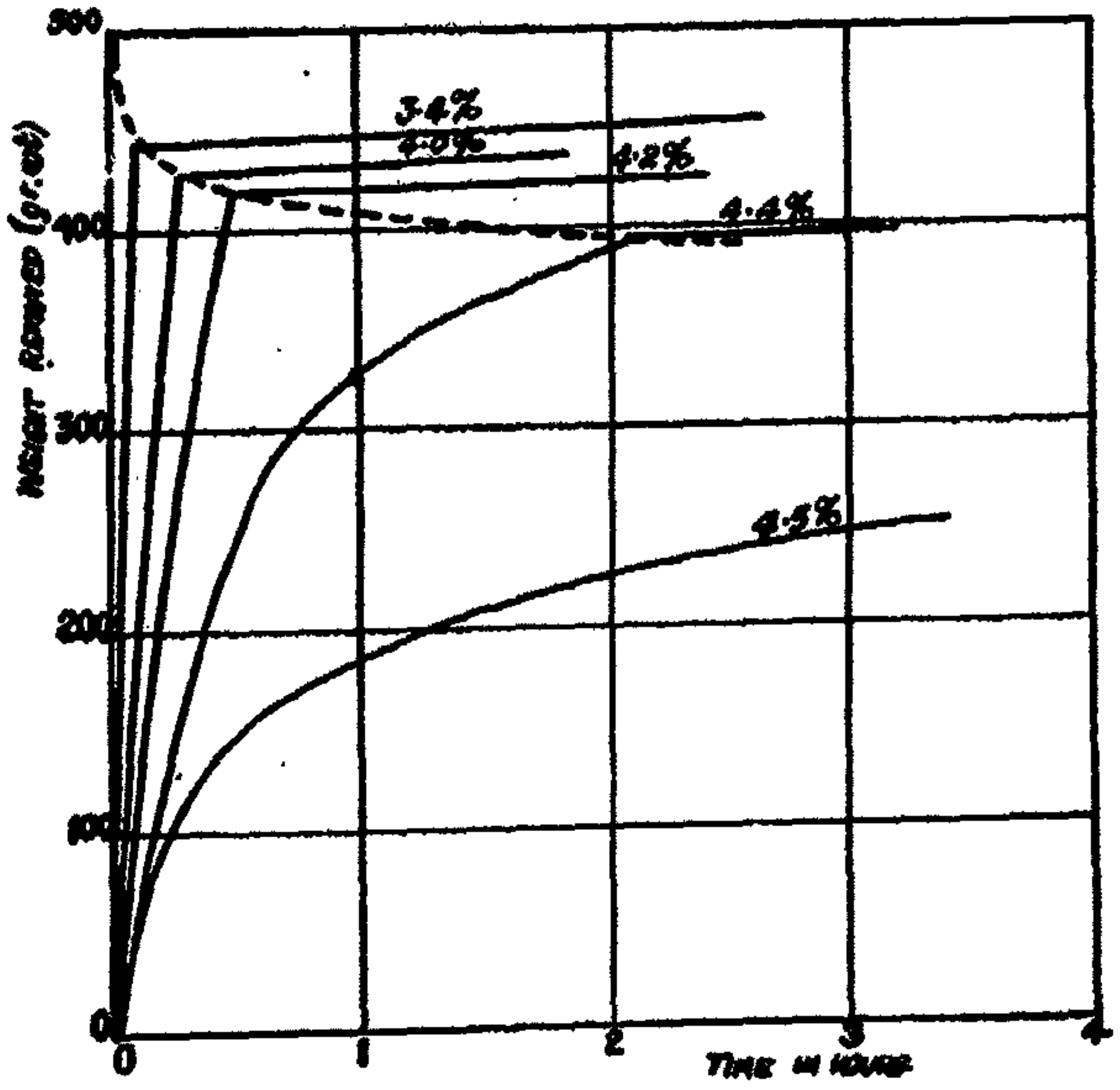

Fig. 7

Recovery of Loaded Gelatin Jellies
(Rankine)

Bingham[3] has pointed out that this agrees with other experiments on the yield values of emulsion colloids, which show that the "yield value" increases rapidly and non-linearly with the concentration.

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[1] E. Hatschek: "Symposium on Colloids," Faraday Society, May (1921).

[2] Rankine: Phil. Mag. ,(6) 11, 447 (1906).

[3] J. Franklin Inst., 197, 115 (1924).

A very interesting observation was made by Freundlich and Seifriz [1] working with quite dilute gelatin solutions—.5 to 2.0 per cent. They used a magnetic method for determining the elastic limit within microscopically small volumes of the sol, measuring the movement of small nickel particles of the order 7 to 20μ. Under these conditions they found a well pronounced maximum for the elastic limit at concentrations below 1 percent (see Fig. 8).

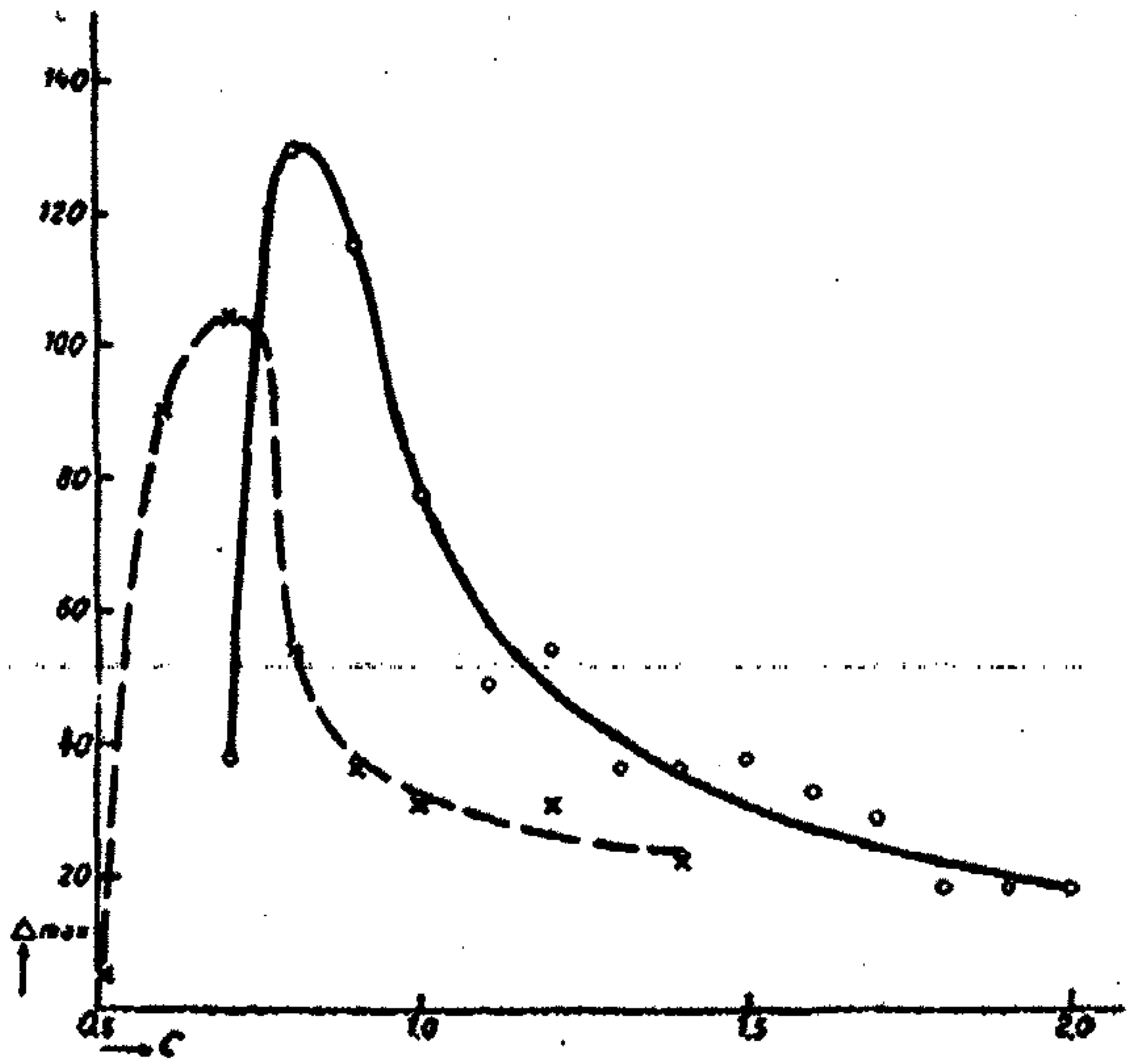

Fig. 8

Elasticity of Dilute Gelatin Sols (Freundlich and Seifriz)

(Explanation of Fig. 8. Ordinate Δ max refers to elastic limit, abscissae C concentration percent. The full curve refers to a commercial gelatin, the broken curve to a purified gelatin). As they point out, this behavior indicates that the more dilute solutions with higher limit of elasticity, but lower modulus of rigidity, resemble rubber more, while the more concentrated solutions, which are solid gels, resemble metals such as steel.

These observations, and the evidence which exist for inhomogeneity of structure of gelatin solutions[2] deserve special attention and demand further experimental work.

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[1] Z. physik. Chem. **104**, 233 (1923).

[2] Cf. Bachmann: Z. anorg. Chem. **73**, 125 (1911), also E. W. J. Mardles, Trans. Faraday Soc., **1922**, 335, for cellulose ester gels.

PLASTICITY AND STRUCTURE IN GELATIN SYSTEMS[1]

BY ROBERT H. BOGUE

The viscosity of gelatin systems has received attention at frequent intervals for a great many years. The concept of plasticity is a more recent development, formerly not separated at all from the concept of viscosity in studies on the flow of gelatin. It is one of those studies which have evolved in an effort to fix more definitely in our minds the structural characteristics of matter. For by a recognition of the laws governing the flow of matter, we come closer to an understanding of the internal complexity which determines the flow. In fact, studies designed specifically to solve some of the mysteries of structure have constituted practically the entire work that has been done on the plasticity of gelatin. Plasticity has served as the tool for attacking the larger and more important problem.

A paper[2] on "The Sol-Gel Equilibrium in Protein Systems" by the writer in 1922 was the first attempt that had been made to utilize the principle of plasticity in an application to the structure of gelatin. Certain other studies however have furnished data which bear indirectly on this field. These will be referred to in their bearing on the problem in this paper.

The controversy on the existence of a definite transition temperature between the sol and the gel form of gelatin brings up prominently the question of difference in structure between the two forms. And since the properties of the two forms are so different, one is justified in expecting that a decided dissimilarity in internal structure exists. Furthermore, since the gel takes the form of a solid, and the sol the form of a liquid, the natural sequence of ideas would lead to the inquiry; are the two forms solid and liquid, respectively, in the classical sense of the terms.

One of the criteria of solid crystalline matter is the existence of a well-defined melting point temperature. Another, more recently introduced, is the requirement of a finite shearing stress to produce flow.

All attempts to obtain a definite melting point for gelatins have failed. Of course values have been given but they have little significance and are not absolute. As Sheppard[3] has said, "both the 'melting point' and the 'setting point' are more or less arbitrary conceptions, and their determination depends mainly upon standardized experimental conventions". As far as we are able to determine, the transition from the hydrosol to the hydrogel condition in these systems is continuous. This would seem to indicate that if the gel is strictly a solid material, and the sol a liquid material, then the change from solid to liquid is a gradual and continuous process, and not an abrupt and discontinuous process, in these systems. The bearing of this conclusion on the significance of plasticity measurements will be referred to later.

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[1] Paper presented at the Plasticity Symposium Lafayette College, Oct. 17 (1924).

[2] R. H. Bogue: J. Am. Chem. Soc., 44, 1313 (1922).

[3] J. Ind. Eng. Chem. 13, 423 (1921).

An attack upon the conditions of transition from sol to gel has been made from another angle by C. R. Smith[1]. He reported that at temperatures above 33° to 35° the specific rotation of gelatin is practically constant at about −123°, while at temperatures below 15° the specific rotation is practically constant at about −266°. At all temperatures intermediate between 35° and 15° the rotation varies between these two limits. Smith arrives at the conclusion that gelatin in aqueous solution exists in two modifications; the one stable at temperatures above 33°–35° which he denotes as Sol form A, the other stable at temperatures below 15° which he denotes as Gel form B. "Between these temperatures a condition of equilibrium between the two forms exists and the mutarotation observed seems to be due to the transformation of one form into the other by a reaction which is reversible with temperature". This work constitutes therefore a second line of evidence indicating that the transition from gel to sol is a gradual and continuous process.

J. A. Wilson[2] has reported points of minimum swelling of pure ash-free gelatin at pH 4.7 and 7.7, and Mathews[3] has shown that the absorption spectrum of gelatin has minimum values for the wave length of maximum absorption in the ultraviolet at pH 4.69 and 7.65. Wilson tentatively interprets these findings to indicate that the gel form has an isoelectric point at pH 4.7 but that between pH 4.7 and 7.7 the gel passes into the sol form and that the latter has an isoelectric point at pH 7.7. He concludes that both temperature and hydrogen ion concentration may have the capacity therefore of transforming, reversibly, the gel to the sol form. A check on this suggestion was obtained by a study on the influence of hydrogen ion concentration on the optical rotation. If Smith is correct in his conclusion that the gel has a specific rotation of −266° while the sol has a specific rotation of −123°, then the variation in this property with pH, at a given temperature, should indicate a transition, if this occurs. This problem was studied by M. T. O'Connell and the writer,[4] using an isoelectric ash-free gelatin obtained from the Eastman Kodak Company thru the courtesy of Dr. S. E. Sheppard. At a constant temperature of 30°, which is the only one yet investigated, the specific rotation of a 2 percent solution was found to very with the pH in a regular manner, rising from −90° at pH 0.3 to −134.5° at pH 2.8, dropping to 94° at pH 4.7, rising to −139° at pH 7.0 and again dropping to 69° at pH 13.4. In no case however was there found any indication of a value of the order of −266° which was the value given by Smith for the gel form. And there was no indication of depression in the curve in the neighborhood of pH 7.7, the point suggested by Wilson as possibly representative of the isoelectric point of the sol form.

It would seem from these studies that whereas temperature could effect the transition, and does effect a gradual and continous transition from gel

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[1] J. Am. Chem. Soc., 41 146 (1919), J. Ind. Eng. Chem., 12, 2878 (1920).

[2] J. Am. Chem. Soc., 44, 2633 (1922); 45, 3139 (1923).

[3] J. Am. Chem. Soc., 46, 852 (1924).

[4] J. Am. Chem. Soc. 47, 1694 (1925).

to sol, yet that hydrogen ion concentration is unable to do so, at least at the temperature of the experiment, 30°. To be conclusive however, the work must be repeated at a low temperature.

The work thus far referred to in this paper has shown in every case a gradual and continuous transition from gel to sol, and seems to indicate therefore a transition of a similar character from the solid to the liquid state.

Remembering Bingham's criterion for the solid vs. the liquid state, based on plastic vs. viscous flow, we would expect, if the above conclusions were substantiated, that the gel would exhibit plastic flow and show a yield value, and that the sol would show only viscous flow. This was substantiated completely in the work reported by the writer[1] in 1922. The angular deflection produced by the use of a MacMichael viscometer was measured, using gelatin solutions of 10, 20, and 25 percent concentrations, at varying shearing stress (revolutions per minute of the cup from 5 to 100) for temperatures from 25° to 60°. The angular deflection was plotted on the abscissa against the shearing stress (R. P. M.) on the ordinates. The curves were then extrapolated to the intersection with the axes.

It was found that in all cases where the temperature was above 34°, the extrapolated curves passed thru the origin of the axes, while at temperatures below 34° the extrapolated curves in general intersected the abscissa at a distance from the origin, this distance increasing as the temperature was reduced. This means that in those cases where the intercept lies on the abscissa an infinitely small shear will result in a deflection of finite magnitude. That is, the gelatin under these conditions offers a permanent and fixed resistance to deformation. It is an elastic body; it possesses a measurable degree of rigidity, and deformation may not occur until after a certain minimum of pressure, exerted against it, has been exceeded. These are the attributed of a plastic substance.

Above a certain temperature, however, (at any given concentration) the curves follow the laws of viscous flow; they converge, when extrapolated to the axes, at the origin. That is, at high temperatures the gelatin appears to be a viscous liquid; at low temperatures, a plastic solid.

A point of considerable interest, however, is the fixing of the temperature of transition, and our data are convincing in this respect. In 25 percent solutions, the highest temperature at which evidence of plastic flow was observed was at about 34°. But in 20 percent solutions it was 33°, while in 10 percent solutions it was 29°. As the concentration of gelatin in the solution is decreased, the maximum temperature at which plastic flow is observed is decreased. Thus, if we may speak of this temperature as the transition temperature, then it becomes obvious that the transition temperature is not a fixed point, invariable for all concentrations, but that it is a concentration variable.

The writer has previously ventured the suggestion that gelatin sols appear to consist of molecules which, upon a lowering of the temperature, cohere

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[1] R. H. Bogue; J. Am. Chem. Soc., 44, 1313 (1922).

into aggregates in the form of catenary threads of more heavily hydrated molecules. The resiliency or elasticity of the jelly probably depends upon the length of these filaments.

It seems also that, in the case of gelatin, elasticity in the gel state is synonymous with plasticity in the liquid state, for on account of the amicroscopic or ultramicroscopic size of these particles and the short filaments characteristic of the sol state, any displacement of them in the fluid would meet with so great a frictional resistance that the property of plastic flow would be imparted to the whole mass. This is what is observed when the curve of viscous flow changes to one of plastic flow.

If it is true that plasticity is an expression of interfibrillar elasticity, and that the elasticity is determined by the length of the fibrils, it must follow that the actual measurement of this property will depend upon the concentration of fibrils in the solution, and this will be proportional to the concentration of gelatin in the solution at any given temperature. But from all the evidence thus far presented, the transition is gradual and continuous, which means that the increase in number, size and hydration of the fibrils procedes continuously over a wide interval of temperature. And no instrument has been observed which will indicate the moment of beginning or of ending of the transition. That is, the exact temperature of transition observed in any given case will depend upon the sensitivity of the instrument used. So while we can say definitely that plastic flow is manifest, for example, in a 25 percent solution of gelatin at 34°, we are not permitted to say that it does not exist at any temperature above this point. The greater the sensitivity of our instruments, the higher will be the temperature at which plasticity will be manifest. There is no fixed point of transition.

The only work which has postulated a definite and exact temperature of transition was contained in a paper by Davis and Oakes[1] in 1922. They reported that at a temperature of 38.03° gelatin sol and gel could exist in equilibrium, while this was not true for any other temperature. They arrived at this conclusion by noting that a "seeded" solution (one to which a little gelatin gel has been added) showed no change in viscosity with time at this temperature, whereas at any temperature below 38,03° a regular increase in viscosity with time was observed, and at any temperature above this a decrease occurred until the viscosity equaled that of a similar unseeded portion at the same temperature.

Sheppard[2] had found somewhat similar results, but Loeb[3] had reported that at any temperature above 35° the viscosity (of a 2 percent solution of gelatin of pH 2.7) *decreased* on standing. The writer[4] designed experiments to bear upon this problem and found a decrease in viscosity with time at 35°

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[1] J. Am. Chem. Soc., 44, 464 (1922).

[2] Discussion at 62nd. Meeting, American Chemical Society, New York, September 6-10, (1921).

[3] J. Gen. Physiol., 4, 107 (1921).

[4] R. H. Bogue: loc. cit.

at every hydrogen ion concentration tested, from pH 2.0 to pH 9.4, with the exception of the sample at the isoelectric point, pH 4.7, in which case there was no change. Seeding had no effect. The nearer the hydrogen ion concentration approached the isoelectric condition, the less was the variation with time. On repeating the test with an ash-free gelatin at the same temperature, and increase was observed at all hydrogen ion concentrations, but on raising the temperature to 37° the curve at pH 4.7 again became horizontal.

The significance of this is as follows. At low temperatures the tendency in the system is for an increase in the size of the molecular aggregates, hence an increase in viscosity with time. At high temperatures the tendency is in the opposite direction—hence a decrease in viscosity with time. At any given temperature, *e. g.* 35°, whether the aggregates will become larger or smaller will be determined by the hydrogen ion concentration, the presence of inorganic ions, and the presence of protein hydrolysis products. Under any given set of conditions there will be some temperature at which neither increase nor decrease will occur. The change in viscosity with time is due to the lag in the attainment of equilibrium. It is a physical or physico-chemical readjustment which requires time for its completion. Given sufficient time under properly controlled conditions, an equilibrium at *any* temperature may be attained at which there will be no change in viscosity—molecular rearrangement—with further time.

This demonstrates that this temperature equilibrium is in no way indicative of a "critical equilibrium temperature" between the sol and gel forms, but is rather only a point on a continuous curve. The equation has been suggested by the writer:

$$\eta_{\text{pH}} = \text{K}/\text{f}(\text{T})$$

where η_{pH} is the viscosity at equilibrium at any given hydrogen ion concentration, f(T) is some function of the temperature, and K is a constant.

Recently Davis[1] has reported that the value 38.03° could no longer be regarded as a definite and fixed transitional temperature. He states, however that he is still hopeful of allocating a definite transition point. Additional evidence of a gradual rather than an abrupt change on passing from the sol to the gel state is indicated by the finding of Walpole[2] that the refractive index of a gelatin—water system is a linear function of the concentration and, when plotted against temperature, shows no discontinuity on proceeding from the liquid sol to the rigid gel. McBain[3] has reported that the sol and gel of soaps differ only thru the mechanical rigidity and elasticity of the gel form.

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[1] Paper presented at the 67th meeting of the American Chemical Society, Washington, D. C., April 21-26, (1924).

[2] Kolloid-Z. **13**, 241 (1913).

[3] J. Chem. Soc., **117**, 1506 (1920).

To summarize: Information on the nature of the transitions and equilibria in gelatin systems between the sol and the gel state constitutes a most valuable means to an understanding of the internal molecular structure of the two forms. An application of the laws of plastic and viscous flow have been found to demonstrate the nature of the transition and the type of the equilibrium. A step further in our knowledge of the structure of gelatin systems is made possible.

Washington, D. C.
October 11, 1924.

PLASTICITY AS APPLIED TO VISCOSE AND ARTIFICIAL SILK*

BY CHAS. S. VENABLE

Plasticity is a fundamental property of artificial silk and fluidity is an important consideration in the preparation and processing of the cellulose solutions from which artificial silks are produced. In spite of these recognized facts but little information from the modern viewpoint of plasticity and fluidity is to be found along these lines in published literature. Prof. Bingham has reported[1] the results of a detailed study of the behavior of nitrocellulose solutions. A recent paper by Carver and Folts before the Cellulose Division of the American Chemical Society[2] dealt in a similar manner with the behavior of cuprammonia solutions of cellulose. A few scattered stress-strain curves for different artificial silks have been published without serious comment. Practically no information is available regarding viscose solutions or viscose silk.

The data here presented must be considered only as the results of a preliminary investigation. It is planned to continue the study, and it is hoped to present a more complete report later.

The essential steps in the production of artificial silk by the Viscose Process are quite familiar. Briefly, cellulose in the form of wood pulp or cotton linters is steeped in strong caustic solutions. The resulting alkali cellulose, after a short aging period, is treated with carbon bisulfide whereby cellulose xanthogenate is formed. This material is dissolved in dilute caustic to give what is known as a solution of viscose. This solution is aged, and is then spun by forcing through suitable small openings into an acid bath, which coagulates the xanthogenate and decomposes it to "regenerate" the cellulose in the form of continuous filaments. These filaments are twisted together to form a thread, which is then washed, reeled, dried, desulfurized, bleached, etc., to give the lustrous product known as viscose silk. The number and fineness of the filaments composing a single thread is varied at will within wide limits. The count or weight of a thread is usually expressed in deniers, one denier being the weight in grams of 9000 meters of thread.

Experimental Data

Plasticity of Viscose Silk

Instructive information can be obtained regarding the plastic mature of viscose silk by a study of its stress-strain-time relationships. The following results were obtained with an ordinary Baer testing machine of the drop weight type, the speed of the drop being set at 6.7 cm per minute. At this

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* Paper presented at the Plasticity Symposium, Lafayette College, Oct. (1924).

[1] J. Franklin Inst. **194**, 731 (1922).

[2] Ithaca meeting Am. Chem. Soc., Sept. (1924).

speed, which represents the maximum at which accurate readings could be obtained on this machine, about 3-1/2 minutes were required to break the thread. Curves of the same general nature can be obtained with the Scott autographic machine by which a break is affected in approximately 10 seconds. However, it was found that the characteristics of the curves are best brought out with the slower rate of stretching.

In Chart I are shown typical curves for No. 80 cotton thread natural silk, and viscose silk when in equilibrium with air of the relative humidity stated, and also when wet with water. The curves for cotton are complicated by the discontinuous nature of the threads, and show but little of the plastic nature of the material. With natural silk, plastic deformation is obvious, though gradual, and the material both wet and dry maintains a remarkable degree of true elasticity through the entire stretch. The case is quite different with dry viscose silk, where as the load is applied the elastic limit and yield point are rapidly exceeded, to be followed by viscous flow and permanent deformation. This behavior, which is likewise typical of nitrocellulose and cuprammonium silks, is a striking example of plasticity. The mobilities and friction values are easily obtainable and furnish useful information both from an operating and research standpoint. As seen from the curves wet viscose silk has no true elasticity and its friction value is practically zero.

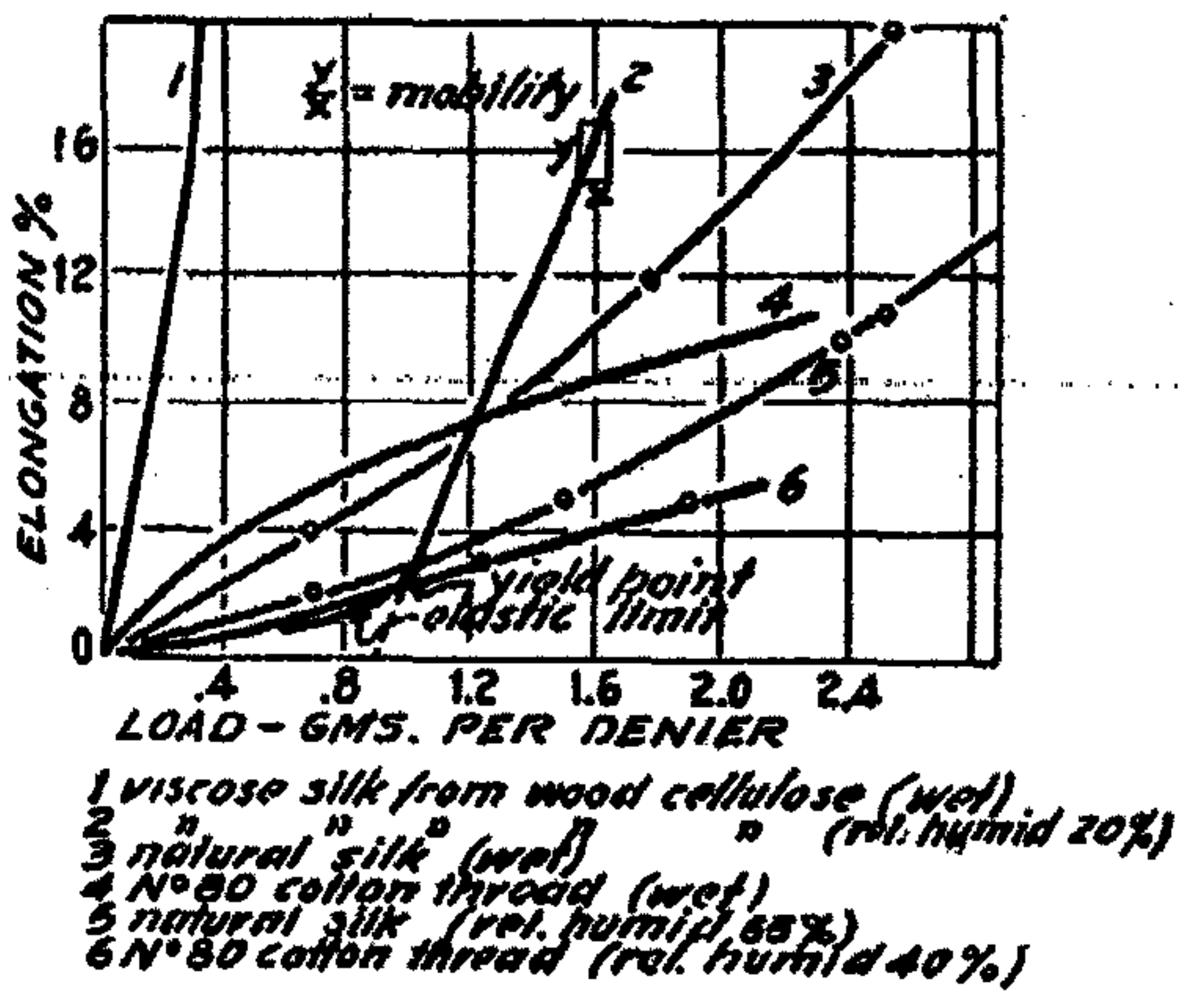

CHART I

Load *vs.* Elongation

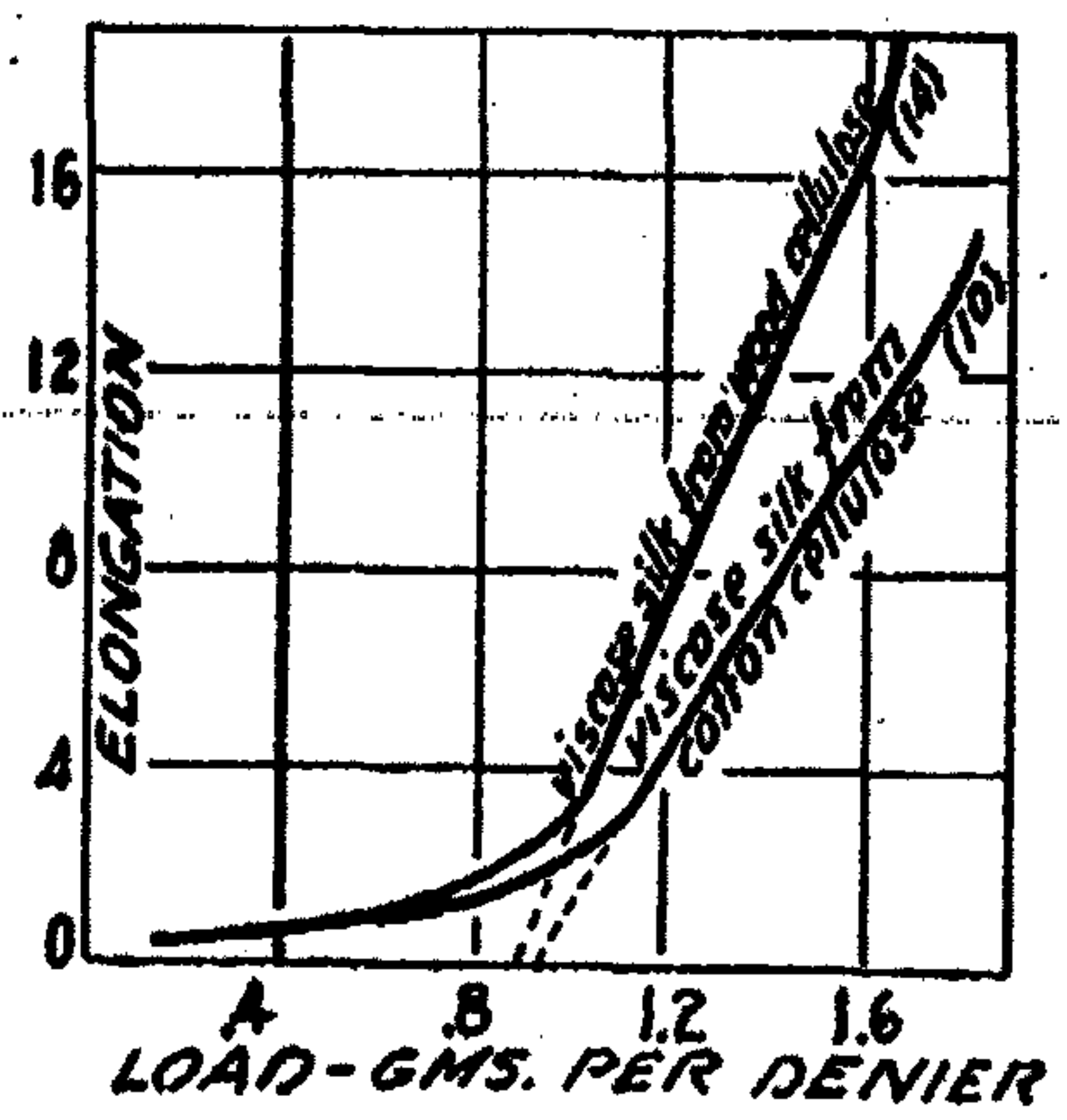

CHART II

Load-Elongation
Viscose Silk-Isodenier—18 Filament
Relative Humidity = 20%.

The mobility and friction value of viscose silk varies with each condition of manufacture. In fact, for reasonable deductions, it is necessary to average the curves of a number of specimens prepared under operating conditions that are identical as far as possible. The influence of processing is illustrated in Chart II, where average curves are shown for silk made from cotton cellulose and wood cellulose by identical procedures.

The degree of stretching of the filaments during the spinning operation has a marked effect on the subsequent plasticity of the material. The friction value increases and mobility decreases with increased stretch. This effect somewhat parallels the effect of the cold working of steels.

The effect of relative humidity on the plasticity of viscose silk is shown in Chart III. A single skein of silk was used for these tests. As the relative humidity increases, the mobility increases and friction value decreases. The large gap between the curves for 97% relative humidity and wet condition is to be expected in view of the tendency of viscose filaments to swell when wet with water. These curves suggest a pronounced lubricating effect of water on the slippage of the cellulose aggregates and emphasize the importance of degree of hydration, or absorptive capacity for moisture, of the cellulose.

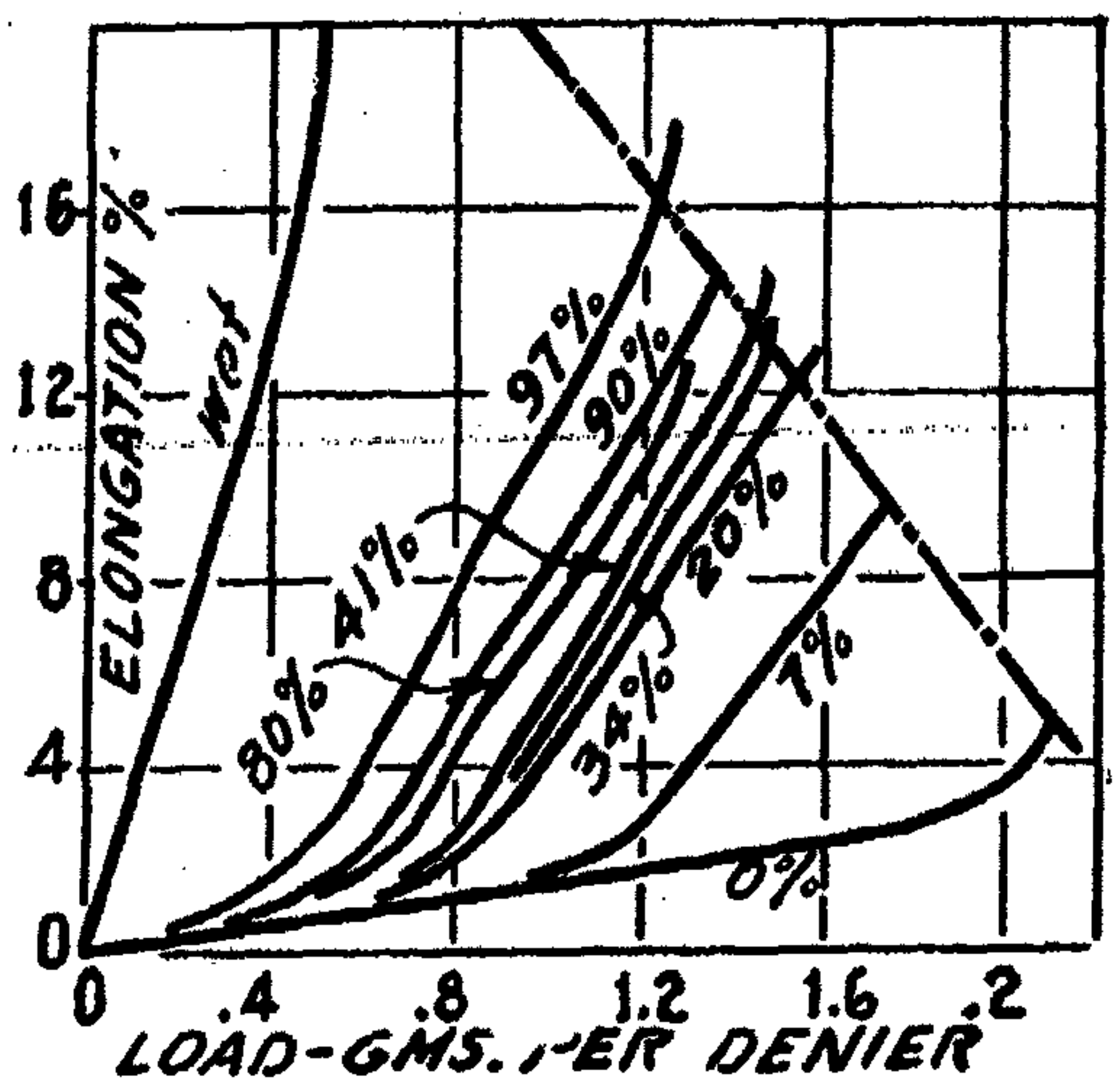

CHART III

Effect of Humidity on Load-Elongation Curve for Viscose Silk

Plasticity of Viscose Solutions

The plasticity of viscose solutions was determined by measuring the rate of flow through a capillary at different pressures. A glass capillary, 16.8 cm long and with an average bore diameter of 3.3 mm was used, the arrangement being such that the viscose solution was drawn by suction from an open container through the capillary into a graduated cylinder. The temperature was controlled to within 0.1° C and the differential pressure to 0.1″ Hg. The time of flow for 100 cc of solution was seldom less than 200 secs.

The performance of this viscometer was tested and standardized by determining the rate of flow of castor oil, these curves being shown in Chart V. Castor oil has approximately three times the fluidity of viscose. The rate of flow for castor oil was found to be directly proportioned to the pressure, as should be the case for a true liquid.

Chart VI shows a rate of flow data characteristic of a technical viscose solution. The solution, containing 7.7% cellulose, had stood at 18° C for 72 hours after mixing. The determination was made at 18° C. The line has been drawn straight in order to bring out the very small friction value. A slightly curved line passing through the origin would connect all points within the experimental error. A very small degree of creep and plasticity is thus indicated.

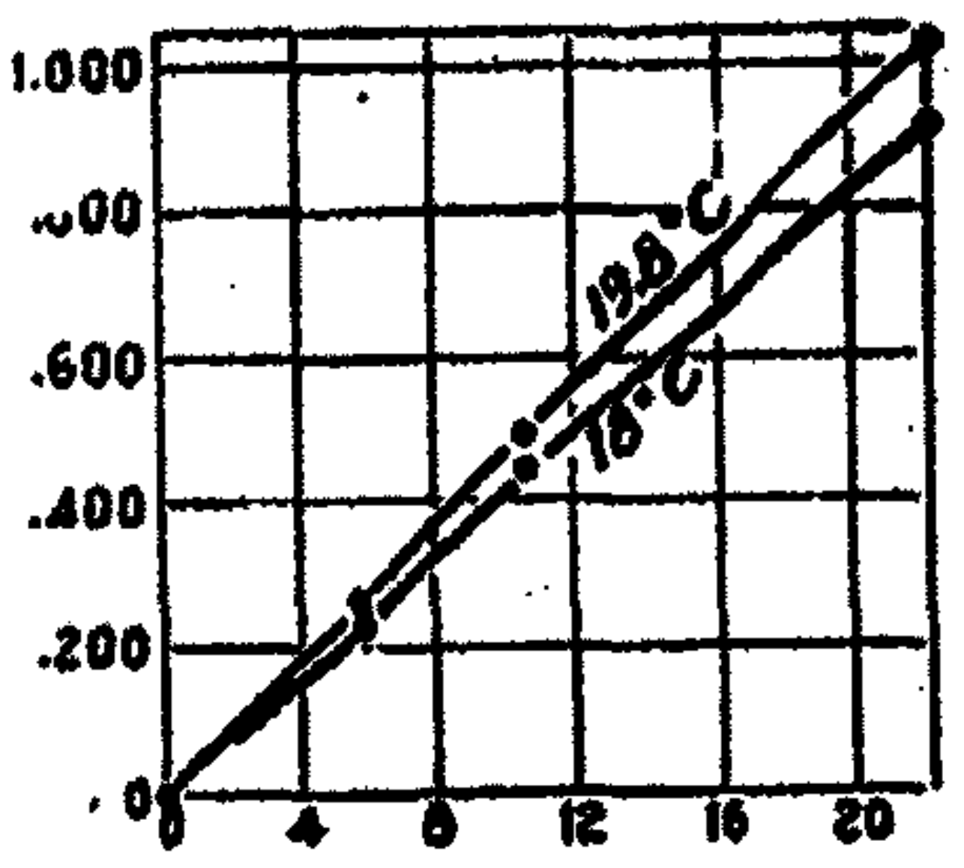

CHART V

Castor Oil—Rate of Flow *vs.* Pressure Viscometer "B".

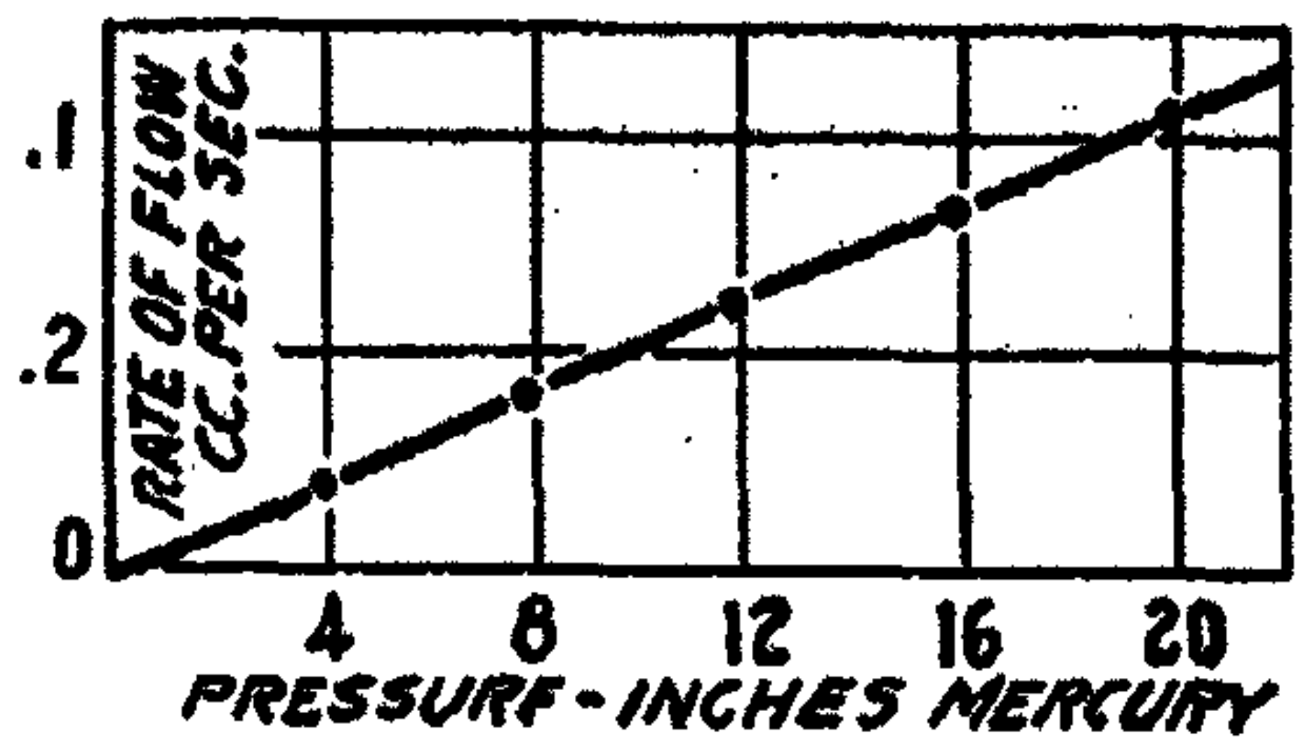

CHART VI

Viscose Solution—Rate of Flow *vs.* Pressure Viscometer = B 18° Cent. Temperature = 18° Cent.

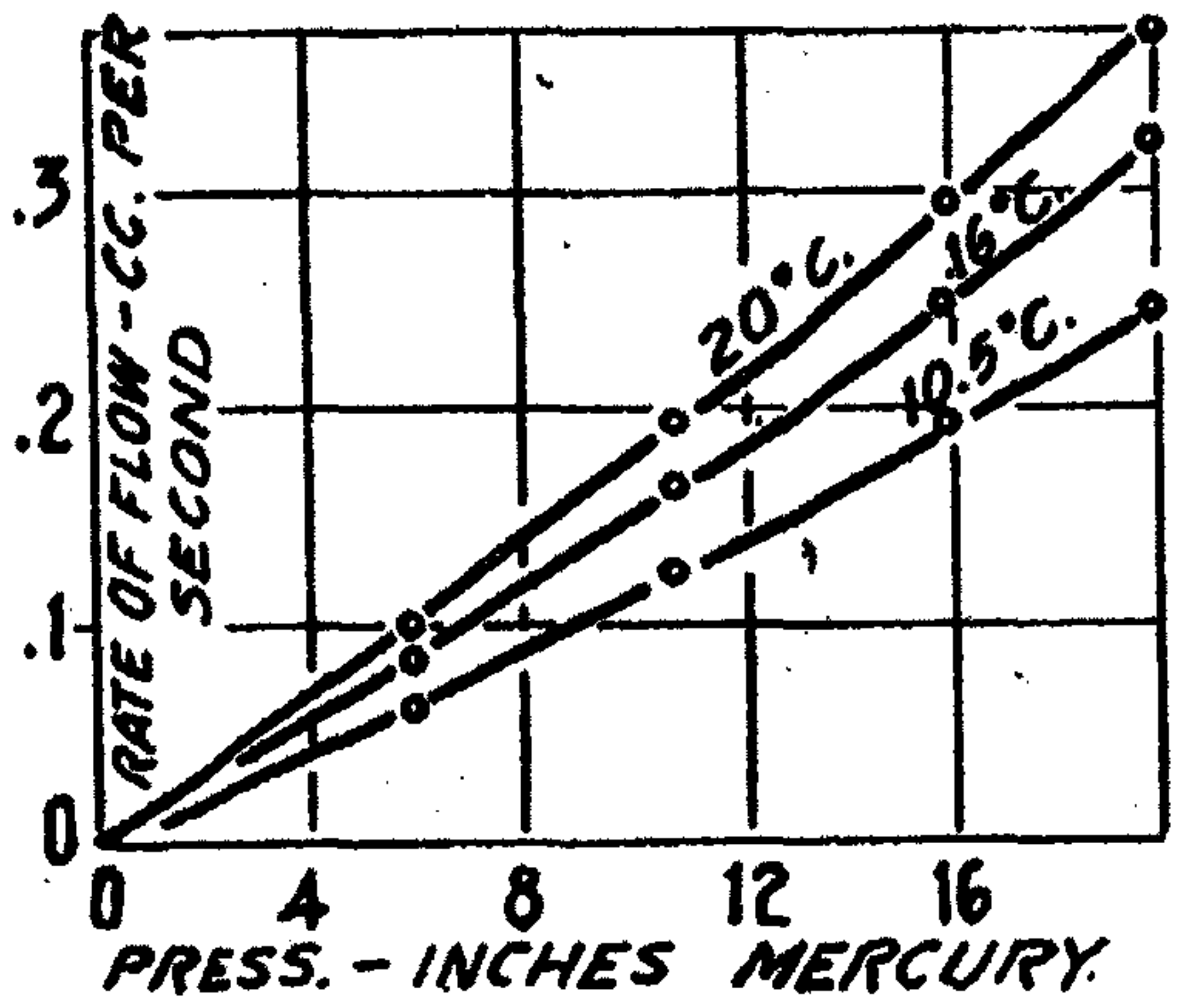

CHART VII

Viscose Solution—Rate of Flow *vs.* Pressure Viscometer "B"

The curved lines have been drawn in Chart VII where rate of flow as against pressure has been plotted for three different temperatures. Straight lines drawn through the last three points for each curve would show that the mobility increases rapidly with the temperature, whereas the small friction value apparently tends to decrease. Undoubtedly friction would increase as the concentration of cellulose is increased.

A viscose solution is seldom used in plant operations at a temperature below 15° C. or at a concentration of cellulose outside the range 7.0 to 9.0%. From the preceding it is seen that within that range a viscose solution follows closely the laws of a viscous liquid. It is to be expected, therefore, that only a very small error would be involved in viscosity measurements made by the gravity efflux method or falling sphere method, and the terms viscosity or fluidity are more or less justified. In actual plant operation, the viscosity of the viscose solution is an important criterion, and for plant control, where relative values accurate to about 3% only are required, these older methods are capable of giving satisfactory results. For investigations requiring an accuracy greater than 1%, only the pressure viscometer should be used.

The effect of temperature on fluidity is shown in Chart VIII. A differential pressure of 22″ Hg was used, and direct comparison made with castor oil, the fluidity of which was taken to be 0.1 at 20° C. Fresh samples from the same lot of viscose were taken for each determination, thus avoiding as far as possible any change in the viscose when maintained at the higher temperatures. Within the range investigated a straight line relationship holds, the slope being rather steep.

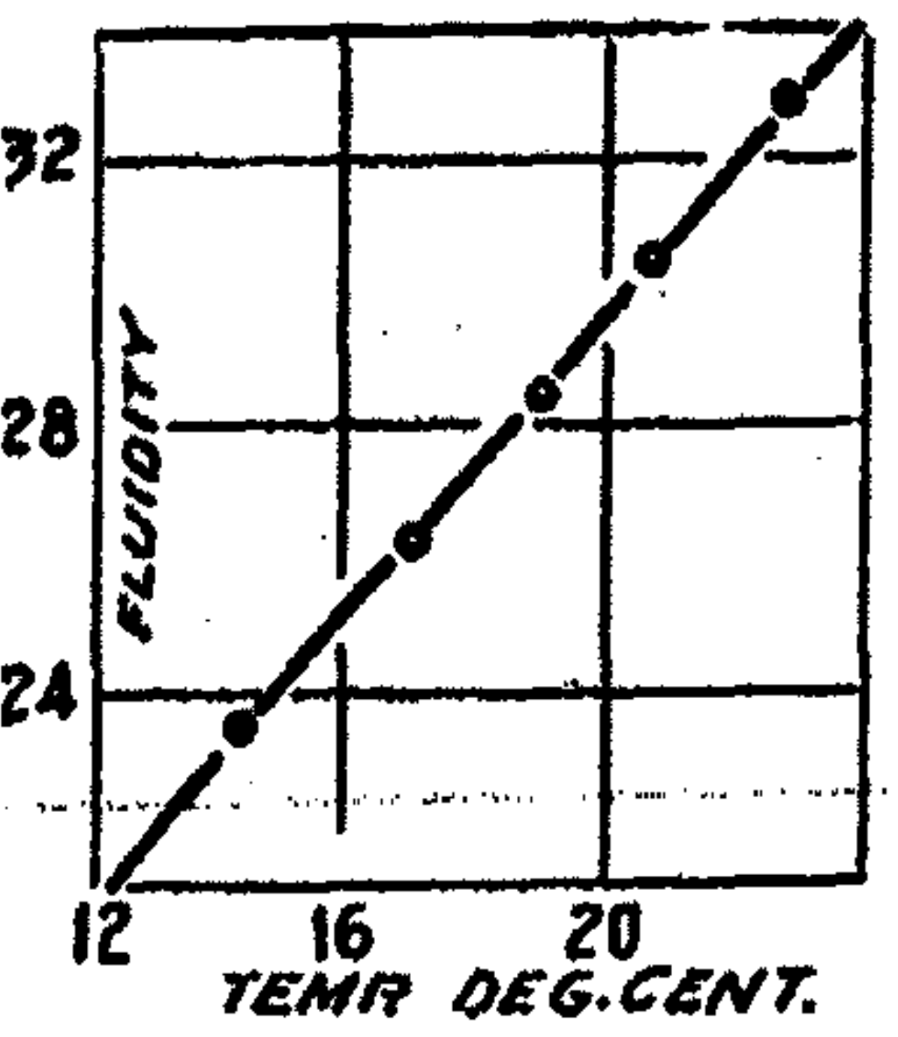

CHART VIII
Viscose Solution—Fluidity *vs.* Temperature.

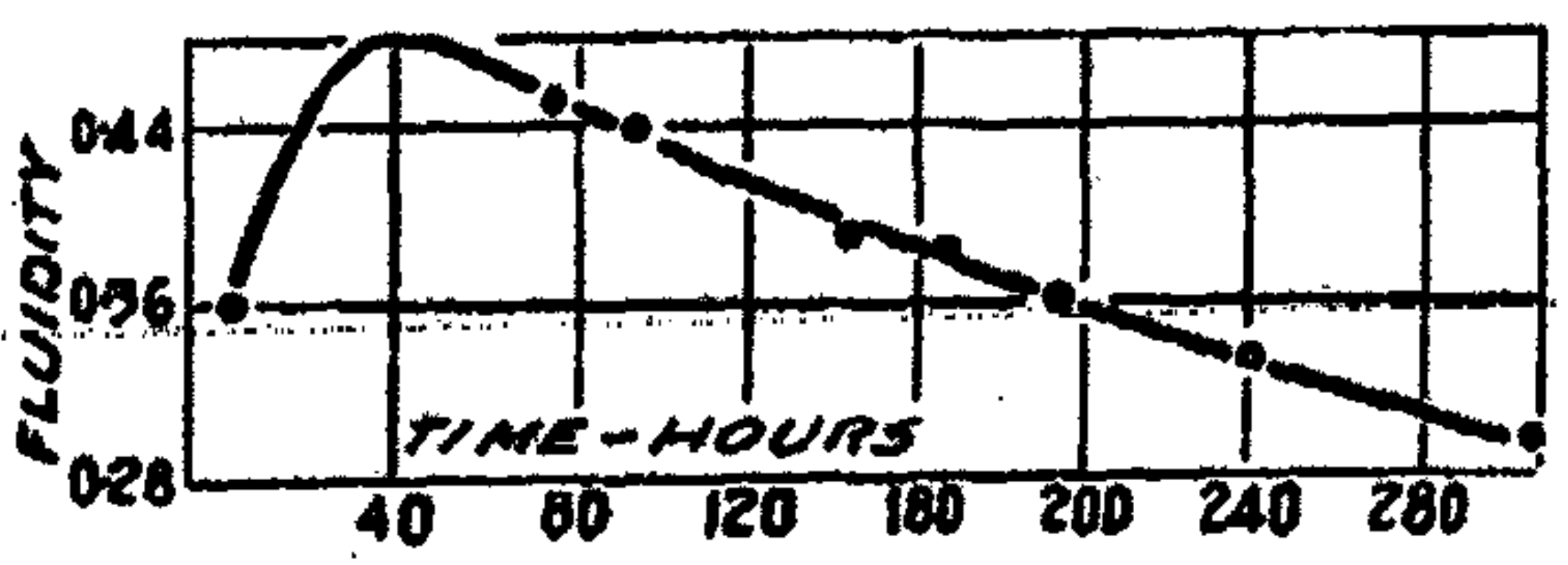

CHART IX
Viscose Solution Fluidity *vs.* Age Temp. 18°C.
Viscometer "B".

The effect of "ageing" a viscose solution is shown in Chart IX, both the ageing process and fluidity determination being carried out at 18° C. This ageing or ripening operation is very important technically, and is also of interest from a scientific standpoint. As yet no really satisfactory explanation has been offered. As a rule the friction values are relatively high for the first 40 hours, but thereafter fall to a more or less constant value.

Conclusions

1. Viscose silk is decidedly plastic in nature, and the determination of its plasticity constants affords valuable information from a technical and scientific standpoint.

2. Curves are given illustrating the effect on the plasticity of the finished silk of modes of processing and of the humidity.

3. Viscose solutions under the conditions of commercial production have only a small degree of plasticity, their behavior being almost that of a true liquid.

4. The effect of temperature and ageing on the fluidity of a viscose solution is discussed.

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PLASTICITY IN RELATION TO CELLULOSE AND CELLULOSE DERIVATIVES*

BY S. E. SHEPPARD AND E. K. CARVER**

Cellulose and its derivatives are similar to other emulsoids in exhibiting plasticity in solution in both sols and gels. A considerable amount of early work on the properties of these solutions has been vitiated, as least as regards its theoretical importance, by failure to recognize the dependence of the total inner friction upon rate of shear. In consequence, many measurements of "viscosity" of these solutions, made at one rate of shear, have been used to generalize too freely. In a valuable paper E. W. J. Mardles[1] remarks "In the last stages of gelation when the sol has a very high viscosity and the falling spheres no longer obey Stokes' law the system assumes the character of a plastic solid such as asphaltum or marine glue since it has elastic properties when a small force is applied for a short time. When a force is applied for a longer time there is plastic flow. Changes continue beyond this stage for a considerable time, the plasticity gradually decreases, and the gel becomes harder and more rigid." While this statement is qualitatively accurate, it is not sufficient to say "In the last stages of gelation," since plasticity can be shown to exist in such solutions at very early stages of "gelation"—depending again upon the concentration and temperature. Although Mardles, in the paper referred to, devotes some attention to the rate of shear in regard to different viscosimeters (Poiseuille-Ostwald, Couette, falling sphere, etc.) he made no systematic study of flow in relation to rate of shear.

With this preface we may pass to consideration of the plasticity of solutions of cellulose itself. Cellulose is dissolved by certain reagents, as ammoniacal cupric oxide solution (cuprammonia), by zinc chloride solutions[2], and by concentrated alkaline thiocyanates[3]. These solutions cannot be regarded as true solutions; the cellulose is strongly hydrated in the process, which is a peptization, and is probably altered both in aggregation and in constitution. But recent work[4] has shown that a study of the viscosity of such cellulose solutions, notably the cuprammonium one, can afford valuable technical information both for the textile manufacturer, and for the manufacture of cellulose derivatives, such as nitrates (celluloid, gun cotton, etc.) and acetates. There exists a danger, however, in the acceptance of "apparent viscosity" measured at one, not always definitely known, shearing velocity, as a com-

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* Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1921).

** Communication No. 225 from the Research Laboratory of the Eastman Kodak Company.

[1] Trans. Faraday Soc., 18, 327 (1923).

[2] Cf. C. G. Schwalbe: "Die Chemie der Cellulose," 153 (1911).

[3] Dubosc: Z. Farbenind. 5, 394 (1906).

[4] Cf. W. H. Gibson and coworkers: J. Chem. Soc., 117, 473, 479 (1920).

plete index of the physical state of the solution. Farrow and Neale[1] used both a falling sphere viscosimeter and a capillary viscosimeter, but without comparison of the rates of shear in the two cases. The use of the falling sphere viscosimeter has been very general in these investigations (cf. Mardles: loc. cit.). W. H. Gibson and L. M. Jacobs are referred to by Farrow and Neale as having "introduced the convenient falling sphere" viscosimeter; actually it had been used in the industry for long previous to their work, and its use of nitrocellulose solutions discussed by Sheppard[2]. None of these authors considered the importance of plasticity and rate of shear in connection with the use of the falling sphere viscosimeter for emulsoids, and this is being investigated at present in this laboratory. Meanwhile it may be noted that for substances showing plasticity there is no necessary validity for the approximate correction for ratio of sphere to diameter of vessel which was obtained mathematically by Ladenburg[3] and adopted by Gibson and Jacobs, Farrow and others. Gibson and Jacobs claim (loc. cit. p. 474) that their results confirm the Ladenburg formula, for not too high values of the ratio, and that further proof of the correctness of this is given by comparison of their value of the viscosity of castor oil with that of Kahlbaum and Raber. They found 9.9 at 20° C., K. and R. give 9.888, and state (loc. cit., p. 478) "The result obtained with the falling sphere viscosimeter is remarkably close to that obtained by Kahlbaum and Raber, and indicates that the instrument may be used with confidence to determine the viscosity of liquids with similar or greater viscosity." As a matter of fact, remarkable closeness indicates nothing of the sort. Gibson and Jacobs make no statement as to the origin, purification, etc., of their castor oil sample. The variation of viscosity of different samples of castor oil, differently prepared, is considerable, and there is no method of selecting or obtaining a true standard of this material. Deering and Redwood[4] in a report on "Castor Oils from the Indian Section of the Imperial Institute", for twenty-three oils found variation of 3 percent over all in the Redwood viscosity at 100° F.; Kahlbaum and Raber (op. cit.) give a value 3.65 poises at 33° C., while J. H. Hyde[5] (Nat. Phys. Lab.) finds 3.80 poises at 33.1° C. for one sample, and others differ again.

Temp.	*Hyde* A	B	*K. and R.*	*Gibson*
20° C.	10.15		9.86	9.90
30° C.	4.68		4.51	
33.1° C.		3.80		3.65

These are much greater differences, and in this laboratory we have obtained variations of the same order. W. H. Herschel's opinion[6] is more favorable,

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[1] F. D. Farrow and S. M. Neale: J. Text. Inst. 157T (1924).

[2] S. E. Sheppard: J. Ind. Eng. Chem. 9, 523 (1917).

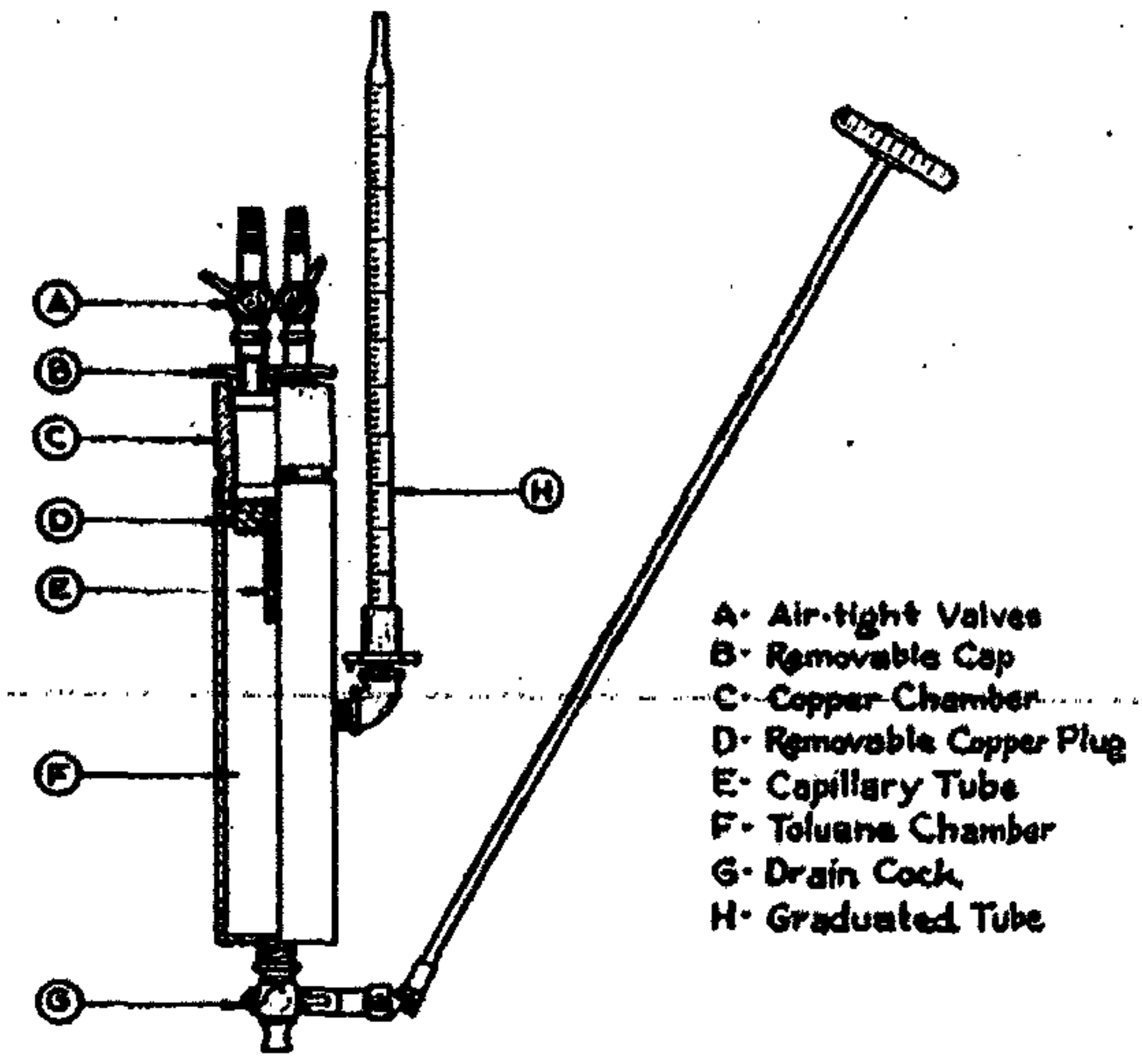
[3] Ann. Physik, (4) **22**, 287 (1907): **23**, 447 (1907).

[4] J. Soc. Chem. Ind. **13**, 959 (1894).

[5] Cf. "Report of the Lubricants and Lubrication Engineering Committee," Department of Science and Industrial Research, Great Britain, 1920, p. 110.

[6] Appendix to Technolog. Paper., No. 112, Bur. of Standards, p. 24.

but is apparently based chiefly on Deering and Redwood's work and that of Kahlbaum and Raber, and he regards the variation as about 2.5 per cent. The validity of Ladenburg's modification of Stokes' law is more seriously in question for colloids. Ladenburg himself[1] used a solution of rosin in turpentine (3 parts colophony and 1 part turpentine oil) following Reiger[2]. He states that Reiger found Poiseuille's law to hold for a solution of this type, of viscosity 10^9 times that of water to within ± 10 per cent, but it is to be noted



MODIFIED BINGHAM PLASTOMETER

FIG. 1

that with tubes of different radius a progressive change in the "friction coefficient" (apparent viscosity) was observed

$$\left.\begin{array}{ll} r = 1.04 & = 5.15\times 10^7 \\ r = .305 & = 6.09\ \text{“}\ \ \text{“} \end{array}\right\} 9^\circ$$

$$\left.\begin{array}{ll} r = .50 & = 6.72\ \text{“}\ \ \text{“} \\ r = .305 & = 8.62\ \text{“}\ \ \text{“} \end{array}\right\} 8.6^\circ$$

for a mixture of viscosity about 6×10^7.

Conclusions as to the validity of Poiseuille's law for "solid" turpentine: rosin mixtures appear very doubtful. For these reasons an investigation was commenced on the influence of rate of shear upon the flow of cuprammonium solutions of cellulose. The preliminary results have been reported by Carver and Folts[3] and will only be briefly referred to here.

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[1] Cp. cit.

[2] Ann. Physik, (4) **19**, 985 (1906).

[3] Ithaca Meeting of the American Chemical Society, September, 1924.

The details of the preparation of the cuprammonium, and cuprammonium cellulose solutions are discussed in the original paper, but it may not be amiss to show the type of plastometer used. In this modification of Bingham's original design, the fluid contained in the space C is forced through the capillary tube into the reservoir F which is filled with toluene. The toluene is forced up into the graduated tube H, and the pressure-flow curve measured by timing the movement of the toluene at various pressures of nitrogen.

The curves of flow; pressure obtained in this way are typical curves for plastic solutions (cf. Fig. 2)

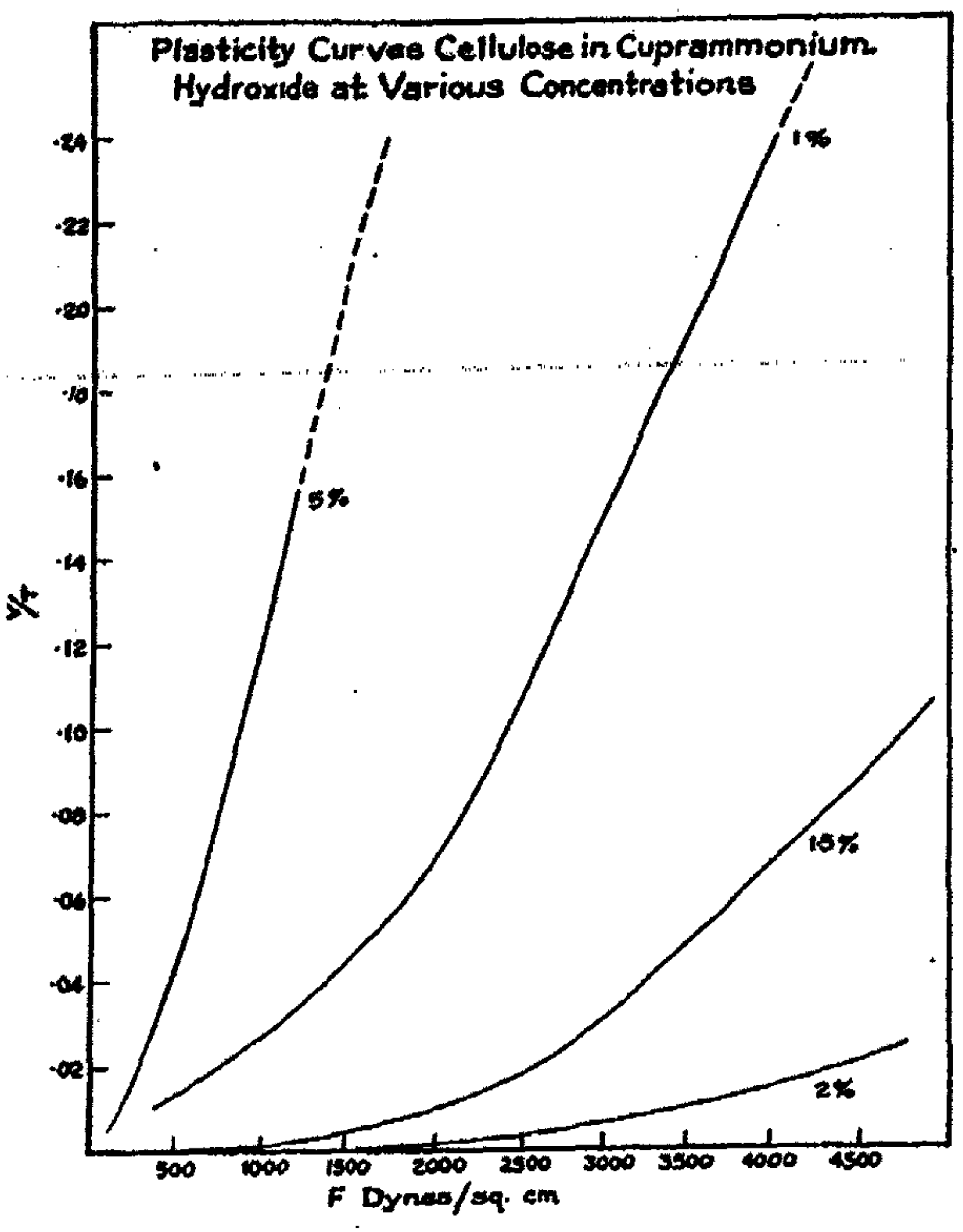

FIG. 2

The nature of the relation between the "yield values" and the cellulose concentration as also between the "mobilities" and the concentrations (and other variables, as temperature) has not been determined as yet but is under investigation. The difficulties in securing reproducibility of the plasticity curves with these solutions are considerable, chiefly due to the effects of small traces of oxygen. It may be regarded as established, however, that the cellulose solutions are plastic. If now the "apparent viscosities" at various rates of shear are plotted logarithmically against the concentrations of cellulose, it is found that the linear relation found by Joyner is only partially confirmed, and at low shearing rates there may be considerable deviations. We are continuing work on the influence of various factors on the flow of cellulose solutions, with the conviction that the flow cannot be properly characterized by one parameter (apparent viscosity) but requires at least two.

Elasticity and Plasticity of Solid Cellulose

a. There has been a large amount of work done on the elasticity of textile fibers and materials. Only the results on single cotton hairs have much interest in the present connection, and while considerable work has been done on the "tenacity" (breaking load) there is not much information on the elastic behavior previous to break.[1]

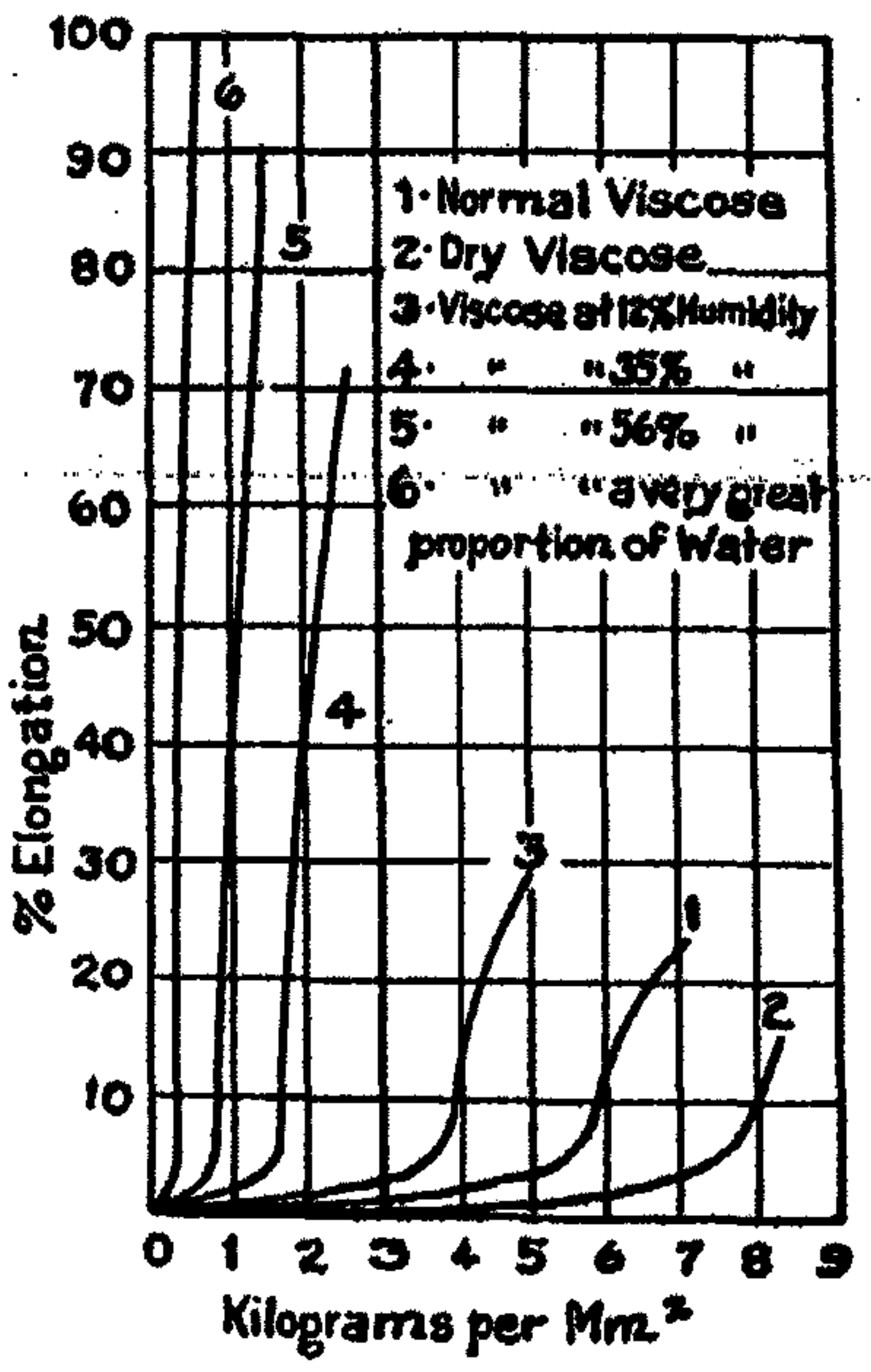

FIG. 3

How far the elasticity of individual cellulose fibers, e. g., cotton hairs, may be related to the plasticity of solutions and strength of subsequent films is quite uncertain. A full and valuable discusion of the nature of fiber elasticity is given by S. A. Shorter[2]. This deals directly with wool fibers, however, and further work on cotton fibers will be awaited with interest. Peirce gives values for the "rigidity" of cotton hairs ranging for different varieties from .010 dynes/cm^2 to .11 dynes/cm^2. The variation is somewhat less for the theoretical coefficient of rigidity n taken for hairs supposed homogeneous cylinders of radius r (with no collapse of walls) going from .029 to .090 $\times$ 10^{11}—from which the average value of .060 $\times$ 10^{11} may be taken. Peirce calculates that "the most probable value of the coefficient of rigidity of the cotton cellulose therefore seems to be about 0.23 $\times$ 10^{11} dynes/cm^2, which is about one tenth that of glass."

Determinations by ourselves of the *modulus* of *elasticity* of cellulose nitrates and acetate films give values of the order 20,000 to 15,000 kg./cm^2, which correspond approximately to moduli of *rigidity* of the order .07 to .05 $\times$ 10^{11} dynes/cm. This would indicate a reduction of rigidity compared with the original cellulose fibers.

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[1] W. Lawrence Balls: "The Development and Properties of Raw Cotton;" J. M. Matthews: "Textile Fibers", 449 (1924); Bowman: "Structure of the Cotton Fiber", (1908); R. S. Greenwood: J. Textile Inst., (Gt. Britain), 10, 274 (1919), on "The Effect of Certain Industrial Processes on the Strength of Cotton Fibers and Yarns". For methods of measurement of elastic constants of fibers, the following references may be cited: Barrett: J. Text. Inst., (1922); Matthews: op. cit., 450 et seq.; F. F. Peirce: J. Text. Inst., 14, 17 (1923).

[2] Textile Inst., 15, 1207 (1924).

b. One form of "regenerated" cellulose, *viz.* from viscose, can be readily tested for elastic properties in film sheet or thread form. The material is considerably affected by moisture.[1] From experiments on sheets it appeared that the modulus of rigidity is higher than that of cellulose nitrate or acetate, but in view of uncontrolled humidity conditions we do not regard this result as conclusive. The accompanying figure, reproduced from Clement and Rivière's work on cellulose[2], illustrates the enormous effect of moisture on the elastic and plastic properties.

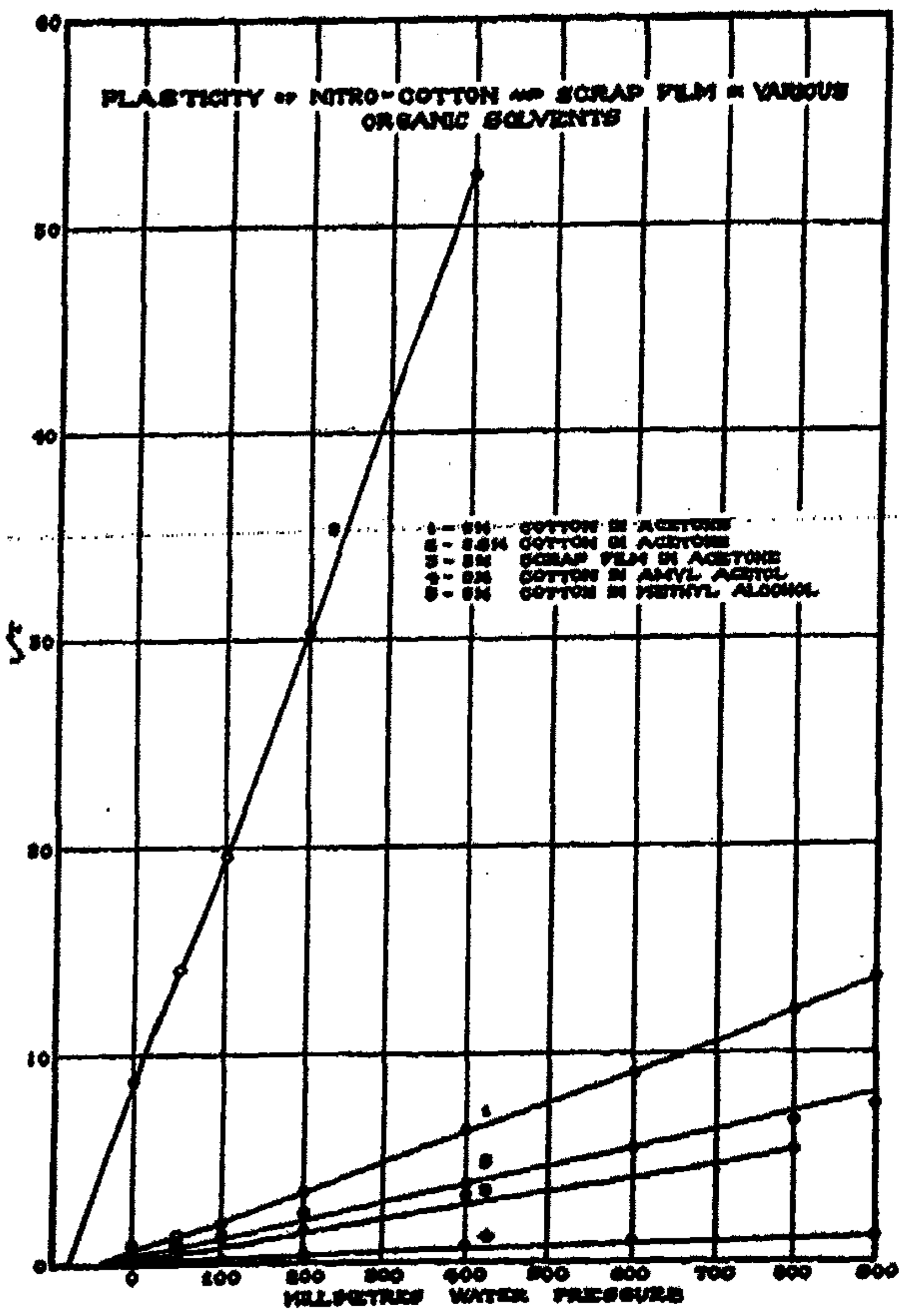

Fig. 4

Cellulose Nitrate and Acetate Sols

It is not necessary to refer to the vast amount of published work on the "viscosity" of cellulose nitrate solutions. Much of it has been of considerable technical value, but the subject has required consideration from the stand-

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[1] See "Plasticity as applying to Viscose and Artificial Silk", C. S. Venable, this Symposium.

[2] "La Cellulose," p. 303 (1920).

point of "plasticity". Shortly after Hatschek[1] had announced the dependence of the inner friction of colloid sols on shearing rate, the flow of collodions, i. e., ether-alcohol solutions of cellulose nitrate was measured in this laboratory, using an Ostwald pipette under different pressures. The flow was found to depend markedly upon the rate of shear, but nothing was published, the results being used only to correct comparative "apparent viscosities". A paper of Bingham[2] makes a valuable contribution to the subject. Briefly summarized, his results showed that the flow is a linear function of the shearing stress, with a definite yield point, for solutions of cellulose nitrate in acetone. As the concentration is raised, or the temperature lowered, the yield value invariably increased. On plotting "yield value" against temperature, a straight line relation was obtained, which indicated a sharp "transition temperature" at 43° C. This was for a 7.7 per cent mixture, and the question as to dependence of the "transition temperature" on concentration was not

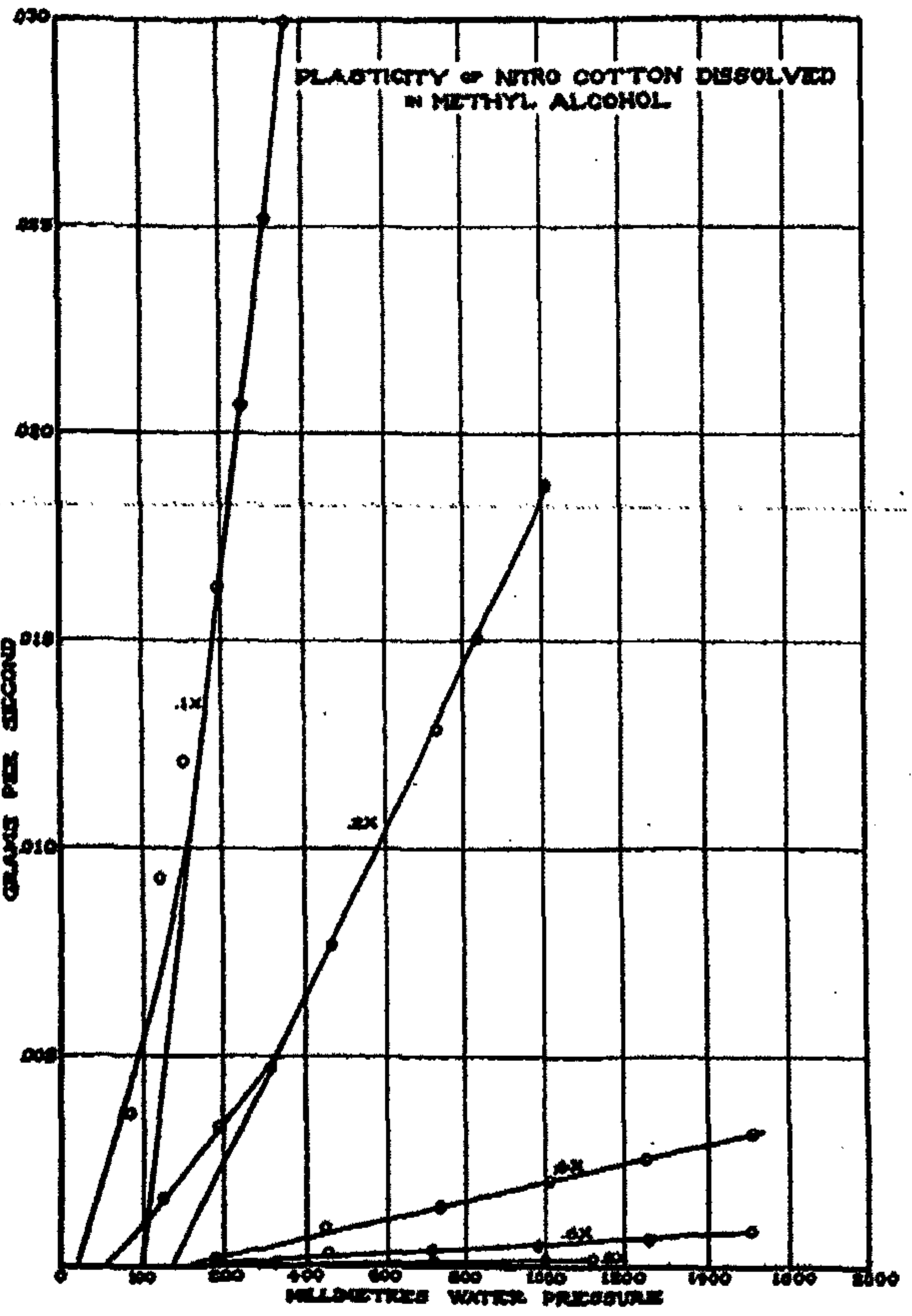

FIG. 5

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[1] J. Franklin. Inst., 194 731 (1922).

[2] Kolloid-Z. 12, 238 (1913).

settled (cf. gelatin). The "yield value" was found to increase very rapidly with the concentration at 20° C., but not linearly, therein differing from clay suspensions.

Bingham points out that the "mobility of nitrocellulose solutions is characterized by its extraordinary depression with very small percentages of solid." This is of course a precise restatement of the well known fact that the "apparent viscosity" of solvated or emulsoid colloids rises very rapidly with concentration of solute. In preliminary work on the plasticity of nitrocellulose in various solvents, it was found that solutions in acetone, methyl alcohol, and amyl acetate respectively all gave flow: pressure curves at 25° C. showing definite plastic yield values. (See Fig. 4).

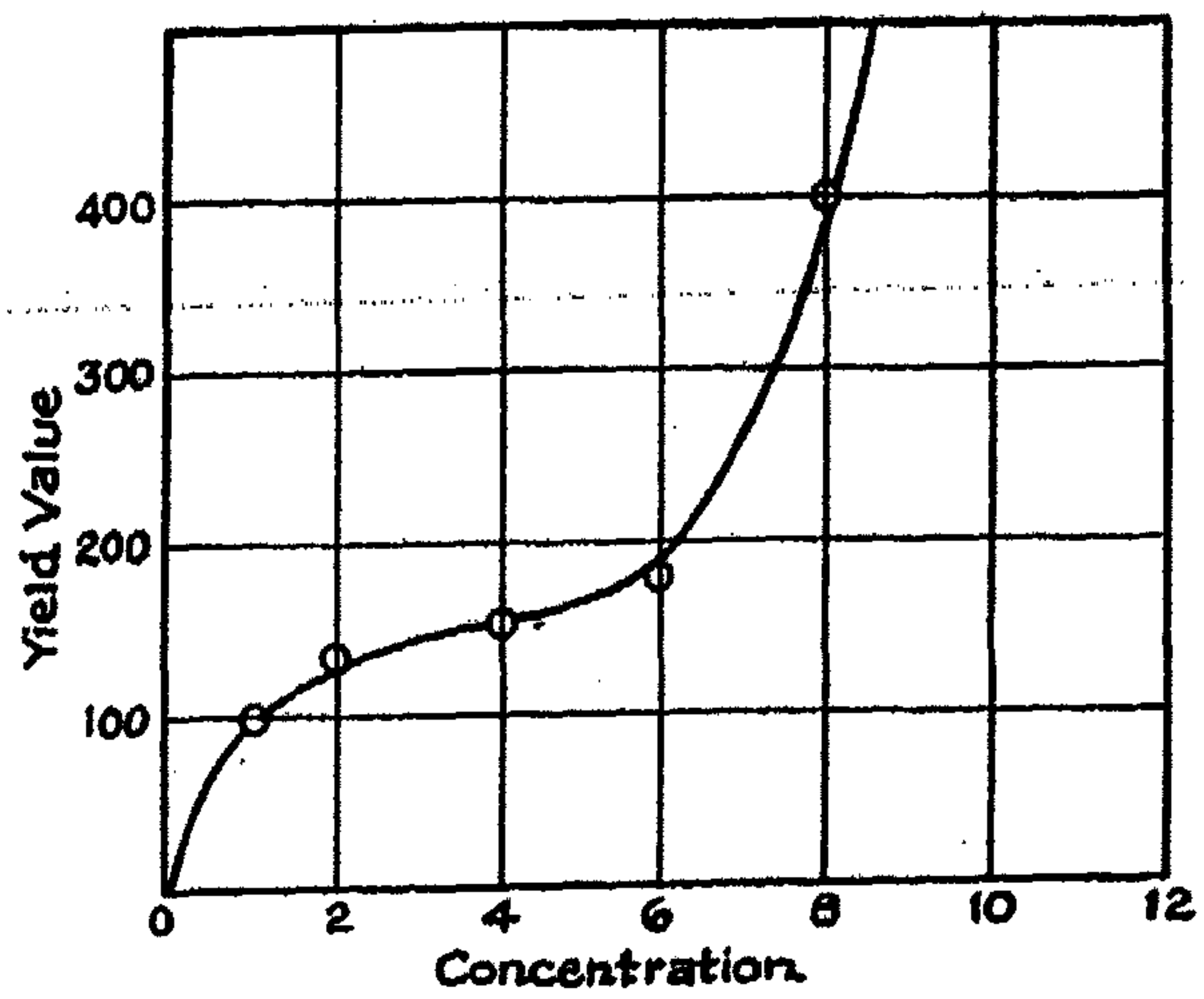

FIG. 6

These results, with a viscosimeter of the Ostwald type, were confirmed with the Bingham plastometer. (See Fig. 5).

In these a series of solutions of nitrocotton dissolved in methyl alcohol were taken, made by diluting an orginal solution of approximately 15 per cent. The "yield values", from the curves, plotted against concentration, are given in Table I.

TABLE I

Yield Value	Concentration
100	.1 x, approx. 1.5 per cent
135	.2 x, " 3.0 " "
153	.4 x, " 6.0 " "
180	.6 x, " 9.0 " "
(400)	.8 x, " 12.0 " "

These give a curve as above: (See Fig. 6).

The particulars of the plastometer capillary in this set were as follows:

Concentration	No.	Diam.	Length
.1 x	6	.273 mm	35.97 mm
.2 x	6	"	"
.4 x	6	"	"
	4	.537 mm.	49.43 mm
.6 x	4	"	"
.8 x	4	"	"

It will be seen that the curve is one of double flexure, differing in this respect from the curve for nitrocellulose in acetone obtained by Bingham[1]. A similar curve was obtained but with less marked inflexion for a nitrocellulose lacquer thinned to various concentrations. Since a mixed solvent: non-solvent combination is used here, these latter results have no great comparative value.

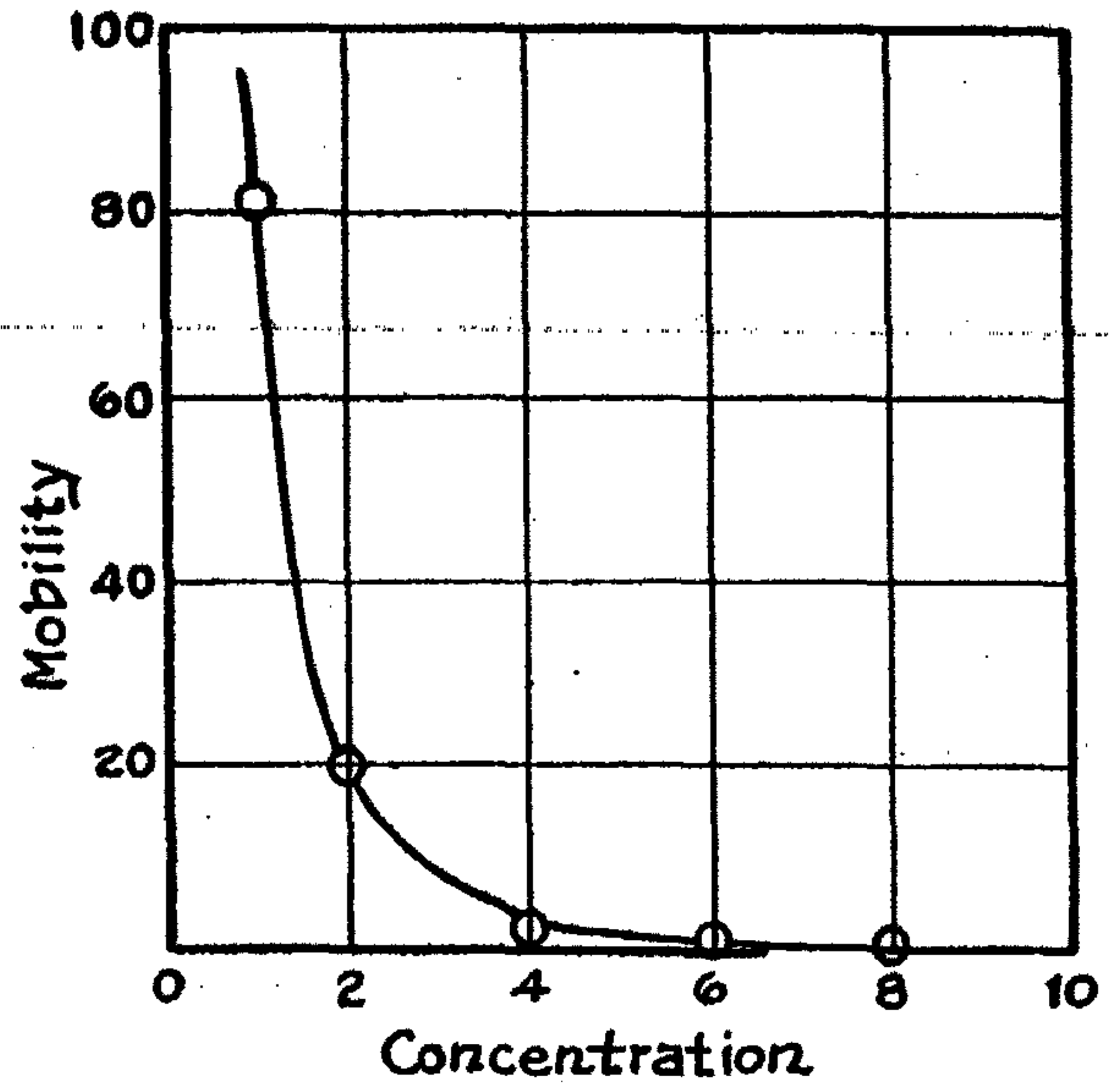

FIG. 7

Further work is in hand to see if this difference is confirmed. For the relation of *mobility* to concentration of nitrocellulose in methyl alcohol a very similar result was obtained as by Bingham for nitrocellulose in acetone.

TABLE II

.1 x	81.5
.2 x	20.0
.4 x	2.3
.6 x	.67
.8 x	.03

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[1] Op. cit., p. 738.

Elastic Properties of Cellulose Nitrate and Acetate Films

Shorter remarks, in the paper referred to, on the lack of knowledge of the tensile elasticity of fibers. "The element of time plays an all important part in such phenomena. Strictly speaking, there is no such thing as a stress-strain diagram of a fiber; the diagrams so-called are really stress-strain-(time) diagrams." This is true, to a limited extent, for the non-fibrous materials derived from cellulose. In a dynamometer we have used for determination of the elastic properties of films of cellulose nitrate, etc., provision is made for autographic recording. The instrument is a Schopper type dynamometer, upon which has been installed a recording device. Instead of a continuously recording pen, the point following the elongation marks off on the record discontinuously, the period being determined by an electric clock which controls the electromagnetic circuit of the stylus. Each chart is therefore at the same time a time chart, while the discontinuous recording avoids lag due to friction. (See Fig. 8).

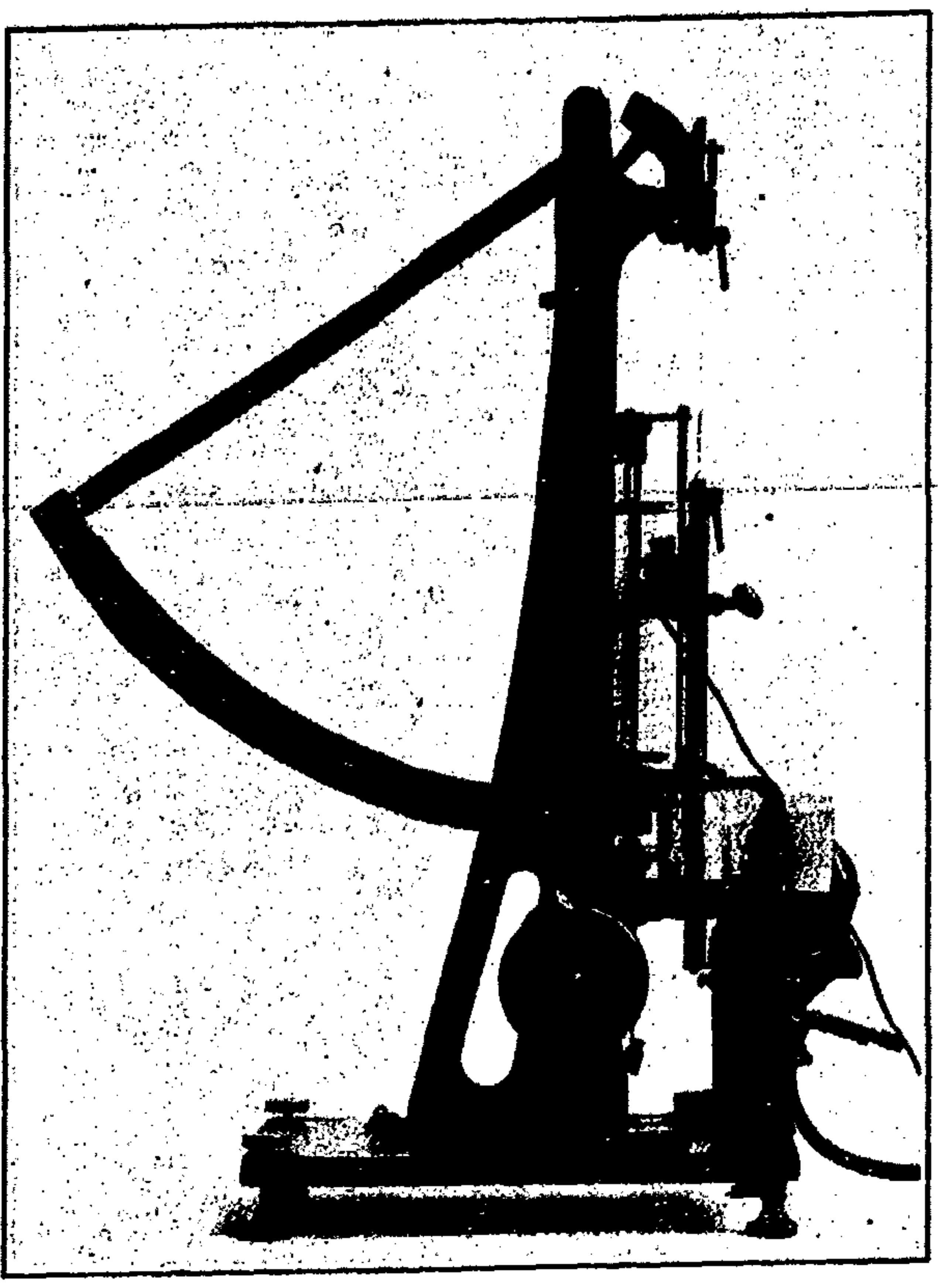

FIG. 8

The typical elastic curve obtained with films of cellulose derivatives is shown in the figure. (See Fig. 9).

It will be seen that the curve consists of several distinct regions (i) an initial straight line, in which the material obeys Hooke's law fairly closely. Deformation is not permanent, i. e., the time of relaxation is very small (ii) a curved portion, where the limit of elasticity is reached, and irreversible effects begin (iii) an upward portion, when plastic flow is evident (iv) a further apparently elastic portion previous to break.

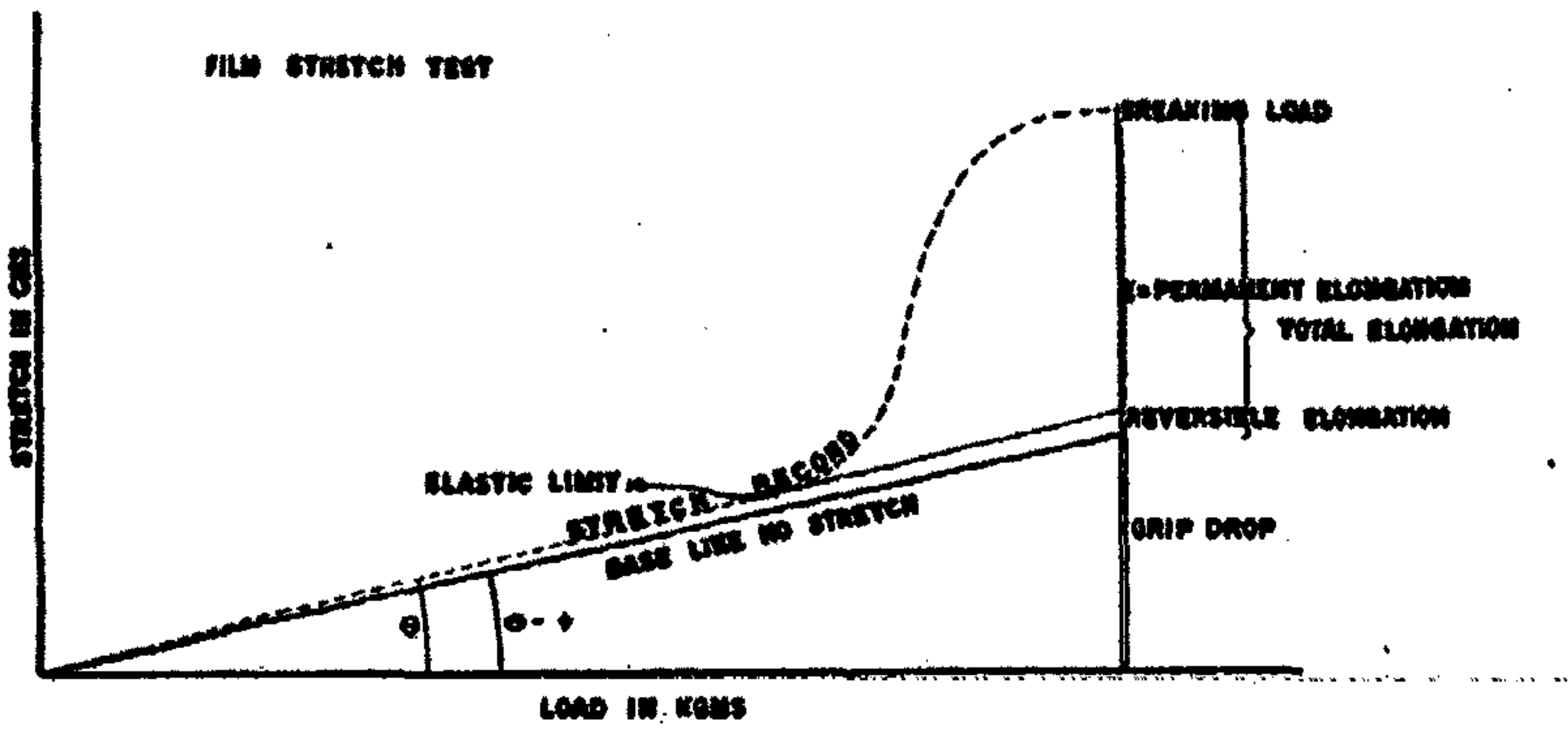

FIG. 9

Actual records are shown in the following figures. (See Figs. 10, 11, and 12).

The results with cellulose nitrate and acetate respectively may be compared with those given by other observers. For pure esters, i.e. without softeners or fillers, Clement and Rivière give the following comparison

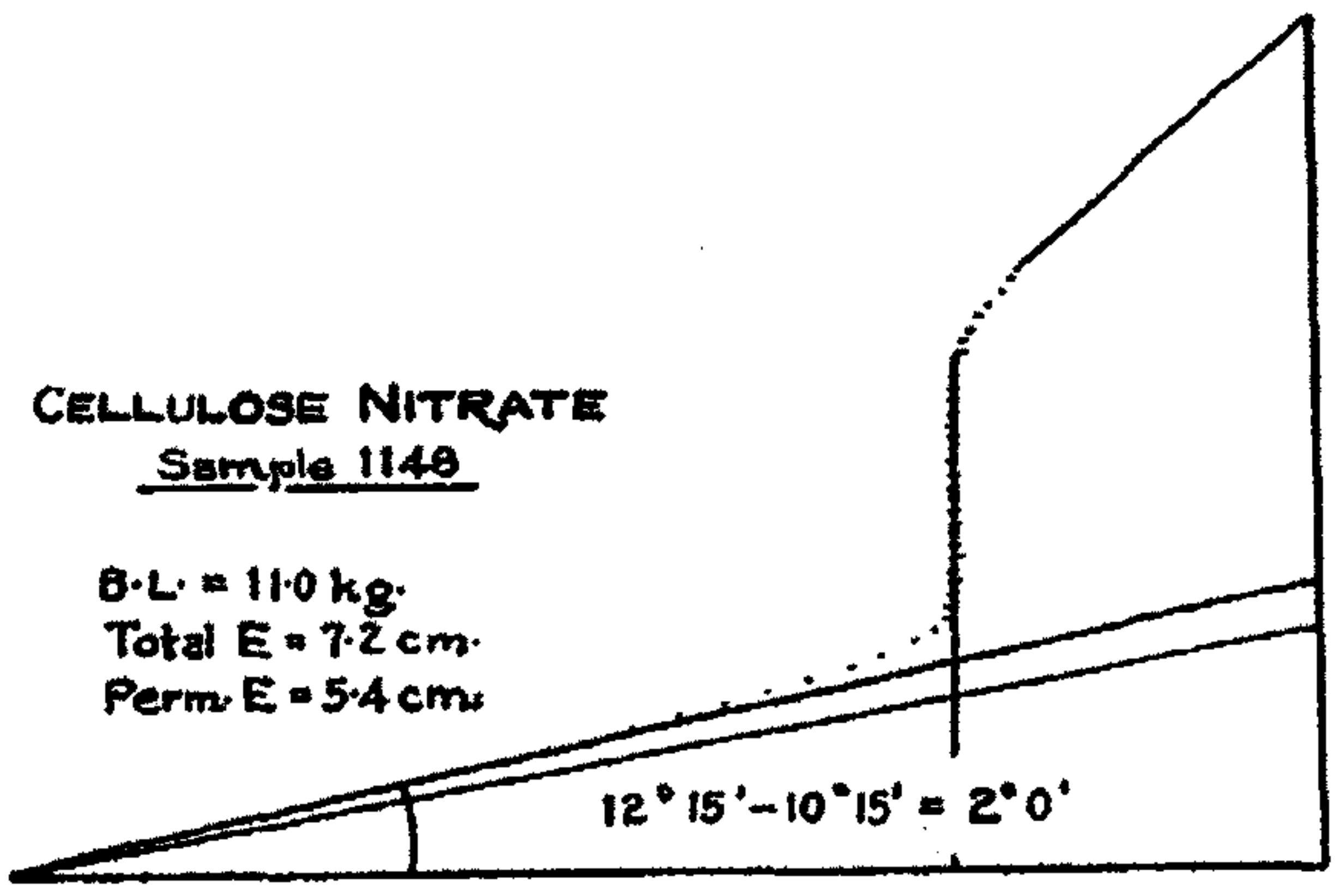

FIG. 10

Substance	Breaking Load kg./mm²	Elongation at Break	Folds No.
Cellulose nitrate	10.1	18.5	50
Cellulose acetate	9.6	14.4	45

It is necessary to state that the values depend very much on the method of manufacture.

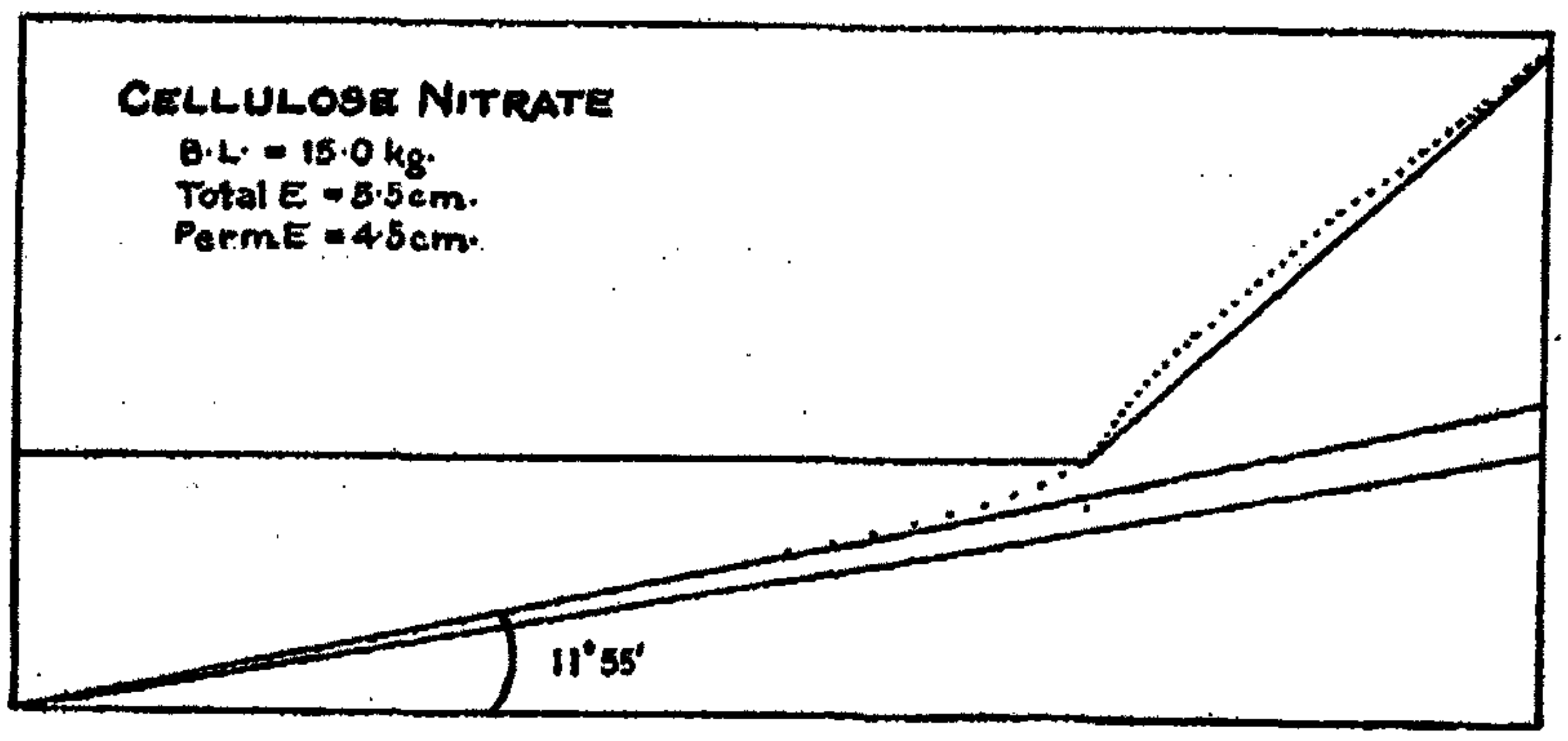

Fig. 11

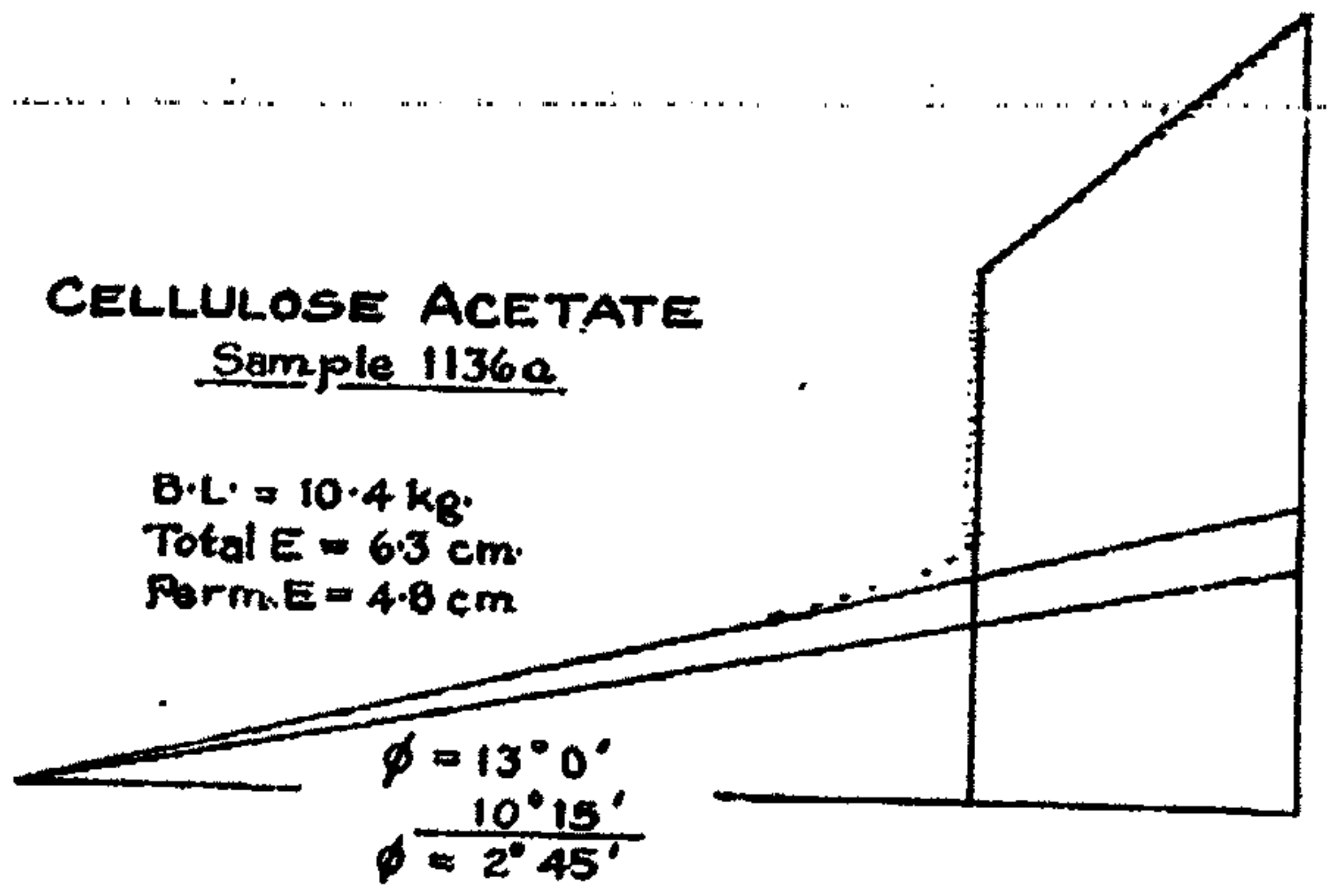

Fig. 12

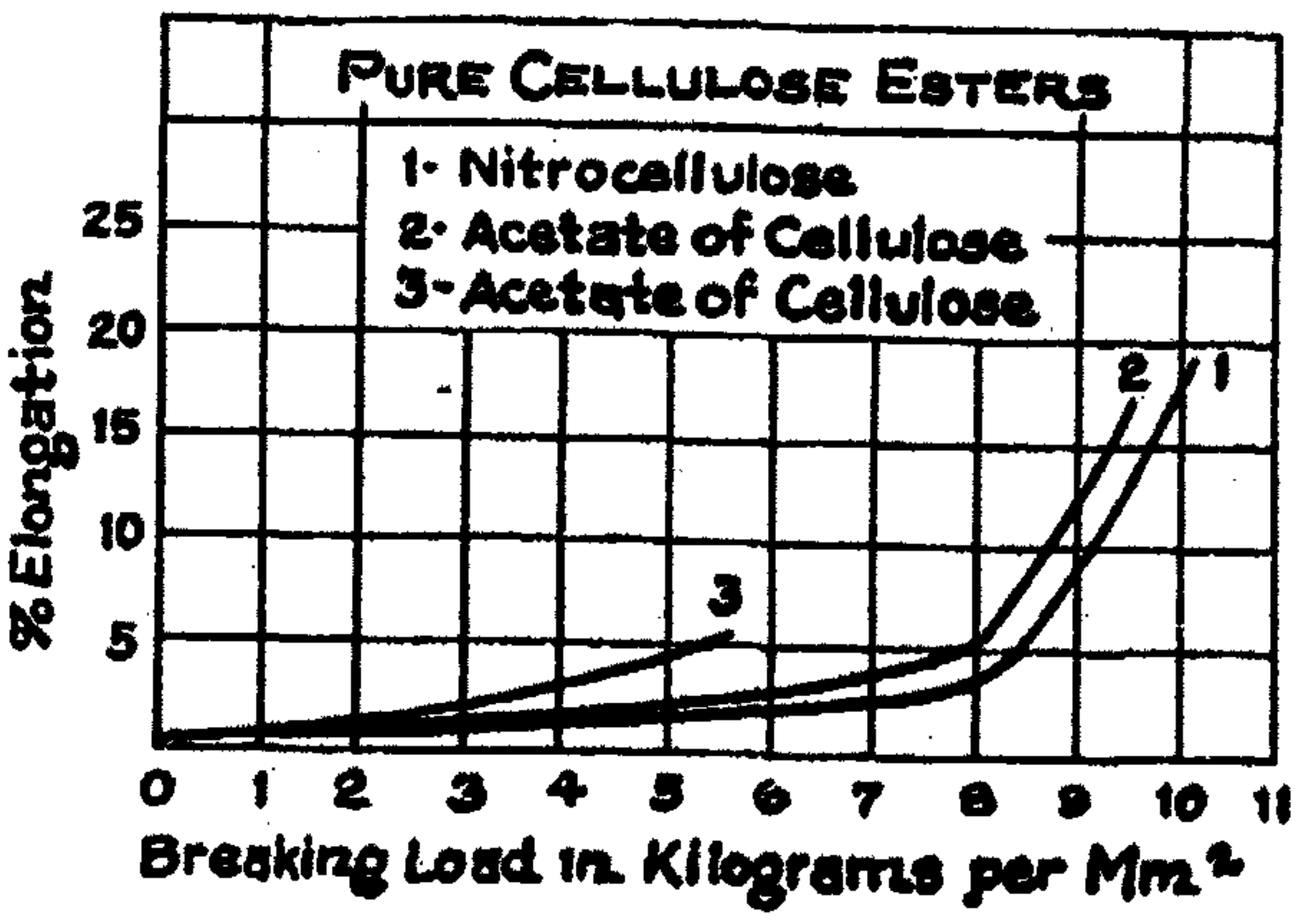

Fig. 13

It will be seen by comparing Figs. 10 and 11 that there may be considerable differences in the elastic behavior past the elasticity limit, depending upon the pretreatment. The pseudo-plastic flow may be greatly increased, and no second period of "perfect elasticity" reached before break. As would be expected, such material shows definite hysteresis on reversing the extension.

As has been pointed out by Clement and Rivière[1] in connection with reversing or alternating traction the greater the number of tensile cycles a material can undergo within a certain definite limit of stress, the greater the value of the material. This is an index that the residual elongation (up to the limit of stress employed) keeps small, in which case the area of the hysteresis loop is the least possible. The behavior under reversing stress is therefore the essential matter in so-called "folding tests" for cinematograph films and the like. The number of folds registered prior to break is approximately the number of hysteresis cycles which the material is capable of enduring within a given limit of stress. Clement and Rivière also state, apparently in specific reference to cellulose esters[2] that after three or four cycles there is practical reversibility. Mardles[3] regards this as supporting his theory of the "development of a metastable phase" of which more later. But it may be remarked here that this tendency to reduction of the hysteresis loop area with increasing number of cycles depends not only upon the composition of the plastic material, but upon the limit stress chosen. Referring again to the typical diagram (Fig. 9), if the limiting stress is chosen at or

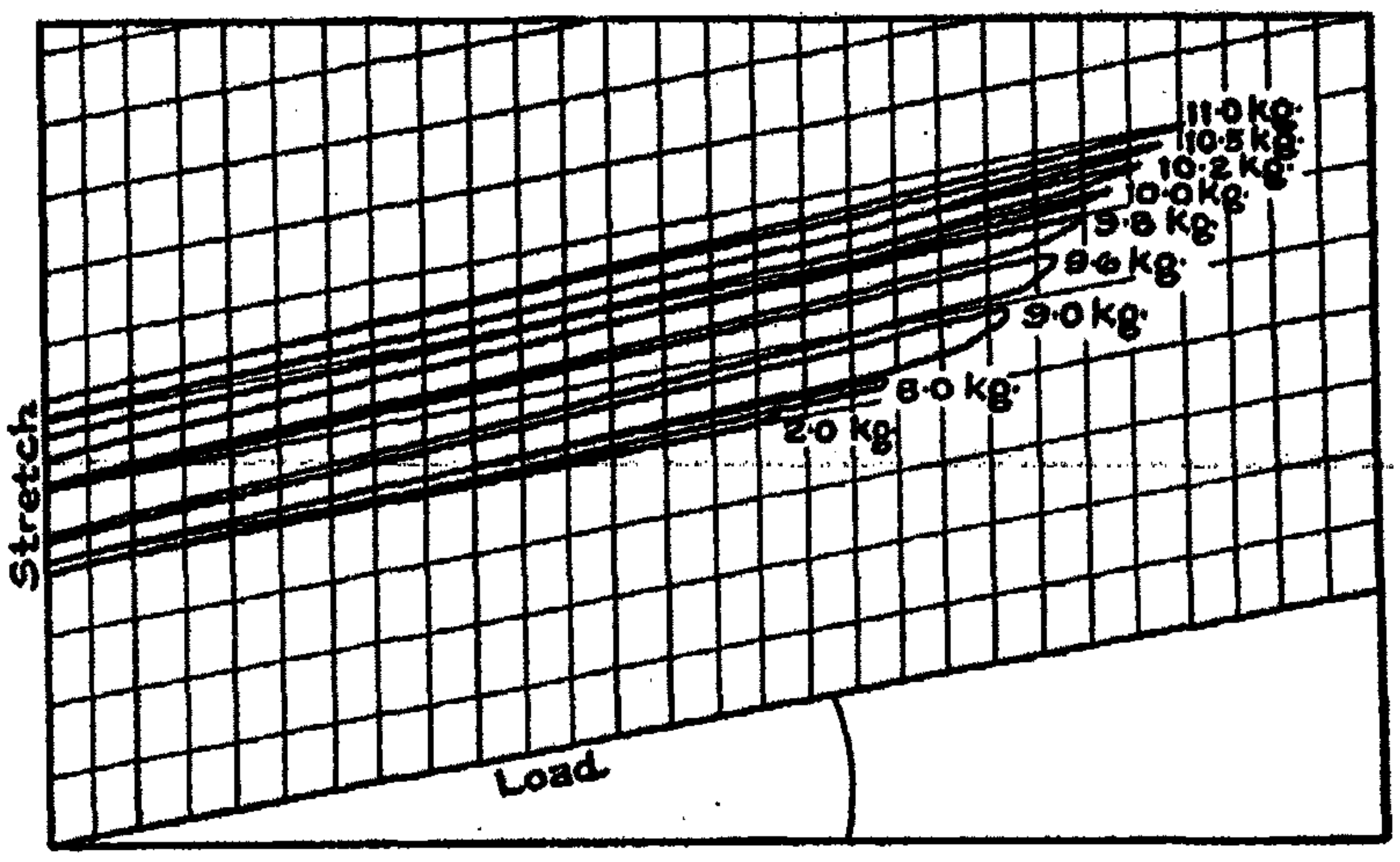

Fig. 14
Hysteresis loops with cellulose nitrate film

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[1] "La Cellulose," p. 298.

[2] Ibid, p. 298, Quoted with reference to cellulose esters by Mardles: Trans. Faraday Soc., 19, 124 (1923).

[3] Op. cit. p. 124.

below the elastic limit, point A of curve, the areas are small and the cycle soon becomes practically reversible. If, however, the limiting stress is taken up to the plastic flow value, the loops are large and do not tend to diminish so rapidly. More work is required with alternating loading applied at different speeds and with different limits before very definite conclusions can be stated. It is, however, in general correct to state with Clement and Rivière that these plastics (celluloids) behave similarly to certain metals on "cold working". The elastic resistance (rigidity) increases, and the specific elongation diminishes, the material becomes more brittle.

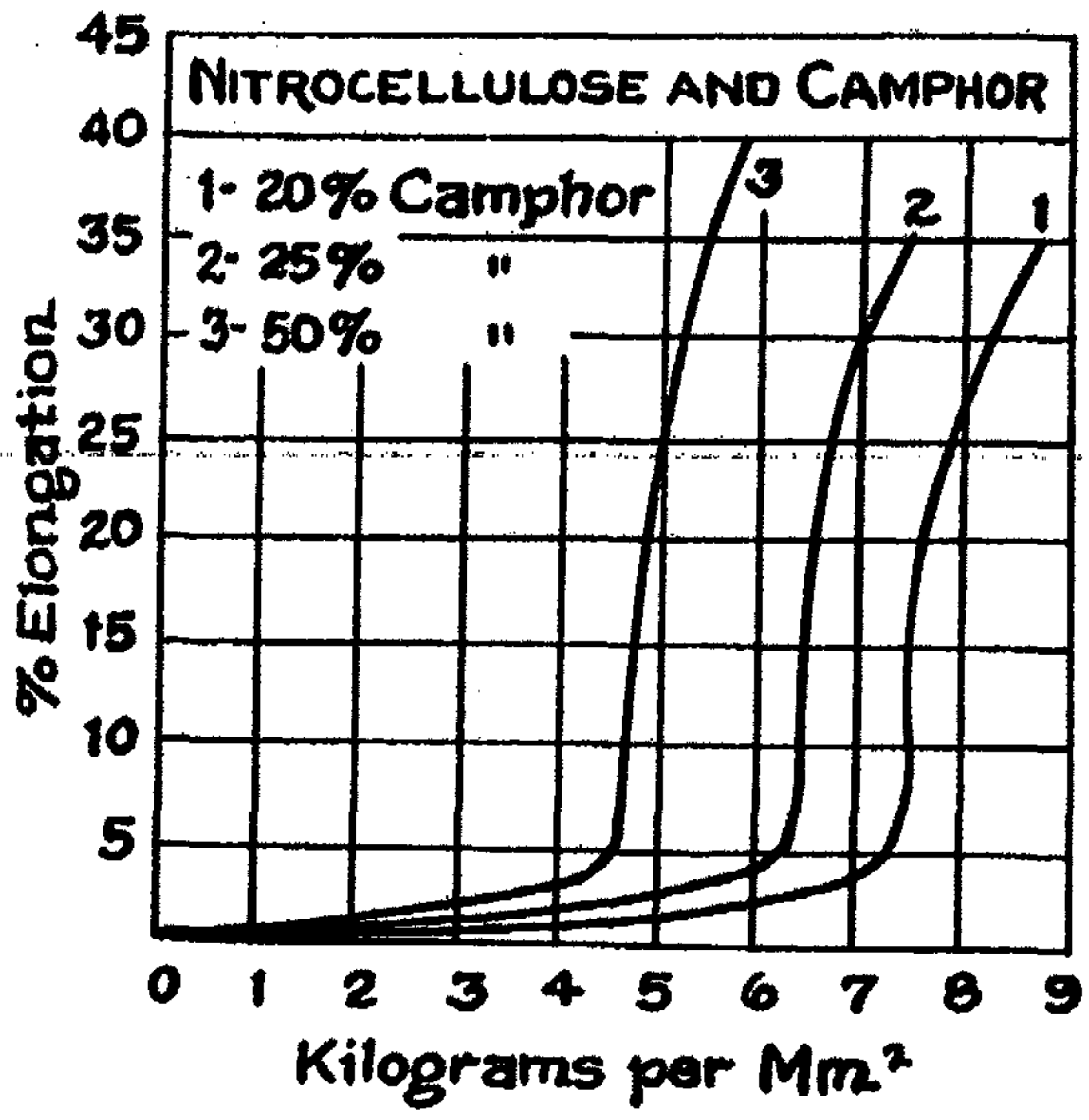

FIG. 15

Influence of Composition

An enormous number of factors influence the elastic behavior of plastics etc. prepared from the cellulose esters. Not only mechanical treatment, just discussed, but temperature, humidity, age, mode of preparation, additions of other substances, are all of great importance. The influence of the last named, or total composition, really requires study in relation to each of the other factors mentioned, but examples of an effect of composition upon plasticity with approximate constancy of the other variables, are of interest. The most noticeable addition agent affecting this is camphor with cellulose nitrate, which greatly changes the mechanical and thermoplastic properties. In general the breaking load and the modulus of elasticity decrease, while the region of pseudo-plastic and plastic flow is increased, as the amount of camphor is increased. This is illustrated in the above set of curves from Clement and Rivière[1].

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[1] Op. cit.

They may be compared with the results of Brandenburg and Mark[1] which give a similar result. On the other hand Heymans and Callingaert[2] find that the modulus of elasticity shows a slight increase up to 18 per cent camphor, then a steady decrease. The change does not appear to be large, however, and the elastic and plastic behavior requires further study at different temperatures. The influence of moisture content and humidity,—which might also be considered as a composition factor—is of great importance quantitatively and practically, but is of less importance qualitatively, that is, does not greatly affect the plastic behavior[3].

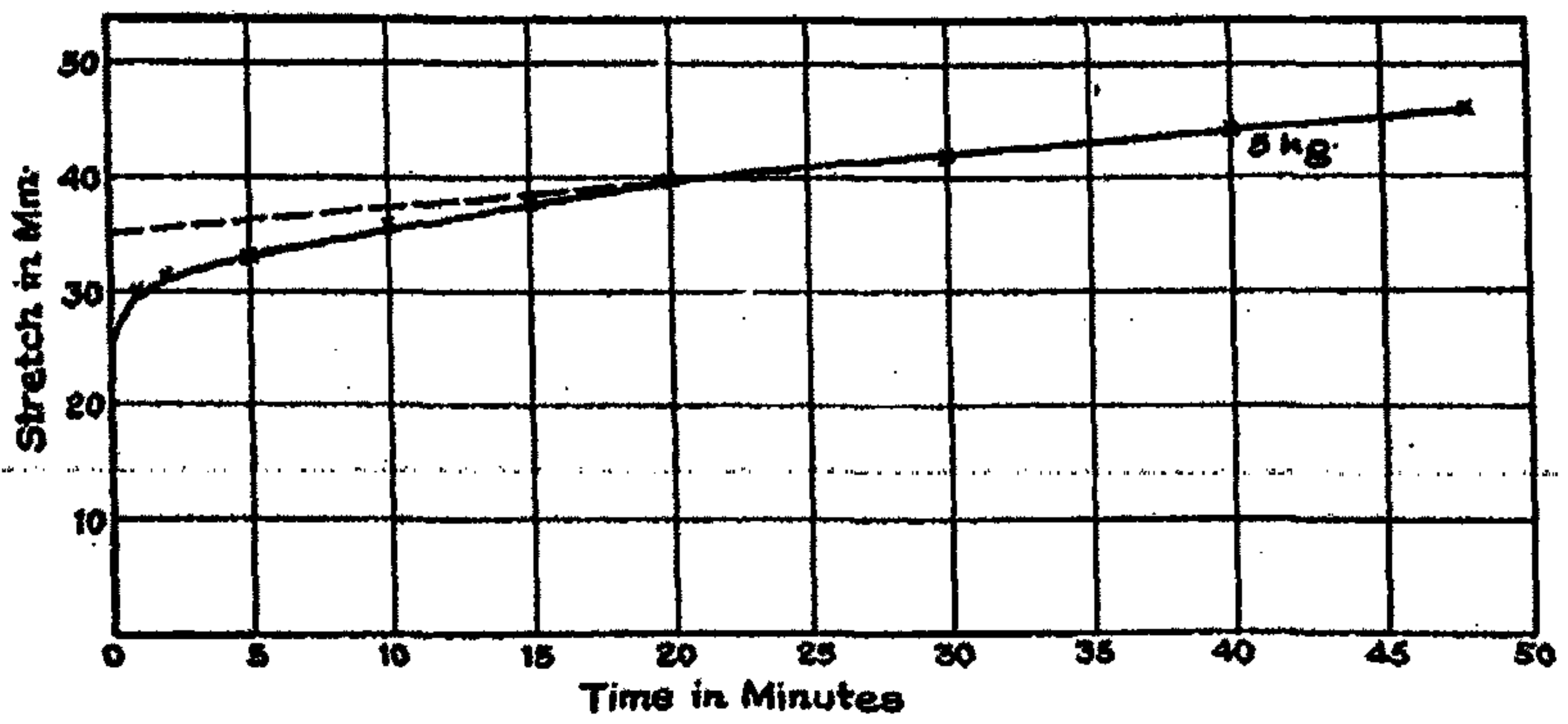

Fig. 16

Behavior under Steady Loads

The behavior under steady loads beyond the elastic limits is such as might be expected in comparison with soft metals (Dalby et al.). In Fig. 16 is shown a typical curve for a film loaded moderately (lower elastic limit). At first there is a very rapid reversible elongation. The strain then increases with time fairly rapidly, then more slowly until a constant rate is reached. This is quite similar to the results of Trouton and Rankine with lead wire, cited by Bingham[4]. If greater loads are then superposed, secondary periods of elastic deformation are followed by steady periods of flow of increasing rate (See Fig. 17) until the breaking point is reached. On plotting the slopes of the elongation: time curves for the steady periods against load, a smooth curve is obtained. It might be thought that this would be a typical flow: time curve (plasticity curve), but on plotting the logarithm of the velocity of stretch against logarithm of load, a straight line is obtained. This indicates (cf. Fig. 19) that there is at any rate a continued curvature of the velocity: time curve, and no linear relation of flow and time.

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[1] Kolloid-Z. 34, 12 (1924).

[2] Ind. Eng. Chem. 16, 939 (1924).

[3] This statement is relative to the material. With regenerated cellulose the effect of moisture (hydration) is very large, with cellulose acetate it is much less, but still greater than with cellulose nitrate.

[4] J. Franklin. Inst., 194, 115 (1924).

The results obtained with cellulose acetate film by Mardles[1] are shown in Fig. 20. In this case a film 28 x 2 cms. thickness 0.17 mm. was loaded at 20° C. with 1000 grams. The immediate reversible extension corresponds to a Young's modulus of elasticity of 0.08×10^{11} dynes/cm², while the immediate retraction was smaller, the original state not being approached until after several hours. Mardles notes that the rate of disappearance of strain did not appear to follow Maxwell's expression

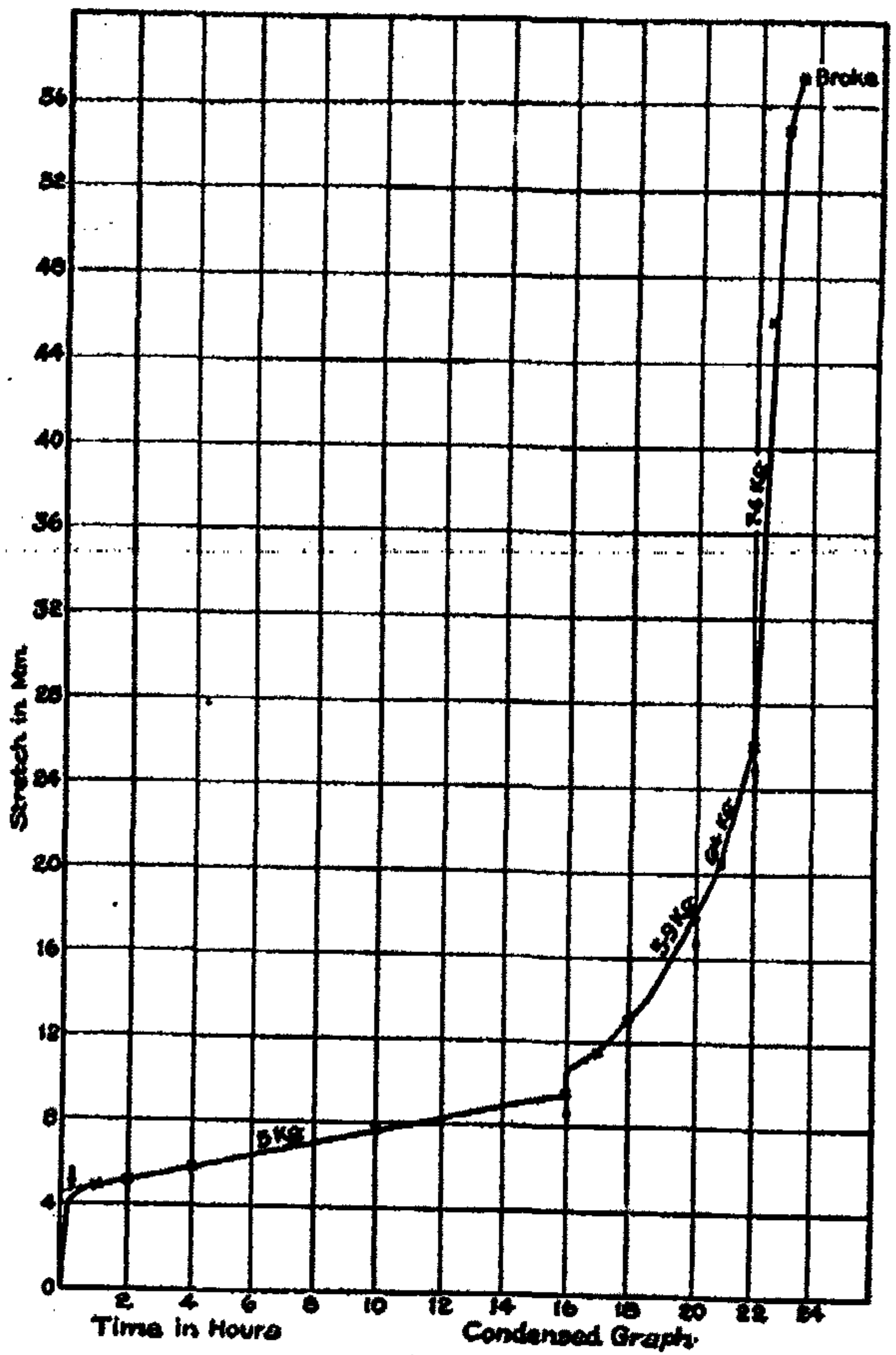

FIG. 17

$$W = W_0 e^{-\lambda t},$$

Conclusion

Measurements on the sols of cellulose and cellulose derivatives—these latter being organosols—show that plasticity is evident in the sol state. The work of Mardles[2] on the reversible sol-gel transition of solutions of cellulose

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[1] Op. cit.

[2] Trans. Faraday Soc., 18, pt. 3 (1913).

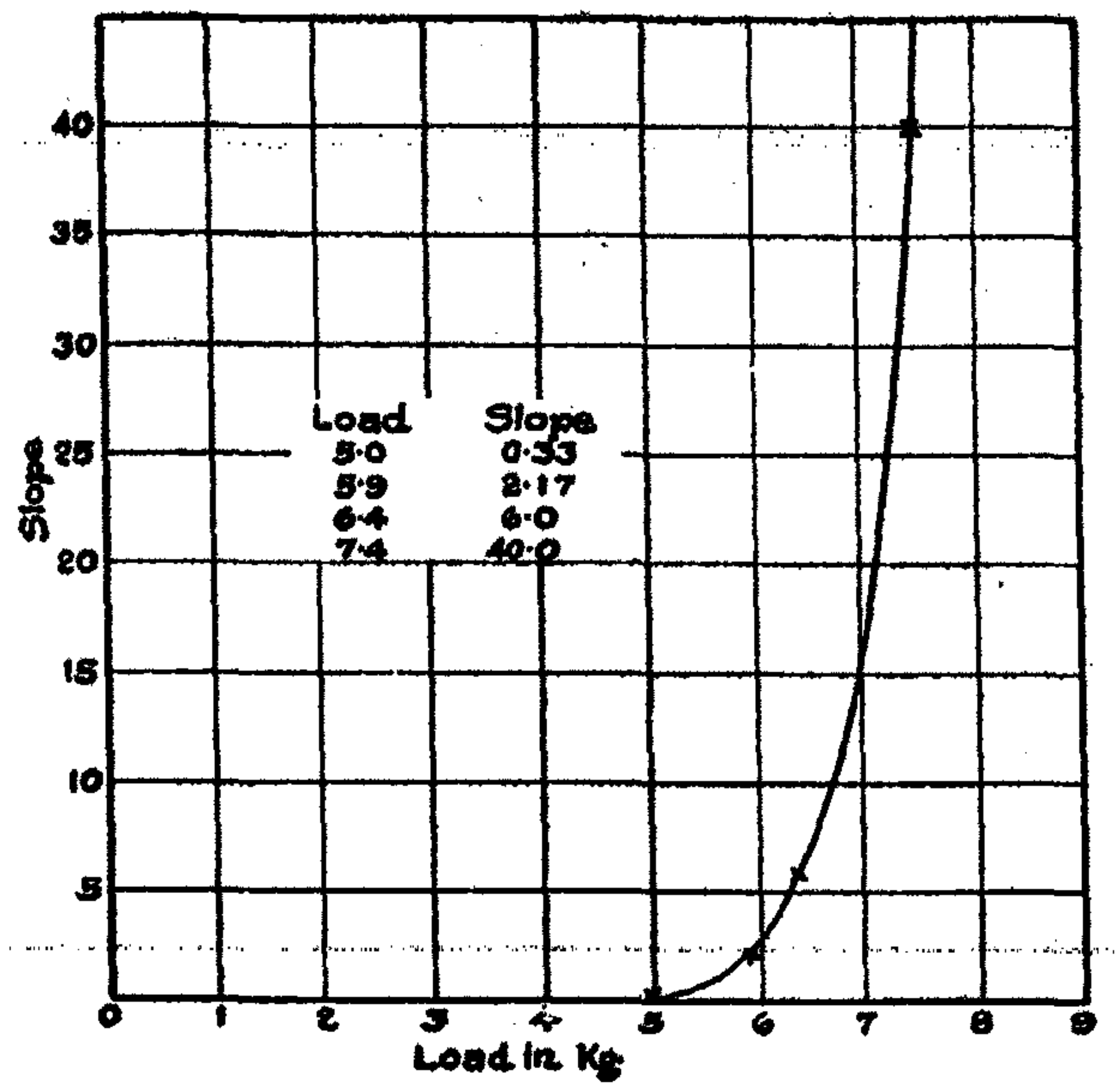
Slope
40
35
30
25
20
15
10
5
0
1
2
3
4
5
6
7
8
9
Load in Kg.
Load Slope
5·0 0·33
5·9 2·17
6·4 6·0
7·4 40·0

FIG. 18

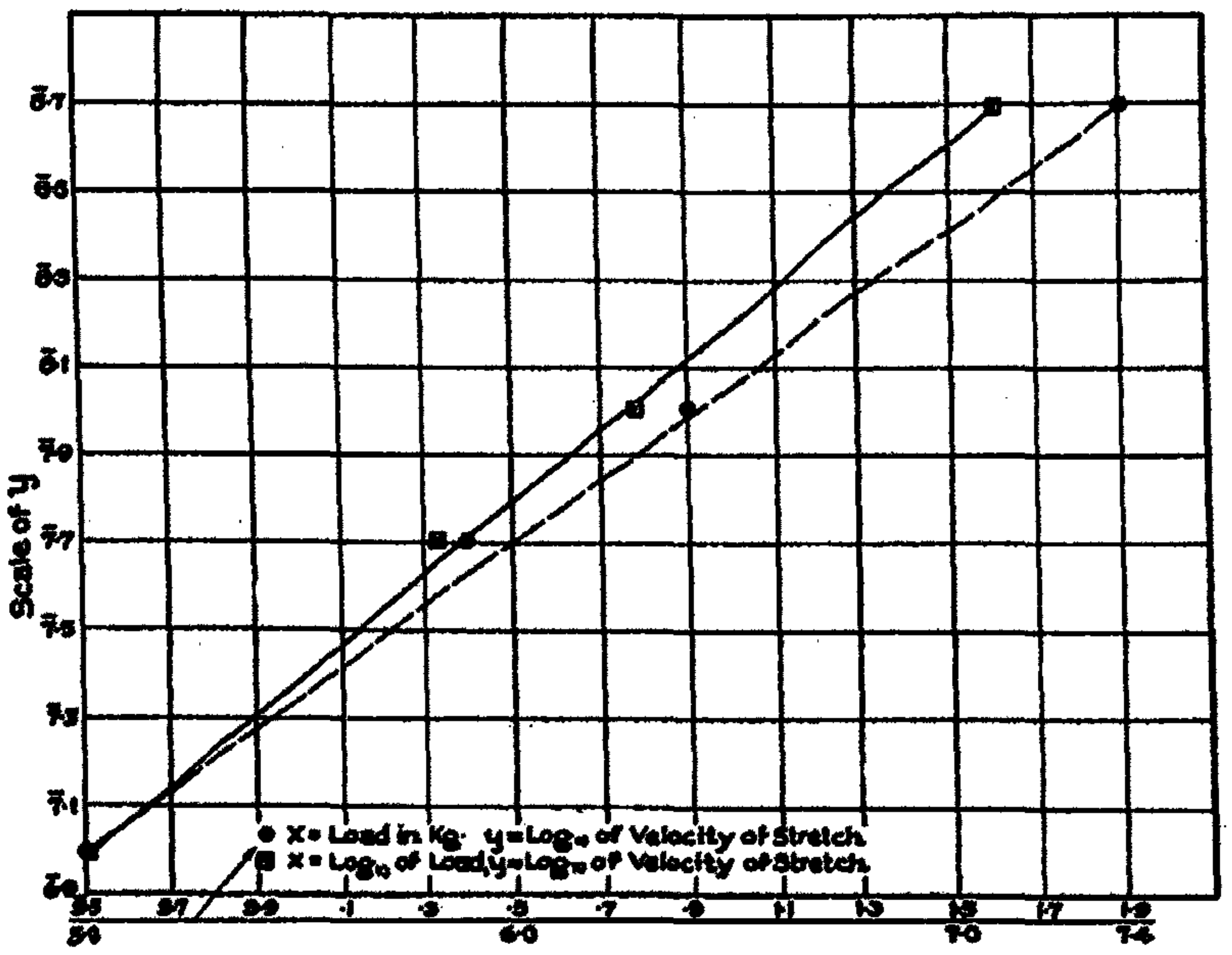
Scale of y
$\bar{3}$·7
$\bar{3}$·5
$\bar{3}$·3
$\bar{3}$·1
$\bar{4}$·9
$\bar{4}$·7
$\bar{4}$·5
$\bar{4}$·3
$\bar{4}$·1
$\bar{5}$·9
·65
·67
·69
·1
·3
·5
·7
·9
1·1
1·3
1·5
1·7
1·9
5·0
6·0
7·0
7·4
● x = Load in Kg. y = Log₁₀ of Velocity of Stretch
■ x = Log₁₀ of Load, y = Log₁₀ of Velocity of Stretch

FIG. 19

esters, and on the elasticity of organogels of cellulose[1] acetate shows that this plasticity becomes more pronouncedly evident *in the transition of sols to gels and gels to sols*; the relation of the elastic properties to temperature here somewhat resembling that of gelatin, e.g., in the parallelism of gelation and solution, (setting and melting) with marked hysteresis.

It is natural to attribute this plasticity to the formation of structures in the solution; the similarity of the organogels and sols of cellulose acetate to the hydrogels and sols of gelatin appears to indicate that chemical changes in the sense of ionization, play but little part here. But the elastic behavior of the solids, i. e., of the limiting concentrations of the gels, which has been described here, demand attention. This behavior is similar to that of the metals, particularly of the ductile metals. Moreover, the elastic behavior of the cellulose derivatives resembles that of the ductile metals more closely than it does that of rubber (unvulcanized pure gum), a typical organic colloid giving organosols and gels. The contrast between rubber and metals is discussed fully by G. S. Whitby[2]; the diagram reproduced from his book, illustrates it clearly. The nature of the contrast is thus described by Whitby "Speaking broadly; the metal is at first resistant to the pull and lengthens only slightly, until it reaches the "yield point" when it "draws out" with little or no increase of stress and then breaks; the rubber stretches easily at first, and then enters on a stage in which it offers greatly increased resistance to the pull and stretches very little as the pull is increased to the breaking point." It is not desirable to over-emphasize this contrast, but the fact that the cellulose plastics resemble the metals rather than rubber has a distinct bearing on structure theories. The elastic properties of metals are in the first place dependent upon an aggregate of crystalline grains, but fundamentally upon the nature of the atomic lattices composing the individual crystals[3]. Although cellulose in the original fibers gives evidence of a crystalline structure under X-rays[4] there is no evidence of this persisting in the dissolved and reprecipitated cellulose esters. The properties of the sols and gels of these are, vaguely, attributed to solvation (swelling) and aggregation of colloid particles[5]. Now, in the case of rubber we can prepare a "solid" rubber

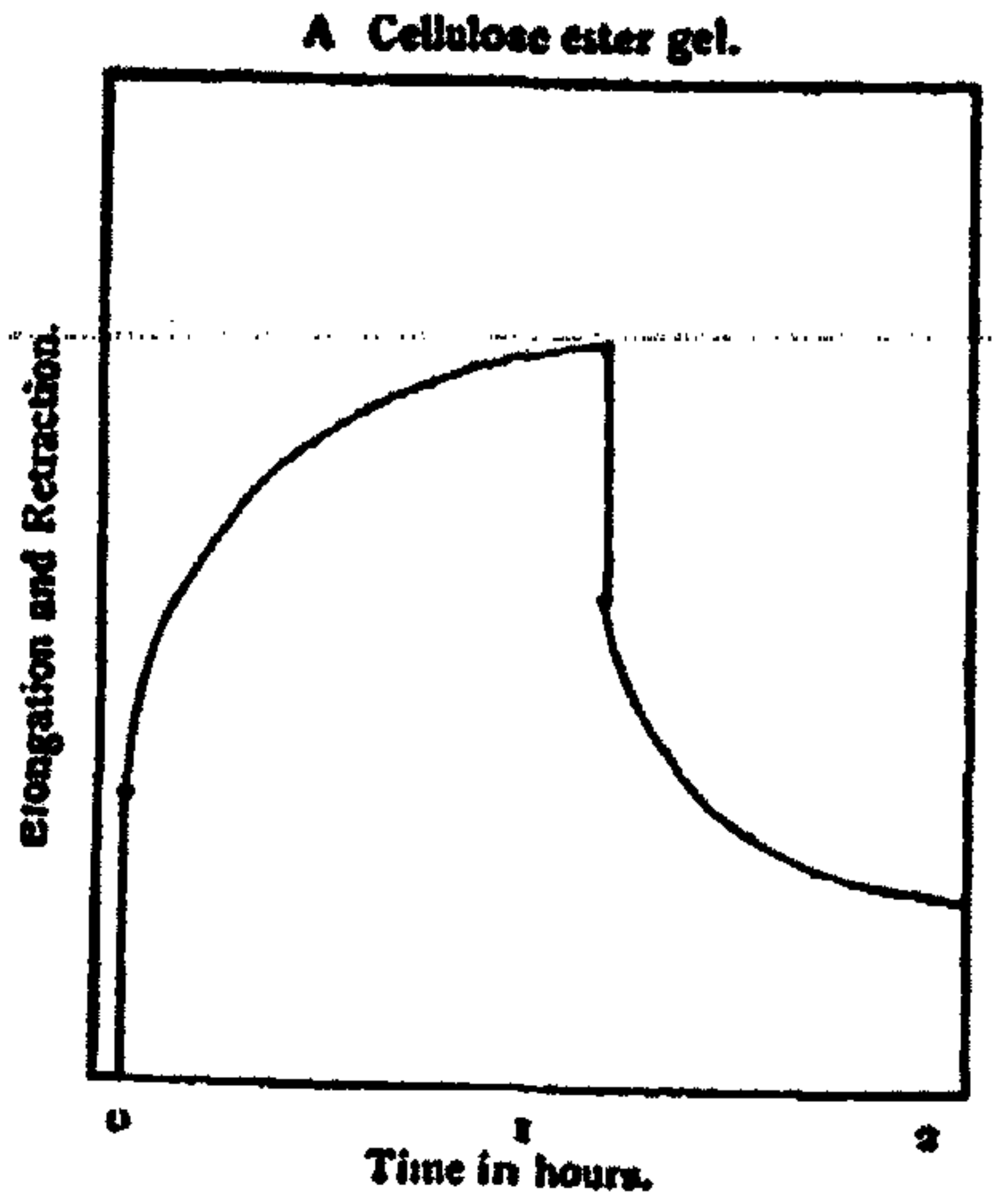

FIG. 20

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[1] Op. cit.

[2] "Plantation Rubber and the Testing of Rubber," p. 219 (1920).

[3] Cf. also W. P. Davey, this Symposium

[4] P. Scherrer: Nachr. königl. Ges. Wissensch. Göttingen, p. 98 (1918).

[5] Cf. Mardles: op. cit.

either by coagulation from an aqueous suspension (latex) *or* by evaporation from an organic solution. As far as fundamental elastic properties are concerned, the two materials thus produced are the same. Now the aggregation of the rubber particles from the latex can be followed microscopically, and the mode of this aggregation has only a secondary influence on the elastic properties[1]. The fundamental properties *of the rubber solid are due to the ultimate rubber particle,* and are only modified in secondary aspects by structure and aggregation of these. That is, a similar relation, *ceteris paribus* obtains as for metals, the properties of which depend on the ultimate crystals.

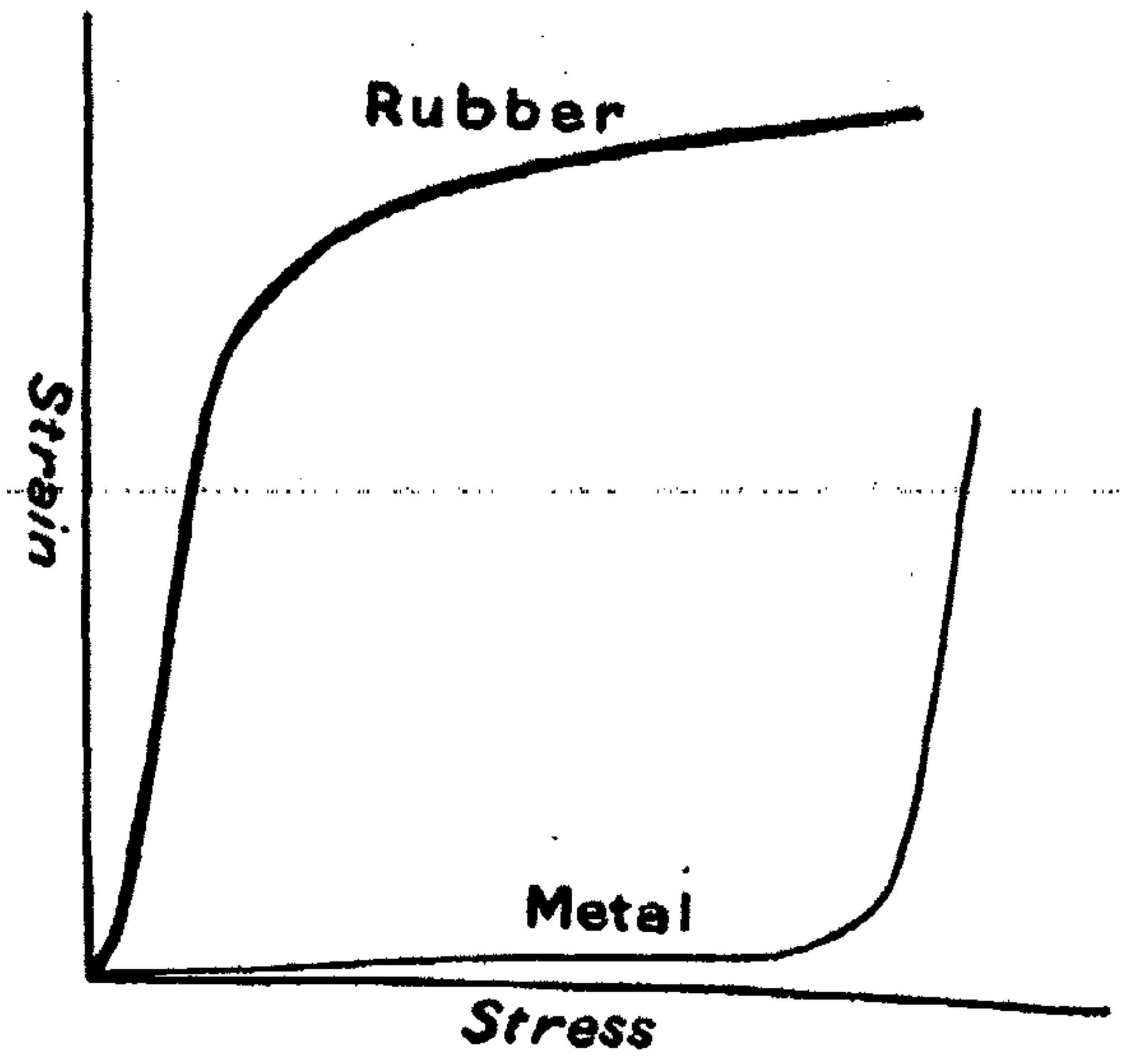

FIG. 21

The aggregation of particles in cellulose ester sols and gels to form the solid body certainly resembles in its main lines the similar process in rubber, much more closely than it does the crystallization of metal from its melt. Yet the resultant solid is more like metal in behavior than like rubber. Here again it is the nature of the ultimate particles of the colloid which is the essential.

McBain[2] from the work of himself and his collaborators on soaps, concludes that the transition from sols to gels with soap solutions is perfectly continuous, and that the particles of the gels are identical with those in the sols. We consider that this is the case also for gelatin and for the cellulose derivatives, as it appears to be for rubber, and that advance in understanding the mechanical properties will depend upon increased knowledge of the nature of the ultimate particles themselves. Failing a crystalline structure which can be revealed by X-rays, much of this advance must be purely chem-

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[1] Secondary in the general sense; as not altering the fundamental character of the rubber solid.

[2] Cf. 3rd Report on Colloid Chemistry, p. 2 (1920).

ical, but the structure of the particles arrived at from chemical considerations must be consistent with the elastic and plastic behavior. At the same time the setting up and testing of "model" particles and "model assemblages" having calculable dynamical properties is a promising procedure. It is only necessary to cite its success in regard to the structure of atoms.

Shorter, in the paper referred to, suggests for the explanation of the behavior of fibers (wool, cotton, etc.) a relatively simple dynamical model, consisting of "three sets of elements, a set of free elastic elements, a set of impeded elastic elements, and a set of viscous or impeding elements. Now, whatever conclusions further investigations may lead to regarding the constitution of the two sets of elastic elements, there is a simple,—almost inevitable —conclusion as to the third set, viz, that those elements consist of the nature of a gelatinous fluid, whose impeding effect diminishes or increases according as the water content increases or diminishes."

It would seem likely that we must regard the ratio of *free* to *impeded* elastic elements in such a model of colloid gels as not fixed, but variable. Shorter's appeal (op. cit.) to the "diminution of viscosity of colloidal solutions caused by excessive mechanical disturbance" really begs this point. Such colloidal solutions are not simply viscous, but plastic, i. e., contain themselves "impeded" elastic elements. Mardles[1] in a study of the "Elasticity of Organo-gels of Cellulose Acetate" finds for these that the determination of elasticity is complicated by the persistence of deformations and optical anisotropy, after the removal of stress, so that elasticity is perfect only for very small stress applied for a short time. These deficiencies of elasticity he ascribes to the formation *with time while under stress* of a "metastable phase, due to the altered orientation of the molecules composing the complexes which have aggregated to form the gel structure." This hypothesis as it stands is too vague to be of quantitative value, but may be helpful in compromise with more specific models of the Shorter type. The most probable hypothesis for the structure of soap[2] and gelatin gels[3], and this may extend to the cellulose ester gels, is that of a fibrillar or filamentous continuous phase; the fibrils bring practically chains of molecules (or micelles) held together by residual valency. It must be assumed that such fibrils are broken in shearing, but are able to regenerate to some extent. On this view, Mardles' "metastable phase" might consist simply of a "brushwood" structure of broken filaments, as compared with the continuous filament structure.

Rochester, N. Y.
November 1, 1924

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[1] Trans. Faraday Soc., 19, 133 (1923).

[2] Cf. J. W. McBain: loc. cit., p. 20, also S. E. Sheppard: "Gelatin in Photography," Vol. I., p. 188 (1923).

[3] Cf. R. H. Bogue: Chemistry and Technology of Gelatin and Glue," p. 147.

PLASTICITY OF STARCH PASTE*

BY CARL BERGQUIST

For many years, a chemical analysis of starch has been used as a criterion of quality. Acidity or pH value, protein, ash, moisture, fat and fibre have been determined. These figures are a check on certain processes in the manufacture of starch. What the customer is interested in, however, is: How does the starch cook up when it is going to be used?

Simple jelly tests have been made, but they leave too much for individual judgment.

The McMichael Viscometer has been recommended. This instrument is not practical, as starch paste actually thins down during the test.

The Scott Viscometer is employed. The objection to this instrument is that it only gives one point on the flow curve, and that pastes of low concentration at fairly high temperatures must be employed.

This is a general objection to most investigations on the viscosity of starch. Very dilute pastes at high temperature have been used as a rule. In practice, generally a concentration of one pound of starch to one gallon of water is the rule. Everybody knows that a paste of this kind does not flow at ordinary temperature. It is not viscous, but plastic; it has both a setting value and a flow value, or, in other words, yield and mobility.

These two values can readily be determined by means of the Bingham Plastometer. A paste containing 7% dry starch is prepared by mixing the starch with cold water, and then heating it to 95° C. for 45 minutes, using a screw agitator. The paste is then poured into the containers for the plastometer, left to set over night at 25° C., and tested in the usual way the next day in the plastometer.

Using a capillary 0.15 cm. in diameter and 2.6 c.m. long, and a pressure up to 850 gms. per sq. cm., the yield value for thick-boiling corn starch will vary between 250 to 400, and the mobility between 0.030 to 0.100. It can definitely be stated that a starch having a mobility higher than 0.055 is not a first grade starch. The yield value does not seem to be so important.

This comparatively large capillary must be used on account of the nature of starch paste. A smaller capillary is more liable to be clogged by impurities or small lumps. A higher pressure or a lower concentration would be required for a smaller capillary, and neither is desirable.

Thus, for the first time, we have been able to determine and express in numerical values two distinct qualities of starch paste. A complaint on starch being thin can be verified without calling on a man's personal judgment.

As mentioned previously, the usual concentration of starch paste in practice is one pound to a gallon. This paste will set to a jelly, but through con-

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* Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1924).

tinued stirring the paste will become semi-fluid. When a starch paste is hot, that is, over 70° C., stirring does not thin it down. Below this temperature, stirring makes it thinner. If stirring is continued vigorously at room temperature, the paste will finally become as thin as water. In our opinion, this shows that starch paste is viscous at a temperature over 70° C., while below that temperature it is plastic. In practice, low temperatures are used. In several places, starch paste is pumped around cold in pipe lines many hundred feet long, and gradually thins down, causing complaints. But this is the very nature of starch paste. A fatigue value is thus introduced.

This is also illustrated in the use of dextrine. As is well known, heavily sized bond papers are hard to stick together. Thin dextrines are used, but many times do not give satisfactory results. A stripping gum, that is, a fairly-thick-boiling dextrine mixed with borax, readily binds this paper. On trying this on the envelope machine, the stripping gum at first gave good results, but in a short time it became too thin. The dextrine had practically no yield value, but the stripping gum had a comparatively high yield value. The very rapidly revolving glue roll in the envelope machine destroyed the yield, and thus thinned down the paste.

We have tried the Murray Tube instead of the original plastometer. This instrument is comparatively simpler to run, and less time is consumed in calculating results. The Murray Tube, however, gives another set of values for yield and mobility. We believe there is adhesion between the starch paste and the glass, and this shows up in the long tube. The curves, where flow is plotted against shearing stress, all have a marked bend towards the origin.

It should be mentioned that values for yield and mobility do not indicate the adhesiveness of a paste. Surface tension has been mentioned as a possible factor. A thick starch paste will give high readings on du Nouy's instrument, but as this paste does not form drops, it must be the tensile strength of the film and not surface tension that is measured. How this adhesiveness or internal cohesion can be measured is a problem for the future.

The plastometer has given us the only values we have for the flow of a paste.

Research Laboratory,
Corn Products Refining Company,
Edgewater, N. J.
Sept. 30, 1924

SOME OBSERVATIONS ON THE PLASTICITY SYMPOSIUM*

BY FRANK G. BREYER

To the layman—and even to the but half-interested technologist—the term, plasticity, is confusing. This is so on account of the fact that the definition of plasticity is not studied with sufficient care, consequently such observers invariably attempt to use the term in a comparative manner, that is they think it legitimate to say that one material, for instance, can be twice as plastic as another. This, of course, as we know, is entirely wrong. Much of this confusion would be eliminated if we would cease to refer to certain materials as plastic and simply state, instead, that they have a finite yield value. Yield value, itself, is a comparable term.

There is another, and very serious, source of confusion—or perhaps it is better to call it a misunderstanding—rising in the field of plasticity, concerning which the technologist is usually misinformed, and that is the nature of the *structure* that will give to a material the property of plasticity.

There are a considerable number of materials such as paint, clay-water mixtures, etc., the structure of which is easily discernible under the microscope, while with others like gelatines, varnishes and glues, the structure is sub-microscopic. Unfortunately, those materials that *are* amenable to microscopic treatment are seldom studied in that manner, and, instead, a structure is visualized from a process of reasoning that is not based on facts, but derived from assumptions in regard to particle-size, shape, and distribution that every one should know by this time are not true.

To be specific, the microscope has long since revealed the facts that particles in plastic materials do not approximate spheres uniform in size, and evenly distributed throughout the liquid phase; nor do they even occur packed in those ideal ways that would enable the technologist to calculate the volume of voids. Instead, a force of flocculation exists, in most cases, causing irregular groupings of the particles that will completely upset any attempt to arrive at conclusions that are based on such a mathematical calculation of the voids. Furthermore, it should be added that the microscope reveals the fact that the force of flocculation is the factor that produces yield value in those materials that are composed of two phases, and where the dispersing phase is liquid.

Palmerton, Pa.
December 10, 1924

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* Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1924).

PLASTICITY OF DENTAL IMPRESSION COMPOUND *

BY WALTER S. CROWELL AND ALBERT SAUNDERS JR.**

Dental impression compound consists of a wax-like mixture of stearic acid, resins, and oils intimately mixed with an inert filler, like talc and a pigment. The unfilled organic part is called compound wax. In use, the compound is softened in hot water, placed in a tray and forced against the interior surface of the mouth. The tray is allowed to remain in the mouth until its contents harden. It is withdrawn and the impression poured with plaster of paris. After the plaster sets, the compound is again softened in hot water and stripped from the model.

The object of a dental impression is obviously to secure a model upon which an appliance can be built which will give continuously satisfactory service in masticating the food. The appliance must be constructed so that it does not interfere with the normal functioning of surrounding organs, and is not displaced by their motion. It must conform closely to the tissues against which it is placed, not only when the tissue is relaxed or at rest, but much more importantly, when the tissue is compressed by the appliance under the stress of mastication.

Plaster of paris is the original impression material. There is no question that it will give an accurate reproduction of the surfaces against which it is placed. Plaster is soft and fluid. In practice, the impression obtained by its use is a copy of the tissues in a relaxed condition. This gives a model frequently differing at certain points form the aspect of the tissues compressed under the plate by the act of mastication. After it has set, a plaster impression can be altered only by scraping or cutting. The outer rim of the impression copies the muscular attachments between the cheeks and the alveolar ridge in one position. Attempts to conform the rim to the motion of the muscles in mastication by carving are seldom sufficiently accurate to be satisfactory.

The need for ensuring freedom of motion of these muscular attachments, when the plate is in place, led to the development of modelling compound impression technique. When compound is used, the rim of the impression can be softened by heat, the impression returned to the mouth and, by moving the muscles, clearance can be cut by the muscles themselves. This "muscle trimming" of the rim of the plate is one of the main features of the compound impression technique developed by the Green Brothers a number of years ago. The importance of tissue compression was not recognized at once. While compound impression techniques gave better fitting, more serviceable plates, the improvement was attributed largely to the lack of interference of the plate with the surrounding organs, particularly the muscles referred

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* Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1924).

** Contribution from the Research Laboratory of the S. S. White Dental Mfg. Company.

to above. Any interference between the plate and these muscles would of course, tend to displace the plate, break the "suction" and cause the plate to drop.

In the Green technique, considerable compression was incidentally obtained because of the necessity for firmly forcing the compound home. Compression plays a large part in the recent Wadsworth technique in which the tissue is pressed into the impression by the actual power of the masticating muscles.

It is apparent that a dental impression compound must do more than simply copy the surface against which it is placed. Its plastic properties must be carefully regulated. At the working temperature, it must be mobile enough to allow of muscle trimming, yet have a yield value high enough to ensure adequate and proper tissue compression. At some temperature above that of the mouth it must be essentially rigid, so that it can be withdrawn from the mouth without distortion.

It has long been known that temperatures up to 50°C. can be readily tolerated by the mouth, while temperatures above 55°C. cause discomfort. Therefore the working range of an impression compound is between the upper limit of toleration, 55°C and the temperature of the mouth, 37.5°C.

The plastic properties of an impression compound are a function of the plastic or fluid properties of the compound wax and the quantity of talc added.

As noted above, the compound wax is the mixture of stearic acid, resins and oils combined by fusion. When this mixture is heated it becomes fluid. On cooling a temperature is reached at which stearic acid commences to crystallize from the melt. The separation of stearic acid in itself reduces the fluidity of the melt, acting like any other suspended solid. Furthermore, the fluidity of the remaining mother liquor is rapidly reduced by withdrawing from it one of its most fluid constituents. The net result is a rapid hardening or setting of the wax in a narrow temperature range.

Broadly, the temperature at which crystallization begins depends upon the quantity of stearic acid present. In practice, supercooling is bound to occur depending upon the fluidity of the particular compound studied at its crystallization point. The fluidity of the compound also affects the rate at which the stearic acid separates. These two factors determine the setting time of the wax and hence the compound. The temperature of crystallization must be above mouth temperature, otherwise the compound will not develop sufficient rigidity to be withdrawn from the mouth without distortion.

The addition of talc or other inert filler to the wax rapidly reduces the fluidity of the mixture and, above a certain volume, concentration changes the mixture from a liquid to a plastic material with a finite yield value.

The complexity of the problem and the lack of data in the literature on similar substances necessitated en elaborate experimental study in order to secure reliable quantitative data.

Both waxes and compounds are studied in the temperature range of 40° C to 56°C.

Preliminary studies indicated that wax No. 4 and the compounds made from it were reasonably satisfactory. It gave favorable results on both laboratory and field tests. This material was selected for detailed study.

The compound wax contained 35% stearic acid, the remainder being resin. Its crystallization point (by undisturbed cooling) was 41.4°C. It was mixed with talc and pigment in the following proportions:

Compound No.	Talc. Weight Percent.	Talc. Vol. Percent.
4C	30.4	14.3
4	51.3	28.5
4A	55.2	31.9

The density of the talc-pigment mixture used was 2.63.

On the wax we set out to determine

1—Fluidity-temperature relation between 37° and 56°.

2—Temperature of zero fluidity.

The flow-shear relations of the three conpounds were studied in the same temperature range and the results used to determine

1—Effect of talc on the fluidity of mixture.

2—Volume concentration of talc giving "zero" fluidity.

3—Effect of talc on yield value.

4—Fluidity, mobility and yield value temperature relation of the three compounds between 37° and 56°.

The plastic properties of the wax and the compounds were studied by the capillary tube method described by Bingham, "Fluidity and Plasticity", p. 319.

The dimensions of the capillaries are given in Table I. Lengths were measured by a micrometer and radii under a microscope equipped with a filar micrometer.

TABLE I

Dimensions of Capillaries Used

Capillary No	Radius Cm.	Length Cm.
5	0.0782	7.635
13	0.1552	7.584
14	0.1581	7.549
17	0.0557	7.922
21	0.0808	7.983

Apparatus

The apparatus used in our measurements was essentially that described by Bingham in "Fludiity and Plasticity", p. 305.

Method of Measurement

Weighed glass test tubes were attached to the plastometers by means of rubber stoppers. The plastometer containing the compound was then placed in the bath, previously set at the desired temperature, and allowed to remain for one hour at that temperature. The temperature of the bath was determined by means of a thermometer calibrated at 32.4°C. the transition temperature of $Na_2SO_4 \cdot 10\ H_2O$. After standing one hour, air from the stabilizing reservoir was admitted above the compound through a needle valve. A stop watch, reading to 1/5 second was started. As soon as the mercury in the manometer became stationary, the height in cms. of mercury was noted. The pressure was maintained constant during a determination by hand regulation. After a sufficient time, usually 50 minutes, had elapsed, the manometer was again read, the pressure shut off, the watch stopped, and the plastometer turned to air by means of another needle valve. During the elapsed time the temperature of the air surrounding the manometer was noted from time to time. The plastometer was taken out of the bath and the glass tube containing the extruded compound removed and placed in an electric oven at 50°C, for one hour in order to remove moisture. After cooling, the tube was again weighed and the weight of the extruded sample noted.

Calculations

Fluidities were calculated from the following formula: $\varphi = \dfrac{8lW}{\pi 9 R^4 \rho t P}$

φ = Fluidity
W = Weight of extruded compound
1 = Length of capillary
ρ = Density of compound
p = Pressure in gms./cm.
R = Radius of capillary
t = Time

Corrections were applied for hydrostatic head and room temperature. Corrections in pressures for various temperatures and mercurical heights were taken from Bingham's "Fluidity and plasticity", p. 302.

Plasticities were calculated by the formula $\mu = \dfrac{8lW}{\pi g R^4 \rho t (P-p)}$

p the "yield pressure" was determined by calculating the intercept on the pressure axis of the weight per second vs. pressure curves by the method of least squares.

Yield values were calculated from yield pressures by the ralation $f = PR/2L$

Notes on Measurements

The measurement of the fluidity of the waxes above 46°C. presented no particular difficulty. Some trouble was experienced in obtaining material free from suspended impurities but this was finally overcome by straining the molten wax through a 200 mesh screen. The .05 and .08 cm. capillaries were convenient for this work and gave corresponding results.

Below 46°C. concordant results were not obtained. The fluidities measured were very low and the errors of measurement sufficient to markedly affect the results. We were unable to accurately determine the temperature of zero fluidity either directly or by exterpolation of the temperature, fluidity curves.

The determination of yield value and mobility of the compounds was still more difficult and uncertain. The mobilities are about 1/10 the magnitude of the fluidities measured. The .05 cm. capillaries could not be used. Better results were obtained with the .08 cm. capillaries but they were still very discordant.

Much of the irregularity was attributed to the presence of relatively large suspended particles. Their effect should be minimized by using larger capillaries. Accordingly some .15 cm. tubes were secured. The results obtained with these tubes were much better, but not in agreement with those obtained with the smaller tubes, the yield value being much higher. When this was called to the attention of Bingham (private communication) he pointed out that with the large tubes, the shearing forces were much greater than those employed with the small tubes. The flow-shear curve at low pressure departs from liniarity and approaches the pressure axis asymptotically. This was confirmed by observations with .08 cm. capillaries at high pressures (and correspondingly high shearing forces.) Under these conditions, the results were in agreement with those obtained with large capillaries.

This departure of the flow-shear curve from linearity deserves special comment. While theoretically two measurements are required to determine yield value and mobility, in practice at least three measurements should be made at widely differing shearing stresses so that any departure from linearity will be observed and the yield value determined from measurements at shears high enough to be in the apparently linear region of the curve.

At best, the results obtained were not in good agreement. Apparently in our hands, the apparatus is incapable of measuring the small mobilities we met to an accuracy of over 5%.

Sources of Error

1—Inhomogeneity of the sample. This was controlled by prolonged mechanical mixing.

2—Suspended foreign particles. Controlled by screening both waxes and compounds through appropriate sieves, under pressure.

3—Trapped air. Screening tends to break up air bubbles and reduces this error to a large extent. In filling the plastometer, however, air is likely to be entrained. Most but not all of it is eliminated by continued heating of the plastometer before running the first determination.

4—Errors in weighing the extruded material. Considerable error may be intorduced by not efficiently cleaning and drying the receiver and by not completely drying the extruded material to constant weight. The quantities weighed were seldom over 1/2 gm., hence it was necessary to take precautions in cleaning and drying, which would be quite unnecessary with larger weights.

5—Flow of compound under its own head. After the pressure has been shut off there is a slight tendency for the compound to continue to flow in minute quantities. This error is very small and may be reduced by removing the plastometer from the bath and chilling the receiver in ice water as soon as the pressure is shut off.

6—Removing the receiver before the compound has solidified. As the compound has a tendency to adhere to the walls of the weighing bottle when soft, a small portion of the compound may be pulled out of the capillary if it is not allowed to first become solid.

7—Cutting the compound from the end of the capillary. The compound is extruded from the capillary in the form of a thread. When the compound has solidified and the receiver is removed, a portion of this thread is attached to the compound in the capillary. Unless care is exercised in cutting the compound from the capillary, a small portion of the compound will be broken off within the capillary giving a high result.

8—Fluctuation of bath temperature. This is a serious source of error, difficult to control when the experiment requires 50 minutes or more. Automatic regulation with toluol regulators proved unsatisfactory and additional hand regulation was resorted to. A part of the variations in our results may be attributed to this cause.

9—Leakage in the system. This was guarded against by frequent inspection of all joints.

10—Errors in the hydrostatic head correction and the manometer reading. At the high pressures used these errors are negligable.

Many of these sources of error would be negligable in the measurement of high mobilities at low pressures but under our experimental conditions they are serious causes of deviation.

The changes in the structure of the wax noted above are reflected in the temperature fluidity relations. At high temperatures the wax is a liquid. As the temperature falls the fluidity decreases, but not in a linear fashion. There is some sag to the curve. This can be attributed to internal changes in the liquid similar to those in water and other associated liquids which show a similar sag to the temperature fluidity curves. At about 46.5° the fluidity commences to rapidly decrease, finally reaching extremely low values. This change occurs in a range of two or three degrees and corresponds to the separation of the stearic acid.

The melting point of the wax determined by undisturbed cooling is 41.4°, while the temperature at which stearic acid begins to separate as indicated by fluidity measurements is 46.5°. The value determined by undisturbed

TABLE II

Fluidity of Compound Wax No. 4

Stearic Acid 35% Capillary No. 17

Temp.	Manometer reading in mm. hg.	Cor. Pressure Gms./Cm.^{2}	Density	Wt. per sec. 10^4	Fluidity × 10^4
44.0°C	113.91	1555	0.9900	10.59	1.47
44.0	113.98	1556	0.9900	12.75	1.77
44.0	115.69	1579	0.9900	9.85	1.35
44.0	119.10	1625	0.9900	12.19	1.62
44.0	149.03	2030	0.9900	14.91	1.57
44.0	150.15	2047	0.9900	14.80	1.58
44.0	210.33	2760	0.9900	20.52	1.68
44.0	207.63	1824	0.9900	21.45	1.64
44.0	257.18	3495	0.9900	25.67	1.59
44.0	258.13	3506	0.9900	25.86	1.59
44.0	298.00	4049	0.9900	29.14	1.55
44.0	300.58	4080	0.9900	30.06	1.59
				Mean $\varphi =$	1.58
44.8	101.90	1392	0.9880	23.83	3.70
44.8	108.62	14.83	0.9880	24.42	3.56
44.8	108.21	14.79	0.9880	24.60	3.60
44.8	141.08	1923	0.9880	31.67	3.56
44.8	144.05	1963	0.9880	31.87	3.51
44.8	148.37	2021	0.9880	33.77	3.61
44.8	201.32	2739	0.9880	46.63	3.68
44.8	200.65	2729	0.9880	46.09	3.65
44.8	259.00	3519	0.9880	58.90	3.62
44.8	259.30	3522	0.9880	58.22	3.57
44.8	296.72	4028	0.9880	67.09	3.59
				Mean $\varphi =$	3.61
45.05	118.86	1623	0.9877	31.95	4.26
45.05	215.95	2936	0.9877	54.03	3.98
45.05	304.71	4137	0.9877	86.71	4.54
				Mean $\varphi =$	4.26
46.10	95.60	1308	0.9843	41.45	6.90
46.10	206.27	2805	0.9843	89.02	6.90
46.10	199.70	2716	0.9843	89.30	7.14
46.10	303.93	4126	0.9843	133.36	7.02
				Mean $\varphi =$	6.99

TABLE II (continued)

Temp.	Manometer reading in mm. hg.	Cor. Pressure Gms/Cm^2	Density	Wt. per sec. 10^6	Fluidity × 10^5
48.0	105.00	1435	0.9790	68.71	10.06
48.0	110.62	1511	0.9790	72.33	10.45
48.0	164.93	2244	0.9790	109.05	10.61
48.0	168.34	2293	0.9790	110.41	10.51
48.0	213.38	2899	0.9790	139.26	10.49
48.0	214.49	2915	0.9790	138.55	10.38
48.0	263.06	3572	0.9790	168.66	10.31
48.0	300.60	4082	0.9790	179.44	9.60
48.0	302.84	4112	0.9790	185.95	9.87
				Mean φ =	10.2
50.0	102.06	1395	0.9735	88.71	13.97
50.0	104.93	1434	0.9735	92.27	14.13
50.0	106.42	1454	0.9735	93.06	14.05
50.0	167.87	2285	0.9735	137.94	13.25
50.0	208.23	2832	0.9735	169.00	13.10
50.0	213.68	2904	0.9735	178.30	13.48
50.0	252.39	3428	0.9735	208.84	13.38
50.0	271.40	3686	0.9735	223.53	13.32
50.0	303.71	4121	0.9735	248.69	13.25
50.0	304.16	4130	0.9735	251.97	13.39
50.0	305.68	4149	0.9735	255.01	13.50
50.0	306.41	4160	0.9735	259.49	13.70
				Mean φ =	13.51
52.0	108.08	1476	0.9680	118.91	17.79
52.0	111.34	1519	0.9680	125.83	18.29
52.0	112.11	1530	0.9680	130.80	18.87
52.0	113.64	1551	0.9680	126.72	17.63
52.0	117.01	1597	0.9680	134.06	18.49
52.0	220.53	2996	0.9680	243.03	17.91
52.0	221.28	3307	0.9680	256.97	18.87
52.0	226.47	3077	0.9680	246.09	17.67
				Mean φ =	18.19
54.0°C	116.68	1592	0.9625	156.16	21.83
54.0	119.91	1636	0.9625	161.22	21.94
54.0	119.55	1631	0.9625	165.63	22.55
54.0	211.88	2878	0.9625	280.23	21.67
54.0	215.76	2931	0.9625	284.71	21.57
				Mean φ =	21.91

cooling is affected by the poor heat conductivity of the wax and its low fluidity, which results in marked undercooling. It is of great practical importance since it is a more accurate measure of the setting temperature in use than the value obtained by fluidity measures.

TABLE III

Fluidity of Compound No. 4C

Talc % by weight = 30.4
Talc % by volume = 14.3

Capillary No. 5

Temp.	Manometer reading in mm. hg.	Cor. Pressure Gms./Cm²	Density	Wt. per sec. 10^6	Fluidity $\times 10^6$
44.2°C	91.05			NIL	
45.0	89.45	1227	1.232	26.01	0.91
46.0	95.20	1305	1.228	62.99	2.08
46.0	142.75	1948	1.228	93.07	2.06
				Mean φ =	2.07
46.1	82.92	1139	1.227	53.40	2.02
46.7	89.95	1234	1.225	68.55	2.40
46.7	145.23	1982	1.225	108.27	2.37
				Mean φ =	2.385
47.1	86.06	1182	1.223	70.64	2.59
48.0	90.98	1249	1.220	88.20	3.07
48.0	146.57	2001	1.220	140.72	3.05
				Mean φ =	3.06
48.3	87.04	1195	1.219	84.16	3.06
49.2	90.10	1236	1.215	106.03	3.74
50.3	92.57	1270	1.211	126.29	4.35
52.2	87.73	1204	1.203	151.51	5.54

As talc is added to the wax, the fluidity is rapidly reduced. The form of the fluidity temperature curve remains the same (see Fig. 1). At this contration of talc, no yield value could be detected by the experimental proceedure used.

Volume Percent of Talc Giving "Zero" Fluidity

The concentration of zero fluidity at various temperatures was calculated (see Table IV). An average value of 19.89 volume percent equals 40.34 weight percent was obtained. It was found to be independent of the temperature within the limit of experimental error.

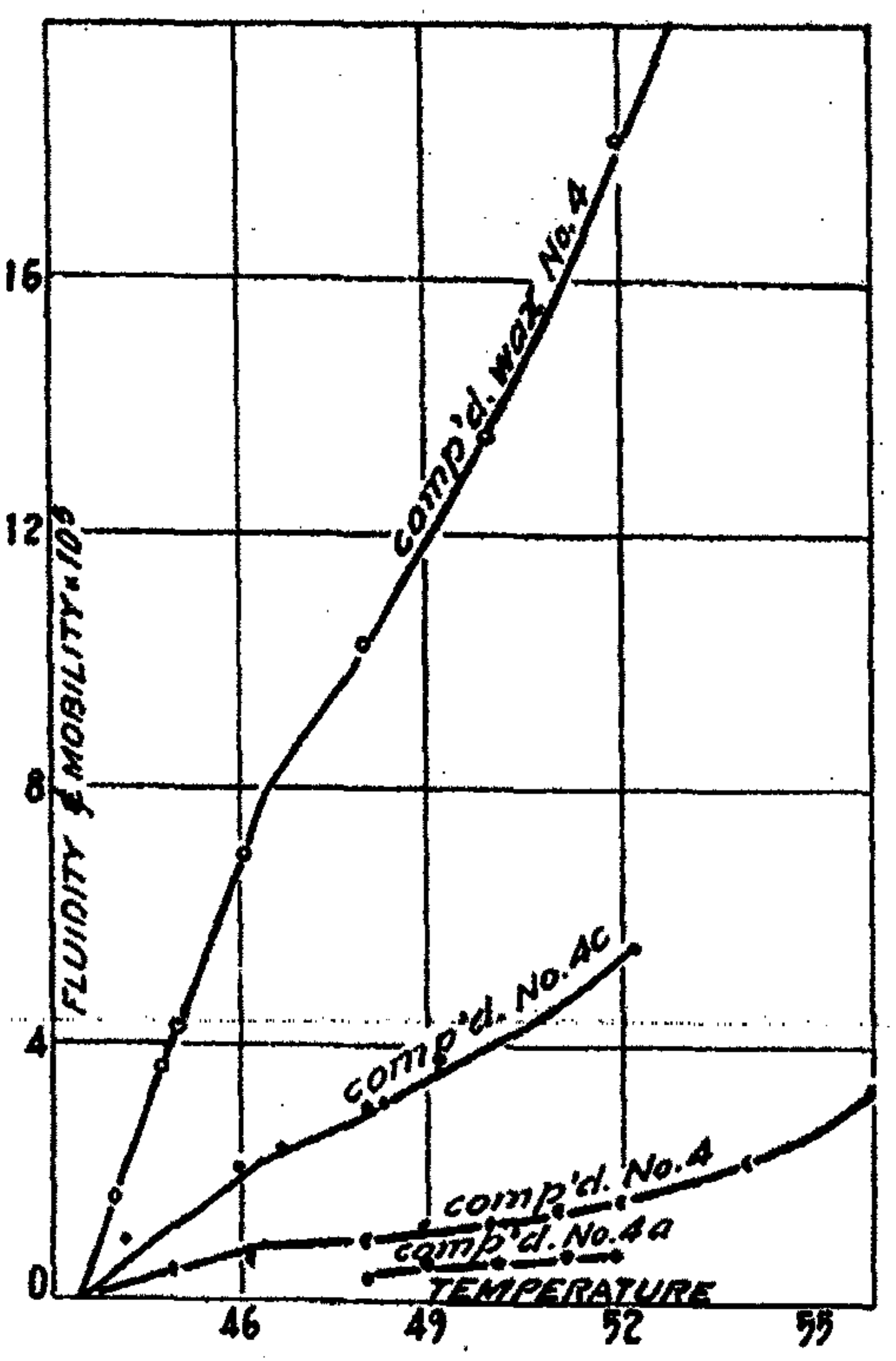

Fig. 1

Waxes and Compounds
Fluidity and Mobility *vs.* Temperature

Table IV

Determination of Quantity of Talc at "Zero" Fluidity

Temperature	Volume Percent
*45°C	17.84
46	19.85
47	19.82
48	20.01
49	20.12
50	20.12
51	19.96
52	19.81
53	19.71
54	19.64

Average volume percent 19.89 = 40.34 percent by weight.

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*Discarded

TABLE V

Plasticity of Compound No. 4

Talc percent by weight = 51.3
Talc percent by volume = 28.5 Average yield value – 2.69

Temp.	Capillary #	Manometer reading in cm. Hg.	Shear = $\frac{PR}{2L}$ gm/cm^2	Density	Wt. per sec. 10^6	Mobility 10^6	
44.0°c	21	115.69	8.02	1.4686	0.76	.024	
44.0	21	149.03	10.30	1.4686	1.22	.027	
44.0	21	300.58	20.12	1.4686	2.61	.024	
						Mean μ = .02	
45.0	21	108.21	7.52	1.466	13.98	.4	
45.0	21	118.86	8.24	1.466	13.83	.4	
45.0	21	108.62	7.54	1.466	13.23	.45	
45.0	21	141.08	9.76	1.466	19.21	.45	
45.0	21	144.05	9.97	1.466	19.45	.45	
45.0	21	148.37	10.26	1.466	20.17	.44	
45.0	21	200.65	13.84	1.466	28.99	.43	
45.0	21	201.32	13.89	1.466	29.56	.44	
45.0	21	251.42	16.82	1.466	36.83	.44	
45.0	21	259.00	17.84	1.466	39.77	.44	
45.0	21	259.30	17.86	1.466	40.35	.45	
45.0	21	304.71	20.69	1.466	47.50	.44	
45.0	21	296.72	20.42	1.466	46.58	.44	
						Mean μ = .44	
46.2	21	95.60	6.65	1.4642	15.61	.65	
46.2	21	199.70	13.78	1.4642	43.19	.65	
46.2	21	303.93	20.91	1.4642	71.53	.66	
						Mean μ = .65	
48.0	21	105.00	7.29	1.4588	25.16	.91	
48.0	21	110.62	7.68	1.4588	27.47	.92	
48.0	21	164.93	11.39	1.4588	45.11	.87	
48.0	21	168.34	11.64	1.4588	47.00	.88	
48.0	21	214.49	14.79	1.4588	69.53	.97	
48.0	21	254.85	18.72	1.4588	81.07	.92	
48.0	21	300.60	20.69	1.4588	98.32	.92	.91
48.0	13	92.28	12.98	1.4588	37.63	.90	
48.0	13	136.50	19.10	1.4588	61.03	.90	.90
						Mean μ = .91	
49.0	13	85.85	12.09	1.457	41.57	1.09	
49.0	13	147.65	20.65	1.457	86.86	1.17	
						Mean μ = 1.13	

TABLE V (continued)

Temp.	Capillary #	Manometer reading in cm. Hg.	Shear = $\frac{PR}{2L}$ gm/cm²	Density	Wt. per sec. 10^6	Mobility 10^6	
50.0	21	107.03	7.44	1.4556	32.66	1.15	
50.0	21	108.18	7.51	1.4556	35.42	1.22	
50.0	21	196.62	13.56	1.4556	75.39	1.17	
50.0	21	204.27	14.08	1.4556	77.44	1.14	
50.0	21	208.23	14.37	1.4556	84.32	1.22	
50.0	21	208.93	14.41	1.4556	81.10	1.18	
50.0	21	265.20	18.26	1.4556	106.10	1.15	
50.0	21	303.71	20.89	1.4556	132.70	1.23	1.18
50.0	13	85.45	12.05	1.4556	47.03	1.24	
50.0	13	141.55	19.82	1.4556	84.88	1.21	1.22
						Mean μ =	1.19
51.0°C	13	84.69	11.94	1.452	53.89	1.44	
51.0	13	145.35	20.34	1.452	101.74	1.41	
						Mean μ =	1.43
51.9	13	85.85	12.10	1.449	58.51	1.54	
51.9	13	144.80	20.26	1.449	112.61	1.57	
						Mean μ =	1.55
52.0	21	113.64	7.89	1.4493	50.92	1.64	
52.0	21	117.01	8.11	1.4493	49.92	1.58	
52.0	21	117.49	8.15	1.4493	50.11	1.54	
						Mean μ =	1.59
54.0	21	108.51	7.53	1.4445	63.17	2.20	
54.0	21	115.44	8.01	1.4445	68.24	2.16	
54.0	21	210.34	14.51	1.4445	155.90	2.24	
54.0	21	215.67	14.87	1.4445	162.44	2.26	
54.0	21	297.08	20.42	1.4445	226.48	2.17	
54.0	21	299.80	20.61	1.4445	229.43	2.18	
						Mean μ =	2.20
56.0	21	110.02	7.64	1.4386	93.06	3.18	
56.0	21	190.19	13.12	1.4386	210.37	3.43	
56.0	21	193.20	13.32	1.4386	212.88	3.41	
56.0	21	211.88	14.60	1.4386	230.95	3.30	
56.0	21	215.76	14.87	1.4386	240.95	3.37	
56.0	21	215.98	14.88	1.4386	243.17	3.40	
56.0	21	304.90	20.97	1.4386	356.90	3.31	
56.0	21	306.19	21.05	1.4386	344.70	3.20	
56.0	21	312.38	21.47	1.4386	352.10	3.20	
						Mean μ =	3.31

When talc is added in excess of the concentration giving "zero" fluidity a finite yield value is developed.

Yield values were calculated from the flow-shear observations given in Table V by the method of least squares and are given in Table VI. There seems to be no connection between temperature and yield value (see Fig. 2), therefore the average value of 2.69 was used in calculating the mobilities given in Table V. The form of the mobility temperature curve is still similar to that of the wax (see Fig. 3). The mobility of the compound is approximately 1/10 of the fluidity of the wax.

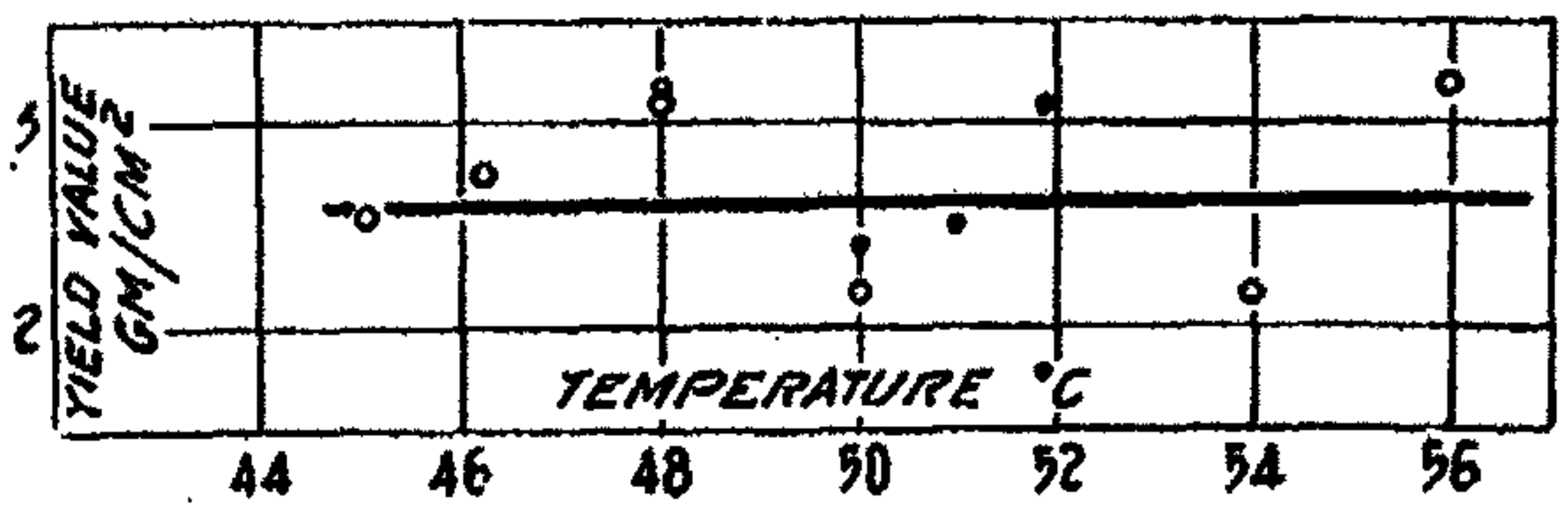

FIG. 2

Compound No. 4

Yield Value *vs.* Temperature

TABLE VI

Yield Value of Compound No. 4

Temperature	Capillary No.	Yield Value gm/cm^2
45.0	21	2.52
46.2	21	2.72
48.0	21	3.09
50.0	21	2.15
52.0	21	3.11
54.0	21	2.16
56.0	21	3.17
Average yield value		2.69(1)
48.0	13	3.14
49.0	13	4.24(2)
50.0	13	2.34
51.0	13	2.48
51.9	13	30.8
Average yield value		2.76
Average yield value, both capillaries		2.72

[1] Used in calculations.

[2] Discarded.

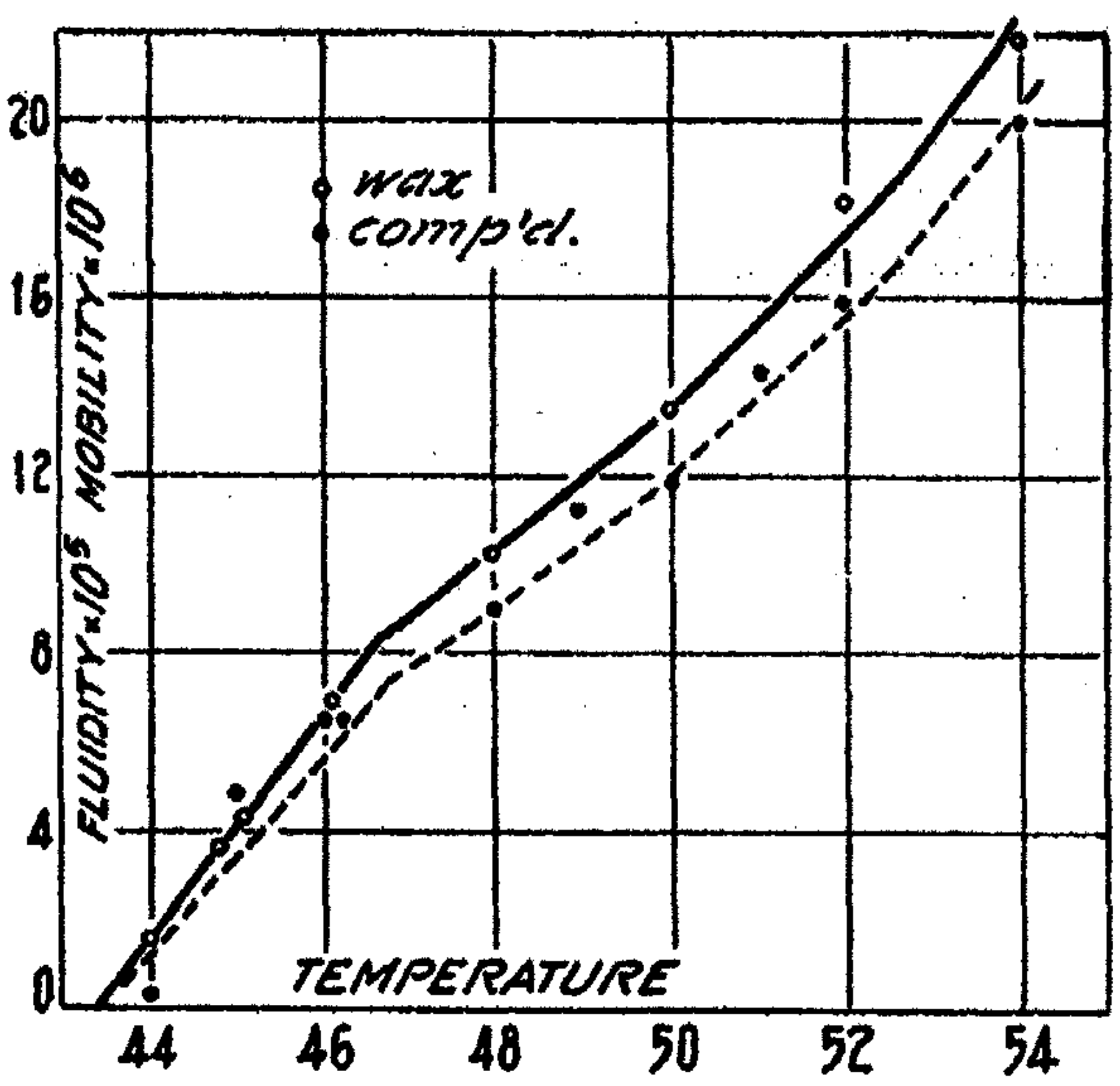

FIG. 3

Wax and Compound No. 4
Fluidity and Mobility *vs.* Temperature

TABLE VII

Plasticity of Compound No. 4A

Talc % by weight = 55.2 Capillary No. 14
Talc % by volume = 31.9 Average yield value = 3.75

Temp.	Manometer reading in mm. Hg.	Shear = $\frac{PR}{2L}$ gm./cm²	Density	Wt. per Sec. 10^6	Mobility 10^6
48.0°C	92.28	65.01	1.489	17.38	.40
48.0	136.50	95.65	1.498	29.42	.41
					Mean μ = .405
49.0	85.85	60 .56	1.495	21.93	.56
49.0	147.65	103.41	1.495	48.14	.61
					Mean μ = .59
50.0	85.45	60.30	1.492	19.9	.51
50.0	141.55	99.24	1.492	39.27	.52
					Mean μ = .515
51.0	84.69	59.80	1.490	23.42	.61
51.0	145.35	101.85	1.490	48.60	.63
					Mean μ = .625
51.9	85.85	60.58	1.488	27.80	.71
51.9	144.80	101.44	1.488	52.58	.69
					Mean μ = .70

Compound No. 4 A

A few determinations have been made at a still higher talc content. The yield value has increased and the mobility fallen off. These results are not sufficiently reliable to certainly indicate that the yield value is a linear function of the volume percent of talc. It is in our opinion, however, that such is the case. (see Fig. 4).

Conclusions

The fluidity-temperature relations of compound wax reflect the physical changes which occur. The crystallization of the stearic acid is indicated by a sharp break in the curve. The temperature of crystallization can be determined to within about 1°C. by fluidity measurements. The addition of talc rapidly reduces the fluidity of the mixture. Above 19.89 volume percent talc, the mixture develops plastic properties. At 28.5 volume percent talc, the yield value is 2.69 gm/cm².

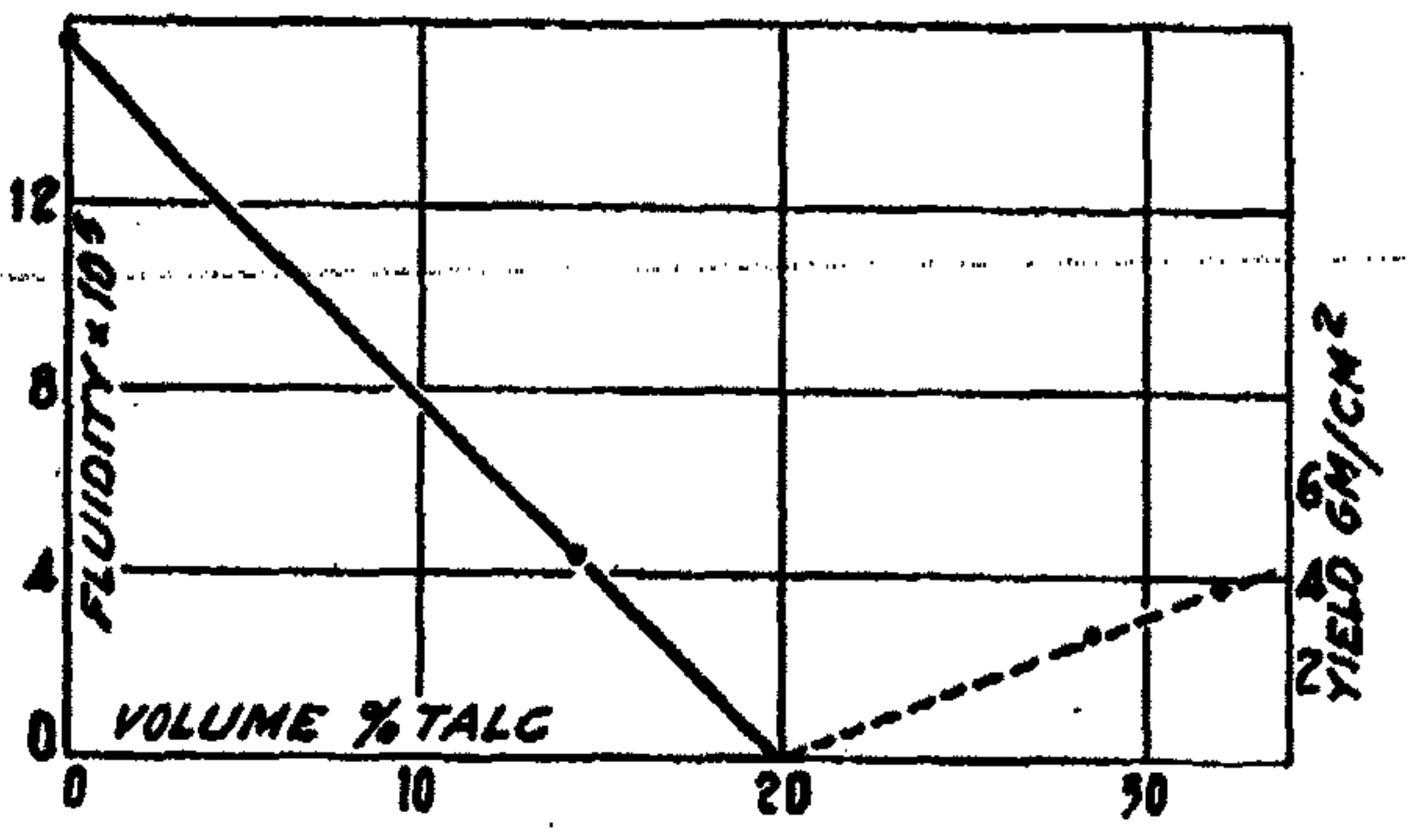

Fig. 4

Compound Wax No. 4
Fluidity and Yield Value *vs.* Volume Percent Talc

Large additions of talc increase the yield value in a seemingly linear manner. Our measurements do not show that yield value depends upon temperature. It seems to be characteristic of the quantity of filler added alone.

The form of the fluidity-temperature curve of the wax is not changed by the addition of talc but the values of the fluidity are rapidly reduced.

When working with plastic substances it is necessary to make measurements at several widely separated shearing forces so that the yield value can be determined from measurements unaffected by the departure of the flow shear curve from linearity at low pressures.

We wish to acknowledge the helpful criticism and advice received from Dr. E. C. Bingham during the progress of this investigation and the support of the S. S. White Dental Manufacturing Company in carrying it out.

September 18, 1924

A SIMPLE PLASTOMETER FOR CONTROL USE WITH DENTAL CREAMS.*

BY E. MONESS AND P. M. GIESY

In April, 1923, before the Division of Industrial and Engineering Chemistry at the New Haven Meeting of the American Chemical Society, Bingham suggested that plasticity measurements could be made by timing the flow of a plastic material over successive increments of length of a capillary, this being equivalent to determining the speed of flow through capillaries of the same diameter and varying lengths. Since the maintenance of uniform consistency is important in the manufacture of dental cream, we decided to use this principle in the development of a simple plastometer which might be used for plasticity measurements on dental creams.

The use of gas pressure involves complicated and expensive apparatus for keeping the pressure constant and measuring it. We decided to try to use a mercury column to supply pressure, measuring the pressure by the height of the column. The dental cream is pushed by the pressure of the mercury through the graduated capillary, and the time at which the head of the column passes alternate centimeter divisions is noted.

Under these conditions $\Delta l/\Delta t$, where $\Delta l = 2$ cm. and Δt is the actual time taken by the dental cream to traverse this length of capillary, is a variable which is a linear function of P/l, where P is the total pressure applied and l the mean length of capillary filled by the material during this time. So, when a curve is plotted with $\Delta l / \Delta l$ as ordinate and P/l as abscissa, a straight line should result, the slope of which is proportional to the mobility of the plastic, and the intercept of which on the X axis is proportional to the yield shearing stress of the material under test.

Apparatus and Method

Fig. 1 shows a view of the whole set-up, and Fig. 2 gives the details of the plastometer proper. This is constructed entirely of standard pipe fittings, as shown. The capillary C is held in a rubber stopper which is kept in position and at the same time compressed against the capillary by the drilled pipe cap shown. The apparatus is easily taken apart and can be readily washed, dried and reassembled.

In making a run the apparatus, not including the capillary with its rubber stopper and the drilled cap and reducing bushing in which this is held, is connected as shown to the rubber tube leading from the mercury reservoir, and the mercury level adjusted by holding the apparatus in a vertical position. The stopcock on the rubber tube is now closed. The dental cream is placed in the reservoir B by squeezing it out from a collapsible tube through a 3 inch long glass tube attached to the mouth of the collapsible tube; the

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* Paper presented at the Plasticity Symposium, Lafayette College, Oct. 17 (1924).

filling is done from the mercury surface upward, care being taken that no air spaces or voids are left in the mass of the dental cream. Next, the apparatus is placed in a horizontal position, pushed through the opening in the wall of the water bath, and the capillary is screwed on tightly by means of the bushing. The whole is then placed in the water bath as shown, covered with water, and the temperature is adjusted to 25°C. and kept there for 10 minutes. The run is then started by opening the stopcock and taking the proper readings, keeping the temperature of the bath at 25°C. throughout the run.

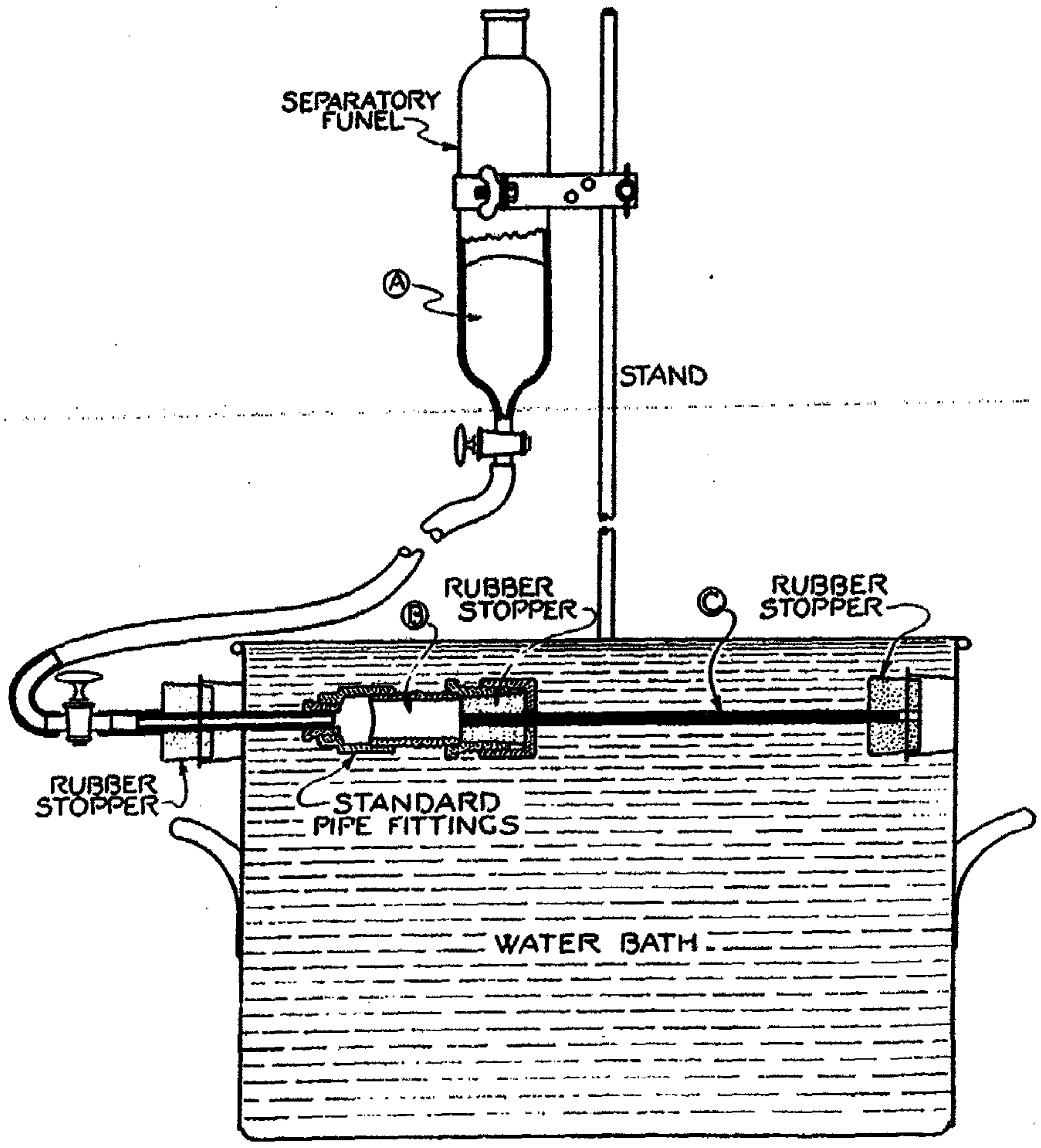

FIG. 1

The capillary can be calibrated by means of the viscometer shown in Fig. 3. The viscous liquid is allowed to flow into a 60 cc. graduated flask, and the time of the flow is taken. This apparatus differs from Saybolt's in that our capillary is used in it directly, and also in that the flow takes place at a constant head, which is maintained as long as the liquid has not yet reached the bottom of the air tube. With a distance between the upper end of the capillary and the lower end of the air tube = 3.8 cm., the length of the capillary 16.8 cm., and the temperature 0°C., two runs on a 37% by weight mixture of alcohol and water gave results of 321 seconds in both cases. Substituting in Bingham's equation (8)[1] $\eta = \frac{\pi g p R^4 t}{8Vl} - \frac{m\rho V}{8\pi l t}$ the values

η = 1/13.9
ρ = 0.9452
g = 980
p = 20.6×0.9452
t = 321
V = 60
l = 16.8
m = 1

we obtain for R, 0.742 mm. A calibration by weighing the mercury thread gave 0.745 mm.

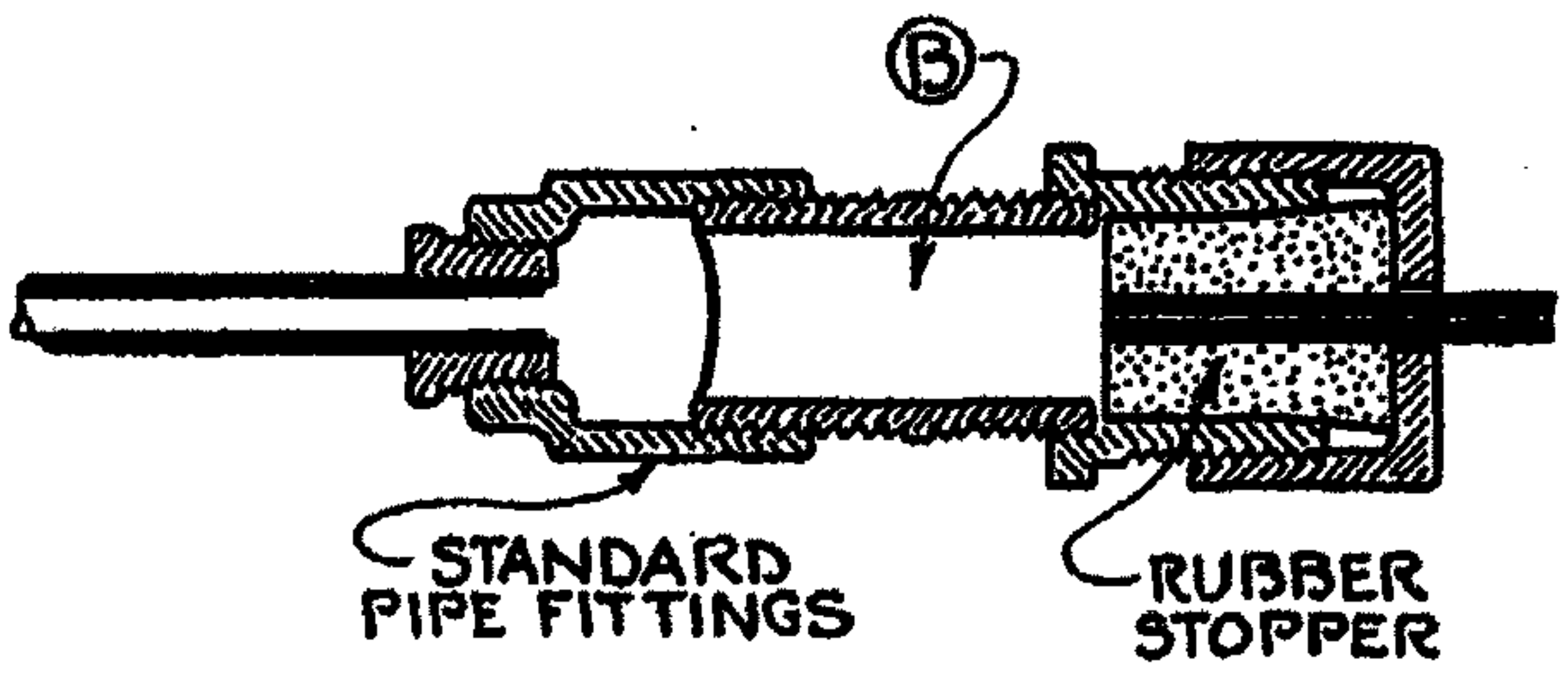

Fig. 2

The first design (Type I) used an oil-cup as the body of the plastometer, the pressure being applied through a tube soldered into the top thereof. With this outfit the mercury channelled through the dental cream to the capillary, frequently entering this before the end of the run. When air pressure was used, the same thing happened. To prevent this, a 3″ × 1/4″ copper tube was inserted between the oil-cup and the capillary (Type II). Duplicate determinations with this checked poorly, due to the mercury entering the tube varying distances. The oil-cup was then omitted, the mercury pressure being applied directly to the copper tube, the pressure thus being exerted over the whole area of the dental cream (Type III). This gave runs which checked satisfactorily, but when the applied pressure was increased the values of the slope also increased:

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[1] "Fluidity and Plasticity," p. 18 (1922).

Pressure (cm. Hg)	Slope
18.9	0.0076
22.6	0.0096
25.8	0.0101
30.2	0.0128

This seemed to be due to flow-resistance not in the capillary, but in the reservoir, which had the effect of an additional length of capillary. We therefore modified the instrument to the form first described. Runs with varying pressures gave the following results:

Pressure (cm. Hg)	Slope	x-Intercept
17.0	0.0156	0.24
20.4	0.0162	0.24
26.6	0.0166	0.22

The curves of these runs are shown in Fig. 4.

It will be noticed that even here the effect of the internal resistance of the reservoir shows itself somewhat. It should be pointed out that it will be impossible to eliminate this entirely with any type of capillary tube instrument. With more fluid materials its effect is less noticeable. In working with fairly thick aqueous emulsions we were able to use the Type III instrument with entire satisfaction; varying the applied pressures did not affect the slopes:

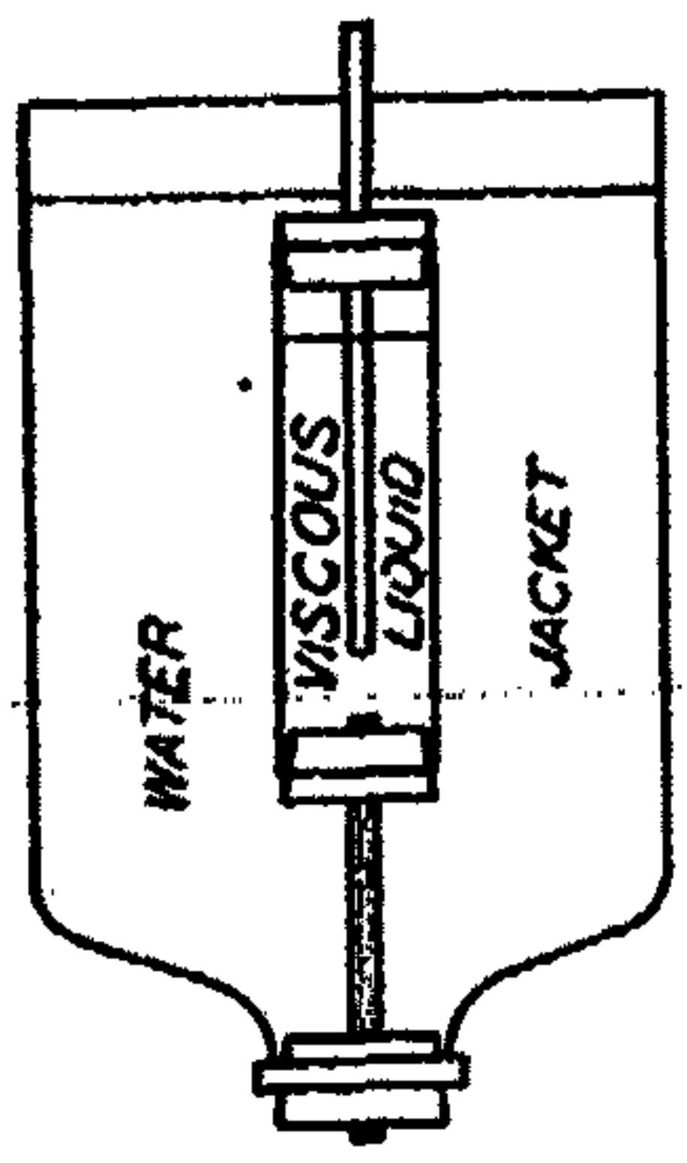

Fig 3.

Pressure (cm. liquid)	Slope	x-Intercept
29	0.0175	1.2
58	0.0175	1.5

Theoretical Part

Bingham and Murray[1] calculated the average shearing stress over the interval $l_2 - l_1$ by integrating $[PR/2l]\,dl$ between these limits, and found it to be $[PR/2(l_2 - l_1)] \log_e l_2/l_1$. They then stated that the volume of flow was evidently $\pi R^2(l_2 - l_1)$, and plotted the speed of flow for different intervals as a function of the average shearing stress. Green in his discussion of this paper, stated that $\pi R^2(l_2 - l_1)$ was *evidently not* the correct V/t to use (he obviously meant V), but gave no reason for the statement. This method is not rigorously correct, for the reason that V is not proportional to F, but to F−f, which has not been calculated.

Our own method is mathematically less rigorous, since we plot average rate of flow over an interval as a function of mean shearing stress over the

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[1] Proc. Am. Soc. Testing Materials, 23 II, 655 (1923).

same interval. To determine whether this was justifiable, we calculated t as a function of l from the equation

$$P/l = a + (1/S)\ dl/dt \qquad (1)$$

which is the equation of a straight line expressing the experimental results. This cannot be integrated as it stands, but by making the substitution $l = 1/z$, the equation reduces to the form

$$dz/dt = Sz^2(a - Pz) \qquad (2)$$

Integrating and resubstituting we obtain

$$t = \frac{P}{Sa^2} \log_e \frac{P - l_0 a}{P - la} - \frac{l - l_0}{Sa} \qquad (3)$$

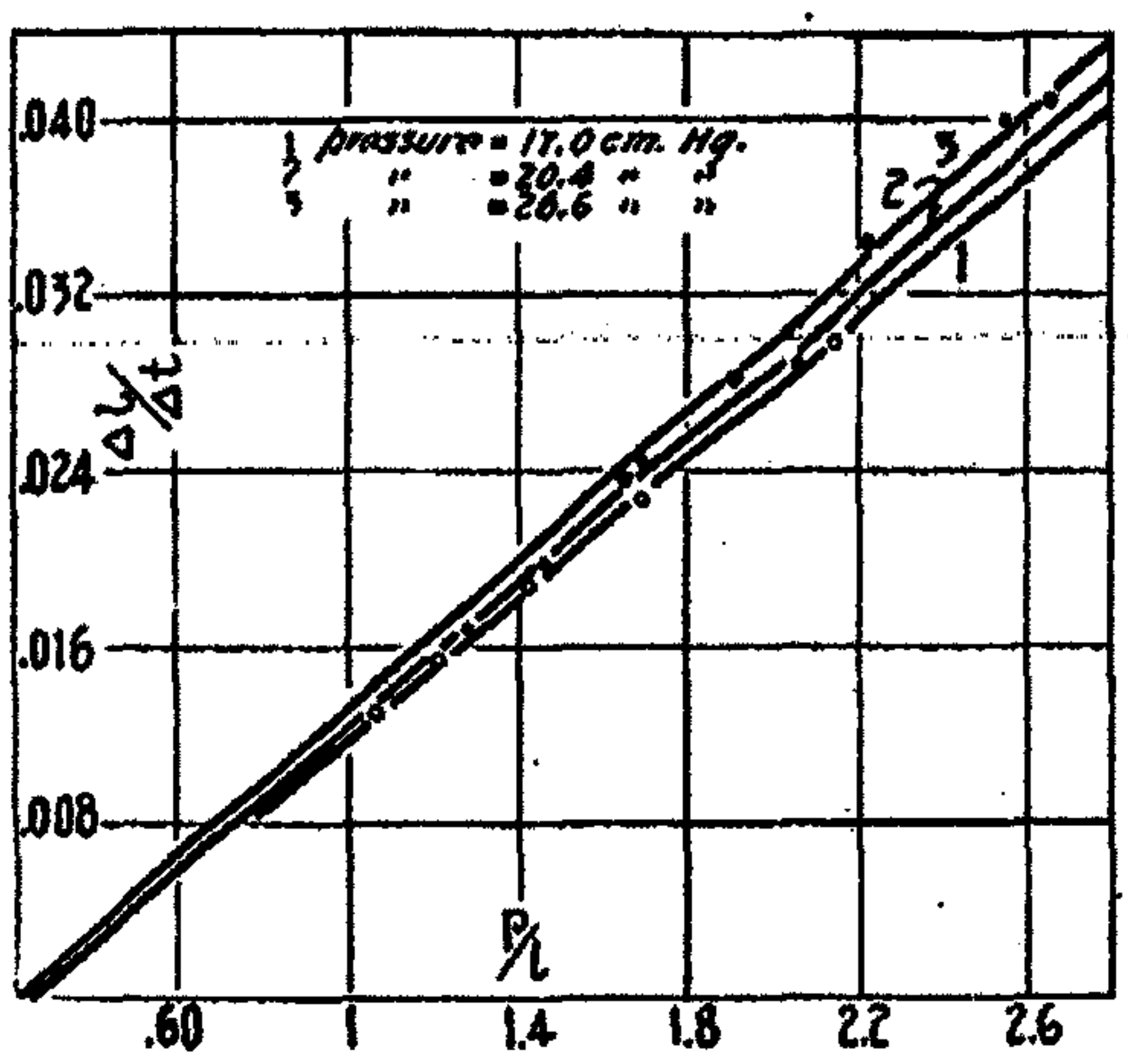

Fig. 4
Plasticity Curves for Dental Cream using varying pressures

where $t = t_0$ when $l = l_0$. In this equation we have substituted the figures from an actual run on a sample of dental cream:

$P = 21.8$ cm. Hg
$s = 0.0086$
$a = 0.17$
$l_0 = 3$ cm.

and have calculated the following values of t, using 8-place logarithms (6-place give an accuracy of only about 1 percent.):

l (cm.)	t (sec.)
3	0
5	44.075
7	111.256
9	202.310
11	318.046

From these values we have calculated $\Delta l/\Delta t$, and from equation (1) dl/dt, with the following results:

l (cm.)	$\Delta l/\Delta t$	dl/dt
4	0.045377	0.045408
6	0.029770	0.029748
8	0.021965	0.021973
10	0.017281	0.017286

From this it is obvious that while the mathematical method is not rigorous, its errors are far less than the experimental ones.

All this, of course, is based on the assumption that a linear relation between F and V/t really exists. But even if this is not strictly so, it will not vitiate the results of this calculation. The differences between $\Delta l/\Delta t$ and dl/dt depend only on the curvature of the l–t curve, and it is evident that it would take a great increase in curvature to make these differences as large as the experimental errors.

Our measurements have shown that when the shearing stress is low enough, the usual departures from the linear relationship of F and V/t take place. But by making measurements with high enough shearing stresses, we have gotten curves which are linear within the experimental errors.

The Bingham formula[1] for plastic flow through a tube is

$$\frac{V}{t} = \frac{\pi\mu R^4}{8l}\left(P - \frac{4}{3}p\right) \qquad (4)$$

Under our conditions, V/t becomes $\pi R^2 dl/dt$, π, μ, R, and P are constants, and l and p are variables. Substituting $2fl/R$ for p (f being constant) we have

$$\frac{dl}{dt} = \frac{\mu R^2}{8}\left(\frac{P}{l} - \frac{8f}{3R}\right) \qquad (5)$$

If, therefore, we plot dl/dt as a function of P/l, as we have done for the sake of convenience, we see that the slope is $\mu R^2/8$, and the x-intercept $8f/3R$. The slope, therefore is proportional to the mobility, and the x-intercept to the yield shearing stress; each value is also a function of the radius of the capillary. As long as the same capillary is used, slopes give comparative mobilities, and x-intercepts comparative yield shearing stresses.

If we plot rate of flow dl/dt as a function of shearing stress, $F = RP/2l$, equation (5) reduces to the form

$$\frac{dl}{dt} = \frac{\mu R}{4}\left(\frac{RP}{2l} - \frac{4}{3}f\right) \qquad (6)$$

Now the x intercept equals 4/3 of the yield shearing stress (or the yield shearing stress itself, if Bingham's formula (89[4] is preferred), and the slope the mobility times one-fourth the radius. To get the mobility directly from the slope we must put the equation in the form

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[1] "Fluidity and Plasticity," p. 225 (1922).

$$\frac{4}{R}\frac{dl}{dt} = \mu\left(\frac{RP}{2l} - \frac{4}{3}f\right) \qquad (7)$$

and plot $4/R\ dl/dt$ as a function of $RP/2l$.

By putting Bingham's equation (88) in the form

$$(4/\pi R^3\ V/t = \mu(F - 4/3\ f) \qquad (8)$$

it will be seen that if we plot $(4/\pi R^3)\ V/t$ as a function of F $(=RP/21)$ the slope of the curve equals the mobility[1]. When speed of flow is plotted as a function of F, as is usually done, the slope of the curve is only proportional to the mobility, being also a function of the radius of the tube.

Summary

A plastometer is described which is composed only of pipe fittings and laboratory apparatus, and which has sufficient accuracy for control work.

A simple viscometer is described which will give absolute viscosity measurements, and which can be used to standardize capillaries for the plastometer.

The Bingham and Murray method is shown to be not mathematically rigorous, but sufficiently accurate mathematically to be within experimental error.

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[1] This has previously been pointed out by F. P. Hall in Technologic Paper of the Bureau of Standards, No. 234, pp. 354, 355.

ELECTRICAL DISPERSION OF LIQUIDS

Phenomena accompanying the passage of an electric current through contiguous immiscible electrolytes

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BY VICTOR COFMAN

When two immiscible solutions each of which separately is a conductor of electricity (e.g. nitrobenzene containing potassium tri-iodide and water containing potassium iodide) are placed in contact and a current is passed through the system, one may generally observe certain interesting phenomena of dispersion, polarization, etc., to which no reference is found in the scientific literature.[1] The importance of any changes occurring at the liquid—liquid boundary under such conditions can be readily appreciated from the following considerations:

According to the ionic theory, *within* the two liquid phases electricity is carried by charged ions, which may be solvated; it is natural to inquire what will happen to these ions when trying to cross from one liquid into the other under the driving influence of the electric force. Given that a steady current is passing through the system, there must be a continuous transfer of electricity across the boundary; this is all that may be definitely stated in advance. There is no *a priori* reason why this transference should take place by means of ions; there are other possible carriers, namely electrons, or larger charged particles. Which of these are actually the agents employed can be deduced from the changes which will accompany the passage of the current:

(1) If *electronic conduction* takes place one should be able to observe at the junction of the two liquids chemical changes similar to those occurring at the electrodes, for instance deposition of metals.

(2) With *ionic conduction* there are several possibilities:

a) the ions may pass freely from one liquid into the other, when little will be noticed, except changes in concentration.

b) the anion may cross the interface at a different rate from the cation—in extreme cases only one of them may be able to cross over. The interface will then play the part of a semipermeable membrane, and polarization, endosmose and other phenomena observed with ordinary membranes, may be expected.

c) the ions may carry with them their atmosphere of solvation. (see (3))

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[1] Nernst and Riesenfeld (Ann. Physik, 8, 600 (1902)) on passing a current through a system phenol-water with KI_3 as solute, observed changes in concentration at the junction of the two solvents. This they explained on the assumption that the ratio of the ionic velocities (or transport numbers) u/v differs in the two solutions. The authors, however, came to the conclusion that nothing more is to be expected: "an der durch Berührung zweier Lösungsmittel gebildeten Trennungsfläche [ist] lediglich ein Transport des Electrolyten, *keine Ionenabscheidung*, zu erwarten." In contradistinction to this, Weber and Gaus (Repertorium der Physik. 2, 118 (1916)) state: "Wenn ein elektrischer Strom die Grenzfläche zweier Flussigkeiten durchsetzt findet an dieser Grenze eine *Abscheidung der Ionen* statt, wodurch die Kapillarkonstante verändert wird". This statement of Weber and Gaus is made in connection with considerations of the mercury-electrolyte interface.

(3) Conduction by means of *larger charged particles*, that is, single ions, or groups of ions, with original solvent attached, would involve a dispersion of one liquid into the other.

A description of some of these phenomena (dispersion, chemical changes) experimentally observed, together with a few remarks concerning the factors which influence them, forms the subject of this contribution.

Experimental Part

Experiment 1. Two grams of KI_3 (molecular proportions of KI and I_2) are shaken in a separator with 50 cc. of nitrobenzene and an equal amount of water. The result is a dark, reddish-brown solution of potassium polyiodide in nitrobenzene, and an almost colorless solution of potassium iodide in water (with only traces of tri-iodide).[1]

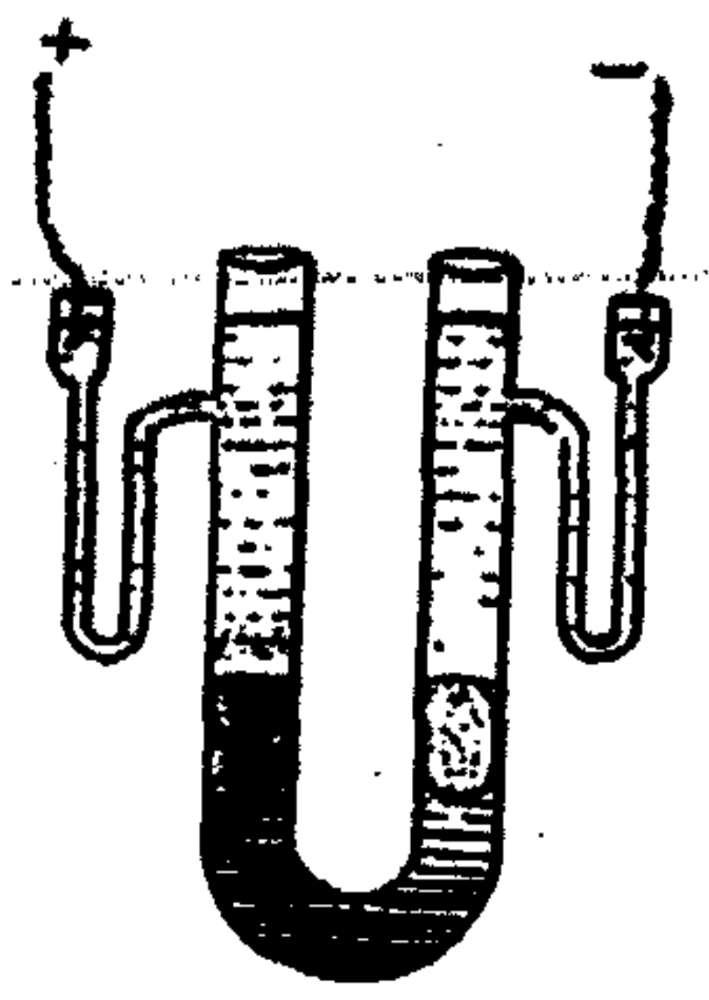

Fig. 1

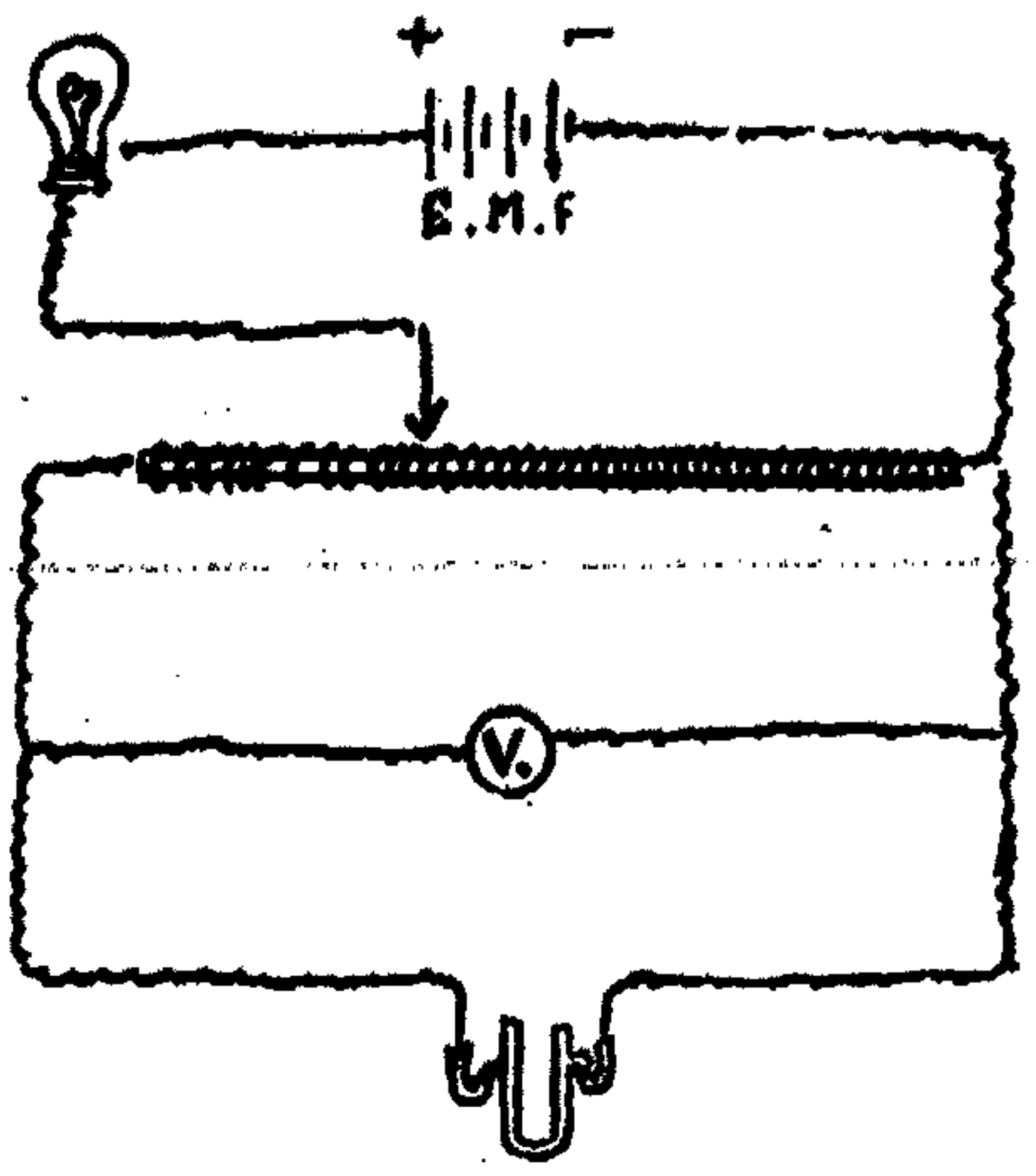

Fig. 2

After separation, the heavier nitrobenzene solution is placed in the lower part of a U-tube and the aqueous solution poured over it in both limbs. Two platinum electrodes dip in the water layers; in Fig. 1 the electrodes are shown placed in separate compartments to prevent the chemical reactions which take place at the electrodes from obscuring the phenomena at the liquid-liquid boundary. The U-tube is connected to a source of electromotive force (220 volts) in series with a lamp resistance and in parallel with a voltmeter and a 1000-ohm rheostat, the latter allowing the potential difference across the U-tube to be varied from 0 to 220 volts (the connections are shown in Fig. 2). The resistance of the circuit amounts to several thousand ohms.

On applying a potential difference up to 10 volts very little change is observed at the junction of the two liquids, except for a slight, skin-deep whiteness on the nitrobenzene surface in the cathode limb of the U-tube. With increasing p. d. (15 to 20 volts) this whiteness develops downwards into the

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[1] Cf. Dawson and Gawler: J. Chem. Soc. **81**, 527 (1902).

nitrobenzene as a turbidity of a cotton-wool-like appearance, and on further increasing the p. d. to 30 volts a white, milky layer is formed which advances steadily downwards. The colored polyiodide in the nitrobenzene withdraws before the advance of this turbidity, except near the wall of the tube, where it creeps upwards in thin streamlets as far as the interface, there to be reflected back and dispersed in the white turbid layer already mentioned.

The milky layer moves downwards at the rate of about 1 cm. per hour; this is not the actual velocity of the particles causing the turbidity since, as will be seen later, theirs is a circular motion; it merely represents the drift of the turbidity as a whole. When the milkiness has reached the lower part of the U-tube it does not advance into the other limb in the same fashion (that is, with a fairly sharp boundary) but merely sends as offshoot a stream of cloudiness which rises rapidly to within one cm from the interface nearest to the anode, where it may stop for an instant and then send forth another thinner streamlet as far as the interface. Eventually the whole of the nitrobenzene layer in the anode limb also becomes turbid, but retains its reddish-brown color.

While these occurrences take place in the nitrobenzene phase, the following phenomena are observed in the aqueous layers, when the voltage rises to 100-150 volts:

In the cathode side a slight stream of turbidity moves upward from the interface and becomes dispersed throughout the water layer. At the same time in the anode limb, just above the nitrobenzene, there appears a *clear*, narrow zone (never more than 2-3 mm. thick), beyond which a slight turbidity is produced. In addition to these changes the usual chemical reactions (liberation of iodine and formation of potassium hydroxide) take place in the electrode compartments.

The phenomena at the interfaces may be studied more closely by means of the microscope, as follows:

Experiment 2. A drop of nitrobenzene solution (same as used in Experiment 1. is placed on a microscope slide with two drops of the aqueous potassium iodide solution, one on either side, just touching it. Two platinum wire electrodes dip into the water drops and, by means of the electrical connections already described in experiment 1, a potential difference of from zero to 200 volts can be applied. The junctions of the drops are observed under a magnification of 100 diameters; the circuit is closed and the potential difference increased gradually, when it is seen that:

(i) Already with low p. d. (from a fraction of a volt to one or two volts) the reddish colour of the nitrobenzene becomes lighter at the junction near the cathode and deeper red at the boundary nearest the anode.

(ii) The junctions of the two liquids approach one another—that is, the water drops move slowly into the nitrobenzene—and, unless some precaution, such as greasing the glass, is taken, the two water drops often join together, spoiling the experiment.

(iii) When the potential difference reaches a "critical" value (in this case 1.5 volts) a new phenomenon is observed; the boundary nearest the cathode becomes turbid on the nitrobenzene side owing to the presence of innumerable minute, dot-like particles, of magnitude of the order $14^{-4}-10^{-5}$ cm. In this case they are formed at the interface and move slowly into the nitrobenzene, forming a turbid zone at the boundary. Because of their minute size the movement of these particles is difficult to follow. After a time, especially if the current be stopped, the small particles coalesce producing larger droplets of a colorless liquid which mixes readily with the water phase and is therefore either water or an aqueous solution.

(iv) With higher p. d. (4 to 10 volts) the movement of these small particles becomes very rapid. They move first in the direction of the negative current (i.e. towards the anode) penetrating a certain distance into the nitrobenzene solution; then they slow down and are finally turned back by streamlets of red-coloured nitrobenzene (cf. Fig. 3). This circular, or spiral, movement continues uninterrupted. The stream of particles as a whole does not remain stationary but advances slowly into the nitrobenzene, but does not reach the opposite boundary. The turbidity (white, milky layer) of the previous experiment was nothing but these streams of particles on a larger scale.

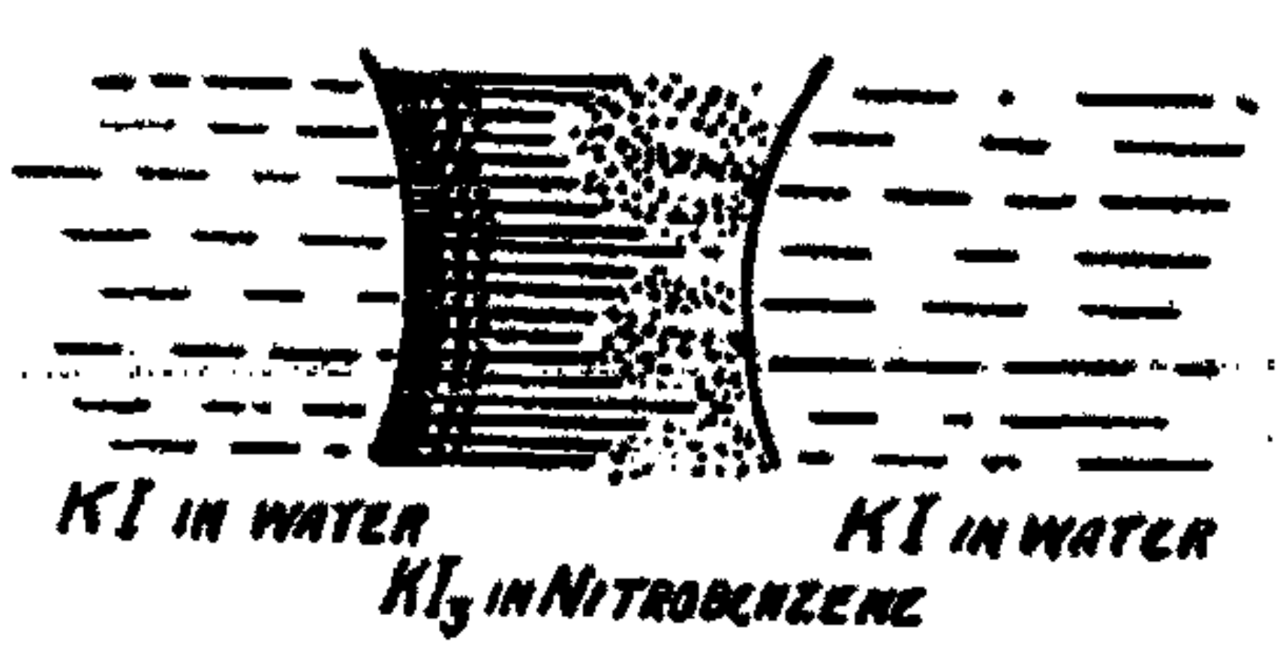

FIG. 3

(v) While the changes described take place at the cathode boundary, the nitrobenzene at the other interface becomes of a deeper red, almost black, color and, when the potential applied is in the neighbourhood of 10 volts, small particles are seen floating in the water. With higher potentials these particles become more numerous, they appear as black dots at the interface and show a circular movement which, however, does not reach the rapidity of that of the water particles previously observed in the nitrobenzene at the cathode side. Some of these dot like particles become attached to the glass slide, others join together producing larger droplets of a dark liquid which is eventually resorbed by the nitrobenzene.

(vi) With still higher p. d. (one hundred volts and over) the positive boundary appears to become rigid owing to the formation of a "skin". Through this membrane water passes into the nitrobenzene in one direction and nitrobenzene into the water in the opposite direction. Drops are thus formed on the two sides of the membrane; they grow to a certain size and then suddenly collapse, being resorbed by the mother-liquid.

The Influence of Concentration

This was investigated by using aqueous and nitrobenzene solutions of various strengths, but always in equilibrium with one another so as to eliminate the disturbing influence of e. m. f.'s of concentration which might otherwise occur. As a result the nitrobenzene solutions employed were in every case of a deep red to black color, while the water solutions were nearly colorless at low concentrations (containing potassium iodide only) but of a deep red color at higher concentrations, showing the presence of polyiodide. This difference not only of concentration, but also of the nature of cation, should be borne in mind when considering the difference of behaviour of solutions of different strength, as described below.

The solutions were prepared as follows:—40 grams of potassium triiodide were shaken with 50 cc. of nitrobenzene and an equal amount of water; after separating, a portion of each was further diluted so as to obtain solutions of "total" concentrations equal to 10%, 5%, 2%, 0.5% and 0.1%. By "total concentration 10% potassium triiodide" is meant therefore that the two solutions of water and nitrobenzene contain potassium and iodine in the proportion in which 10 grams of KI_3 would distribute itself between 50 cc. of nitrobenzene and 50 cc. of water. The immiscible solutions were shaken together and reseparated before use in experiments *2a* to *2f*.

Experiment 2a—total concentration 0.1% KI_3 ⎫ Other arrangements as in
Experiment 2b—total concentration 0.5% KI_3 ⎬ experiment 2.
Experiment 2c—total concentration 2.0% KI_3 ⎭

The phenomena observed with these three concentrations are essentially the same as already described in experiment 2. Small particles render the nitrobenzene turbid at the negative (cathode) boundary. The movement of the turbidity as a whole is slower with decreasing concentration. The particles are very minute and tend to attach themselves to the glass.

At the positive (anode) boundary the color of the nitrobenzene solution deepens (in experiment 2b a pink color replaced the reddish-brown when high voltage was applied—probably due to some chemical action). As the concentration of the solutions employed increases so does the "critical" potential, which has to be applied in order to obtain dispersion.

Experiment 2d. Total concentration 5% KI_3. In this case it is only when the p. d. rises to 15-20 volts that the cathodic interface becomes dotted with numerous droplets. Soon after that the interface gives a jerk and all the droplets disappear; streams of moving particles are also seen but they keep near the interface and only advance deeper into the nitrobenzene when the p. d. is further increased; when the latter reaches 100 volts arborescent crystals (potassium iodide?) are deposited at this interface on the nitrobenzene side.

Experiment 2e—"total" concentration 10% KI_3

Experiment 2f—"total" concentration 40% KI_3

The water now contains a large proportion of polyiodide and it no longer becomes dispersed into the nitrobenzene at the cathodic boundary; it is the nitrobenzene which is now dispersed in the water at both interfaces, but the disperse systems so formed are much less stable than the milkiness due to the water particles in nitrobenzene. The disperse particles of nitrobenzene in water have a much greater tendency to attach themselves to the glass or coalesce and be resorbed.

Influence of Nature of Solute

Two series of experiments were conducted; in one the nitrobenzene solution contained potassium polyiodide; in the second series, tetra-ethyl ammonium iodide. Various substances were used as aqueous solutes, in concentrations of about 1%.[1]

First series: nitrobenzene-polyiodide solution same as in Experiment 1.

Experiment 3. Aqueous solute: sodium chloride.

The phenomena observed were similar to those of expt. 2. Water is dispersed in the nitrobenzene at the negative interface; at the positive (anodic) interface there is a deepening in the colour of the nitrobenzene and, with higher p. d. water penetrates in endosmotic fashion as described under expt. 2 (vi).

Experiment 4. Aqueous solute: magnesium sulfate.

Phenomena similar to the above; the formation of disperse water particles can be clearly seen with a p. d. of 15-20 volts. In this case the negative (cathodic) interface breaks up explosively, streams of water particles being sent thereby intermittently into the nitrobenzene. At the positive boundary there is no dispersion, but the nitrobenzene, which has become almost black in colour (with occasional deposition of opaque crystals) advances bodily into the water towards the anode.

Experiment 5. Aqueous solute: sodium acid phosphate.

Results as in expt. 4. There is a very marked tendency of the water droplets which enter the nitrobenzene at the negative interface, to attach themselves to the glass.

Experiment 6. Aqueous solute: sodium diethyl-barbiturate.

At the negative interface: usual dispersion of water in nitrobenzene; also small arborescent crystals deposited. At the positive junction usual increase in concentration of polyiodide in nitrobenzene.

Second series of experiments, using as middle phase a saturated solution of *tetraethyl ammonium iodide* $(C_2H_5)_4NI$, *in nitrobenzene.*

Experiment 7. Aqueous solute: tetra-ethyl ammonium iodide.

With p. d. up to 20 volts no immediate change is observed. With 100 volts dispersion is observed at the positive interface in both liquids, but is not very marked; acicular crystals are deposited on the water side.

Experiment 8. Aqueous solute: potassium iodide.

Amphoteric dispersion on the cathode side, exactly like that occurring at the positive boundary in expt. 7, accompanied as before by the formation of acicular crystals in water. At the positive interface the usual "violent" dispersion of water in nitrobenzene is now observed.

Experiment 9. Aqueous solute: potassium polyiodide (saturated).

In this case as soon as the two phases are brought into contact—before applying an external p. d.—the red colour of the aqueous solution is seen entering

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[1] The two phases were not in equilibrium as in the previous experiments but this introduced complications only in Experiment 9.

the nitrobenzene. This is accompanied by strong amphotheric dispersion. We shall return in a later paper to this phenomenon of *spontaneous dispersion* which is met with frequently, perhaps always, when two phases not in equilibrium with one another, are brought into contact.

The result of applying an external p. d. is to cause further dispersion of water in nitrobenzene at the positive boundary. At the negative interface the dispersion of nitrobenzene in water is increased at first; but soon after, following upon the disappearance of the red color (polyiodide) from the water, the dispersion is reversed.

Experiment 10. Aqueous solute: silver nitrate.
A new factor is introduced in this experiment owing to the insolubility of the compound formed at the interface (silver iodide) in both solvents. When the two phases are brought into contact, even before passing a current, a precipitate of silver iodide is slowly formed at the boundary. Careful microscopic observation shows the presence of minute, rapid moving particles constantly bombarding the interface; it is these particles which apparently settle down producing a narrow zone of precipitated silver iodide (of different crystalline appearance on the two sides of the junction. After a short time the interaction comes to a stand still.

When an external p. d. is applied the precipitate at the positive boundary grows and forms a thick membrane across which endosmosis takes place, water passing into the nitrobenzene and vice-versa. The water which passes through carries with it some silver ions since a precipitate is formed round the water bubbles on the other side of the membrane. These fairly large (lmm.) bubbles show a violent circular motion of the liquid in their interior, and are from time to time resorbed.

With a p. d. of about 100 volts iodine is liberated on the nitrobenzene side of the interface and silver is deposited on the water side. The silver is black and amorphous at first but soon develops into dendritic crystals with metallic lustre.

While all these changes take place at the positive boundary, very little is noticed on the negative sides, except for a few crystals formed in the water, and sometimes slight endosmosis. The occurrence of dispersion is shown in Table I.

Results with other Solvents

A few other solvents besides nitrobenzene and water were tried, e.g. amyl alcohol, olive oil and guaiacol. Dispersion was obtained in every case when electrically conducting solutions could be obtained but as a rule it was much less marked than with nitrobenzene-water solutions.

From the foregoing table one significant fact is clear, namely that *the type of dispersion depends upon the substance which is formed at the interface* during the passage of the current. For instance when potassium iodide is produced, as in expt. 1 at the negative and in expts. 8 and 9 at the positive interface, then water is dispersed in large amounts in the nitrobenzene. When potassium

TABLE I

Experiment	Substance formed at negative interface	Dispersion observed in	Substance formed at positive interface	Dispersion seen in:
1	potassium iodide	nitrobenzene	potassium polyiodide	water
2	potassium polyiodide	water	potassium polyiodide	water
3	potassium chloride	nitrobenzene	sodium polyiodide	—
4	potassium sulfate	nitrobenzene	magnesium polyiodide	—
5	potassium phosphate	nitrobenzene	sodium polyiodide	—
6	potassium barbiturate	nitrobenzene	sodium polyiodide	—
7	tetra-ethyl ammon. iodide	—	tetra-ethyl ammon. iodide	both solvents
8	tetra-ethyl ammon. iodide	both solvents	potassium iodide	nitrobenzene
9	tetra-ethyl ammon. polyiodide	water	potassium iodide	nitrobenzene
10	tetra-ethyl ammon. nitrate	—	silver iodide	endosmosis

polyiodide is formed then nitrobenzene is dispersed in water, though less vigorously. With tetra-ethyl ammonium iodide the dispersion is on both sides. In general it is found that *dispersion occurs in the solvent in which the substance formed is insoluble or only slightly soluble.*

When the compound formed is insoluble in both solvents it is deposited at the interface. Electro-endosmose and chemical reactions (electrostenolysis) are then produced as in the case of ordinary membranes. These same phenomena are also met with occasionally even when no solid precipitate (except perhaps a "skin") is present. This proves that *the transfer of electricity from one electrolytic phase to another is not always carried out by single ions only,* but also (i) *by means of groups of ions associated with original solvent.* (ii) *by means of electrons.*

Related Phenomena

As previously mentioned, apart from the experiments of Nerst and Riesenfeld, no investigations seem to have been made in this field. Certain known phenomena, however, which appear to be related to those discussed in the foregoing paper may be briefly referred to:

a) Lehmann[1] describes experiments in which liquids are dispersed, apparently by means of high electrostatic potentials. In the so-called "electric

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[1] "Molekularphysik," 1, pp. 825 et ff. (1888).

heart" experiment (Fig. 4) the electrode (A) is surrounded by molten sulfur and immersed in hot turpentine; as the potential of the electrode is increased the molten sulfur takes the shape of a heart from whose pointed end droplets of sulfur break off and are dispersed in the hot turpentine.

De Waha's "electric fountain", (Fig. 5) is a similar experiment in which petroleum is dispersed in air in the form of a fine spray, by the application of a high potential.

b) Kossogonow[1] gives an interesting account of the electrolytic dispersion of lead and other metals by means of low e. m. f.'s. The phenomena observed by him resemble somewhat those obtained in our experiments. W. Ostwald[2] refers to the above phenomena as proof of the existence of a "negative" or "expansive" surface tension.

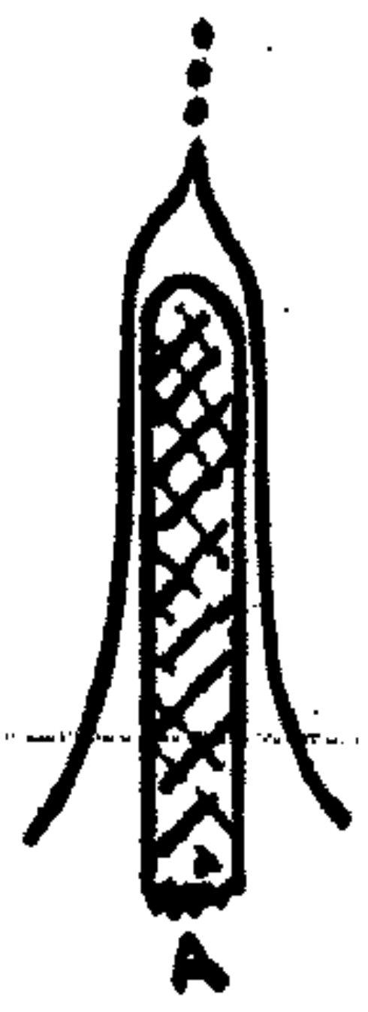

FIG. 4

FIG. 5

Theoretical Considerations

In our introductory remarks it was briefly pointed out what type of phenomena may be expected to happen at the junction of immiscible electrolytes when a current is passing, and subsequently a number of experiments were described showing that many of those phenomena do occur. An attempt will now be made to consider some of the factors which have a bearing on the observed facts.

(1) *The Solubility.* The influence of the substance produced at the interface has been noticed in the experimental part. If as in Fig. 6, the immiscible phases (I) and (II) contain the ionized substances A^+B^- and C^+D^- respectively, it will be seen that on passing a current in the direction shown by the arrow, the ions A^+ and D^- are brought towards the boundary while B^- and C^+ move away from it. In consequence, it is the ions A^+ and D^- that are mainly responsible for the facts under investigation.

There are three possibilities:

(a) The ions A^+ D^- form a compound which is insoluble in both phases (cf. expt. X, where AgI is formed). The result is a precipitate which behaves

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[1] Kolloid-Z. 7, 132 (1910).

[2] "Handbook of Colloid Chemistry," 2nd ed. pp. 68 et ff. (1918).

as a membrane and gives rise to phenomena of electro-endosmose, polarization and stenolysis.

(b) The compound AD is soluble in both phases, and will then tend to distribute itself between the two liquids in accordance with its solubility ratio. A restricted case (i.e. when the substance AD is present originally in the two liquids) was investigated by Nernst and Riesenfeld who showed that owing to differences in the transport numbers in the two media, there generally occurs a change in the concentration of the solute at the boundary as a whole, that is within a narrow zone on either side of the interface. The changes to be expected in our case will be dealt with later, in connection with the influence of the transport numbers.

(c) When AD is soluble in one of the liquids only, a curious situation results. Looking at Fig. 1 and assuming that AD as soon as formed dissolves in phase II only, it seems as if the net result will be that A-ions will pass from I to II but that no D-ions will cross in the opposite direction; that is, the interface would behave as a semi permeable membrane. Further an anomalous condition arises on the phase I side of the boundary where B-cations are leaving without other cations taking their place. It is evident that under these conditions we may expect interesting developments.

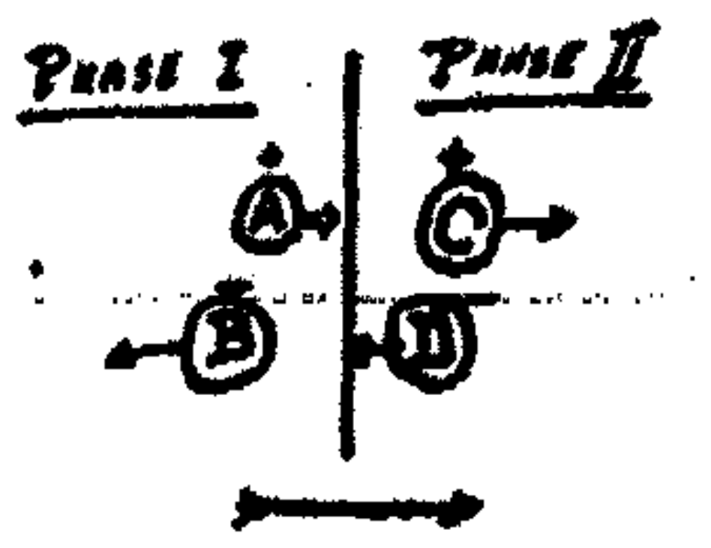

Fig. 6

In fact, in expt. 1 where potassium iodide is formed, soluble in water but not in nitrobenzene, what happens is that negatively charged water particles (phase II) enter phase I. Apparently, under the impelling electric force, negative ions surrounded by their atmosphere of solvation break through the interface and penetrate into the nitrobenzene. Whether these solvated ions enter singly and then coalesce as described in the next paragraph, or whether they enter bodily in "endosmotic" fashion carrying with them a portion of solvent which is in excess of their solvation, it is not possible to state definitely at present. Possibly both cases occur, according to experimental conditions.

(2) *The solvation of the ions.* If the ions which cross the boundary from one phase into the other carry with them part or all of their atmosphere of solvation, then the formation of a disperse system is to be expected. Single ions, even when solvated, would indeed be too small to be visible as a turbidity; but, as shown by Donnan[1], Lewis[2], and Knapp[3], there exists for disperse particles a size of maximum stability (in the neighbourhood of 10^{-5} cm. diam.) and therefore it is probable that several ions will coalesce to form larger particles of that magnitude. The clear narrow zone observed in experiment I just above the interface may correspond to the stage where the ions have not yet joined in sufficient numbers to cause cloudiness.

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[1] Z. physik. Chem. 46, 197 (1903).

[2] Kolloid-Z. 5, 91 (1909).

[3] Trans. Faraday Soc. 17, 457 (1922).

Further, it is interesting to note that the charged particles formed by the union of many ions would move, under the influence of the electric field, with a much greater velocity than the separate ions, owing to the smaller frictional resistance. This would account for the fast movement of the droplets noted in expt. II *et seq.*

The fast moving particles consisting of (say, negative) ions surrounded by their original solvent, will meet oppositely charged ions and their interaction will determine the course of the particle. According as the compound resulting from the union of these oppositely charged ions is more soluble in the particle or in the surrounding medium, positive ions will enter the particle or negative ions depart from it. Hence the particles may have their charges reduced, neutralized, or even reversed. In our initial experiment, for instance, admitting that the droplets entering the nitrobenzene at the cathodic boundary consist of an aqueous phase charged with negative ions, the latter will attract the positive potassium ions moving towards them in the nitrobenzene. The K-ions will thereupon enter the water neutralizing the charge of the particle. In the end the water particles would become positively charged[1] and their direction of movement would be reversed. This seems to be the simplest explanation of the circular motion of the dispersed particles observed in our experiments.

(3) *The ionic mobilities.*—In Fig. 7 let

a_1 = fraction of current transported by A^+ ions in phase (I) = product of transport number of A-ions, and their concentration, divided by the sum of the similar products of all ions concerned.
b_1 = fraction of current carried by B^- in (I)
d_1 = " " " " " D^- in (I)
a_2 = " " " " " A^+ in (II)
c_2 = " " " " " C^+ in (II)
d_2 = " " " " " D^- in (II)
a_3 = " " " " " A^+ from phase (I) to (II)
d_3 = " " " " " D^- from phase (II) to (I)

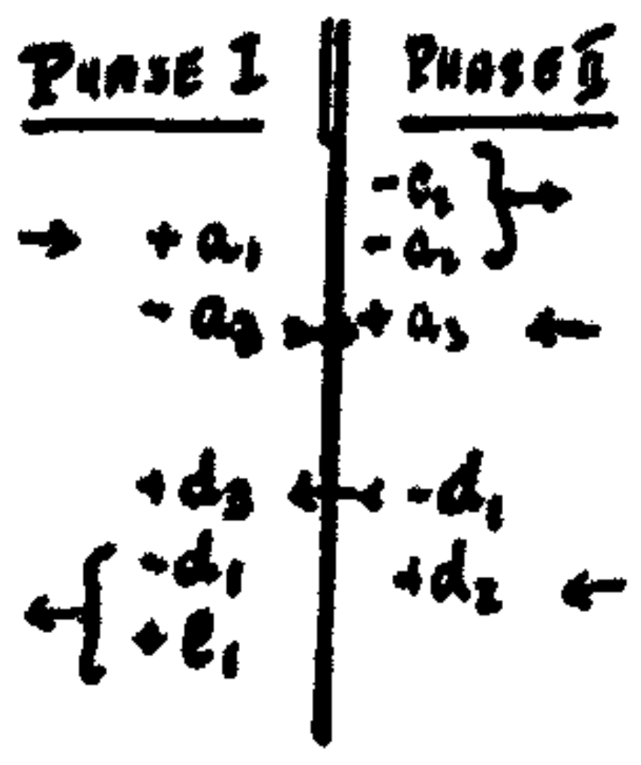

Fig. 7

The following relations hold (when ionic conductance alone takes place):

$$a_1+b_1+d_1=a_2+c_2+d_2=a_3+d_3=1.$$

It has been pointed out already how the value of a_3 and d_3 depends on the solubility of the compound AD in the two solvents: other things being equal, a higher solubility in phase (II) corresponds to greater value for a_3 than for d_3.

But a_3 and d_3 are also functions of the ionic mobilities in the two liquids. It can be readily seen that when a_1 and a_2 are both small compared with d_1

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[1] The formation of a potential difference between immiscible liquids, due to the distribution of interacting ions has been investigated by Beutner: "Die Entstehung elektrischer Ströme in lebenden Geweben"

d_2, the left side in Fig. 7 will lose more AD molecules than the right-hand side; consequently more of the AD molecules formed at the interface will go to phase (I), resulting in a larger number of D^- ions crossing the interface.

When AD is soluble in both solvents then the ions B^- and C^+ will gradually be eliminated from the interfacial zone, and it can be deduced that

$$a_3 = a_2 + (a_1 - a_2)\ D_1 s_2 / D_2(s_1 + s_2)$$

and

$$d_3 = d_1 + (a_1 - a_2)\ D_1 s_1 / D_2(s_1 + s_2)$$

where s_1, s_2, D_1, D_2, are the solubilities and the diffusion constants of the substance AD in phases (I) and (II) respectively.

In these equations $(a_1 - a_2)$ represents the total change in the number of molecules at the interface as a whole, when 1 F = 96.540 coulombs of electricity have passed through the system. This will distribute itself between the two liquids in proportion to the solubility and the diffusion constant of AD in liquid. a_2 and d_1 represent the loss in AD which will have to be made good before the excess (or deficit) $a_1 - a_2$ remains to be distributed. The formulae show that both the relation between a_1 and a_2 as well as that between a_1 and d_1 (a_2 and d_2 resp.) exert an influence on the relative amounts of A^+ and D^- ions crossing the interface.

(4) *The valency of the ions* would also affect the course of the phenomena, but it appears from experiments 3, 4, and 5, that the influence is of a quantitative rather than qualitative nature, at least in so far as the anions are concerned.

(5) *The electromotive force and the interfacial tension.* The ion, or particle, trying to cross the boundary of the two liquids under the influence of the electric force applied, is subjected to two opposing forces. On the one hand the electrical force urges it in the direction of the current (if it is positively charged), on the other hand "molecular forces" endeavour to prevent it from escaping from one liquid into the other. The surface tension, or the interfacial tension in this case, is a measure of these molecular forces. If they are great (i.e. when the interfacial tension is large as with solid-liquid boundaries) then the ion cannot escape and either no current flows or, if the e. m. f. applied is very high, electrons will jump across the interface and the ions, losing their charge, will give rise to the usual chemical reactions observable at electrodes. But if the molecular forces as measured by the surface tension are relatively low and the electrical force applied sufficient to overcome them, then the ion or group of ions will escape from one phase into the other.

According to this hypothesis the e. m. f. must reach a given value, depending on the interfacial tension, before electricity crosses the interface. With e. m. f.'s below that of the "critical" value, the two conducting liquids, separated by the non-conducting interfacial zone, form together a condenser

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[1] Cf. Nernst and Riesenfeld: Ann. Physik, (4) 8, 600 (1902).

of very high capacity, so that a charging current may flow through the rest of the circuit without crossing the interface. The capacity of such a condenser would be $KS/4\pi z$ c. g. s. units (K = dielectric constant; S = area of interface; z = thickness of interfacial zone), and the charging current = $KSV/4\pi z \cdot 1/10^4$ coulombs.

It follows further than an electric double layer would be produced at the interface and it can be shown that such a double layer would exert a twofold influence on the interface, namely[1]

a *pressure* perpendicular to the interface $= \dfrac{K.V^2}{8\,\pi z^2}$ per cm.^{2}

a *tension* parallel to the interface $= \dfrac{K}{8\pi}\displaystyle\int_0^z \left(\frac{dV}{dx}\right)^2 dx$ per cm.

It is to be noted that these magnitudes have the same dimensions as the *internal pressure* (M, L^2, T^2), and *surface-tension-per-cm.* (M. L, T^{-2}), and that the formulae which express them bear a striking ressemblance to those deduced by van der Waals and his pupils for the "molecular" surface forces, e.g.:

$$\sigma = k\int \left(\frac{d\rho}{dh}\right)^2 dh \text{ where } \frac{d\rho}{dh} = \text{fall in density near surface.}$$

On substituting probable values for k and z in the above formulae, it can be easily seen, moreover, that the electrical forces will become greater than the "molecular" forces of surface tension as soon as the potential difference exceeds a relatively low value. With an interfacial zone having a thickness of the order 10^{-7} cm. and a dielectric constant of about 50, a potential difference of 0.5 or 1 volt would suffice to overcome the interfacial tension. Conversely, from the minimum voltage necessary to obtain dispersion it should be possible to deduce, at least approximately, the thickness of the interfacial zone.

The relations between surface and electrical forces are of special interest in view of the recent theories of Debye[2] and Frenkel[3] in which surface tension and internal pressure are explained as results of electrical forces.

In the opinion of the writer the surface energy associated with the formation of dispersions in some of the experiments described is derived directly from the electrical energy supplied. When direct dispersion takes place it does so because it leads to a decrease in potential energy, that is, under those conditions work is gained as a result of an increase in surface. Expressing it in mathematical language, if dF = change in free energy, Q = electrical energy and V, S, and σ have their previous meaning, then $\sigma dF = dS + VdQ$.

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[1] Hertzfeld: Physik-Z. 21, 28 (1920).

[2] Physik. Z. 21, 178 (1920).

[3] Phil. Mag. (6) 33, 297 (1917).

At equilibrium $(\delta\sigma/\delta Q)_{T.S} = (\delta V/\delta S)_{T.Q}$ which means that *if the surface tension decreases with increased electrification then an extension of surface is accompanied by diminution of potential.*[1]

The intrinsic potential difference between the liquid phases and the induced polarization. The electrical potential on the two sides of a liquid-liquid interface has not, in general, the same value, even when the phases are in equilibrium[2]. The existence of a potential difference is equivalent to the presence of an electrical double layer which acts, as previously pointed out, in opposition to the molecular forces and reduces the surface tension.[3]

When the interface is not freely permeable to the ions, there is induced, upon the passage of an electric current—a polarization effect[4] which may either strengthen or reduce and reverse the original double layer, according to the direction of the current. Hence in our experiments the *initial* effect of the polarization would differ at the anode and the cathode interfaces in one case there being an increase and in the other a decrease of surface energy.

Summary and Conclusion

In the experimental section of this paper are described certain phenomena of liquid dispersion, chemical reactions, endosmosis and polarization occuring at the boundary of immiscible liquids upon the passage of an electric current. They show that the transfer of electricity from one electrolytic phase to another does not take place in every case by means of ions only, but that it is also carried out by *electrons* and by *larger complexes of ions and solvent.*

In the theoretical section some of the factors which will have to be taken into account in order to obtain a complete explanation of the phenomena, are briefly discussed. The writer is fully aware of the sketchy and inconclusive nature of this contribution but, not being able to continue the investigation himself, has brought forward these facts and suggestions in the hope that others may be induced to enter this field of research which promises to throw some light on the, as yet, obscure relation between solvent and solute.

In conclusion the writer wishes to express his thanks to Prof. Griffiths, Dept. of Physics, Birkbeck College, and to Prof. F. G. Donnan, Dept. of Physical Chemistry, University College, London, in whose laboratories part of the experimental work has been done.

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[1] Freundlich ("Kapillarchemie" p. 411) states that electric polarization has no effect on surface tension. This statement should be received with caution since Barnett, whose work is quoted by Freundlich, in order to reach his values for "true" surface tension as against what he actually measured, made various allowances for the effects of electrical charges. Whether the perpendicular pressure and the parallel tension exerted by the polarization on the interface are to be considered as *external* agents opposed to a "true" surface tension, (whatever that may be); or whether they are assumed to modify the surface tension itself, depends on the hypothesis one makes concerning the ultimate forces to which surface tension is due.

[2] Beutner: Z. Elektrochem. 19, 319 (1913) and *loc. cit.*

[3] Weber and Gaus: *loc. cit.*

[4] Chapman: Phil. Mag. 25, 475 (1913); Hertzfeld: Physik. Z. 21, 28 (1920).

THE LIMITED SIGNIFICANCE OF HYDROGEN ION CONCENTRATION AS A FACTOR IN DETERMINING THE CONDITION OF LYOPHILIC SOLS

BY H. R. KRUYT AND H. C. TENDELOO

In the papers which Jacques Loeb wrote during the last four years of his life, he aimed at two things: in the first place, he wished to show that solutions of proteins are molecular-disperse and follow stoichiometric laws. In the second place, he emphasised strongly that hydrogen ion concentration of the medium is the all-important factor determining the condition of these systems.

Our conception of lyophilic systems[1] differs entirely from that of Loeb. We, moreover, wish to begin by pointing out that in his latter papers Loeb[2] largely abandoned the former of the above points of view. He was soon obliged to assume that there is a mutual action between the particles themselves and the water which is present, so that according to Loeb's own ideas, the colloidal system cannot be represented in any other way than as composed of multi-molecular particles which in some way or other have united with part of the water.

In the present paper we desire to show that Loeb was also in error as regards the second point of view. The significance which Loeb attaches to hydrogen ion concentration is quite exaggerated. We do not of course wish to deny that the actual concentration of hydrogen ions is more important than to deny that the actual concentration of hydrogen ions is more important than the titer of the added acid (on this point Loeb undoubtedly was right). Misled by erroneous theoretical premises, Loeb, however, considered quite incorrectly that the hydrogen ions (or hydroxyl ions) play a part of their own, *qualitatively* different from that of all other ions[3], and he recognised no continuity between the colloidal chemistry[4] of suspensoids and that of emulsoids, view to which physiologists in general are inclined[5]. In our opinion, however, the colloidal chemistry of lyophilic and lyophobic colloids forms one whole, and in the lyophilic all the properties of the lyophobic colloids are again encountered; earlier investigations in this laboratory have shown this in detail[6], especially after we had for the first time recognized the elec-

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[1] Kruyt and de Jong: Z. physik. Chem. **100**, 250 (1922); Kruyt: Kolloid-Z. **31**, 338 (1922); Nature, **115**, 827 (1925).

[2] J. Gen. Physiol. **3**, 827; **4**, 73 (1921).

[3] Cf. the introduction to his book "Proteins and the Theory of Colloidal Behavior.'

[4] Loeb does not recognise a colloid chemistry at all. He prefers speaking of the so-called colloid chemistry; cf. Science, **56**, 741 (1922).

[5] Buttuzzi: Koll. Beitr. 3, 161 (1913); Wo. Pauli: "Kolloidchemie der Eiweisskörper," (1920).

[6] Kruyt and de Jong: Z. physik. Chem. **100**, 250 (1922); Kruyt and van der Made: Rec. Trav. chem. **42**, 277 (1923); Kruyt and Eggink: Proc. Roy. Acad., Amsterdam, **26**, 43 (1922); Bungenburg de Jong: Rec. Trav. chim. **42**, 437 (1923); **43**, 35, 109 (1924); de Jong: Diss. Univ. Utrecht (agar); Lier: Diss. Univ. Utrecht (casein); Van Postma: Diss. Univ. Leiden (silica).

tro-viscous effect in an emulsoid sol. Among suspensoids the influence of valency of the oppositely charged ion has a great effect in determining their properties. This valency rule is broken by a few definite ions or groups of ions and the hydrogen ion is one of these. In suspensoids the hydrogen ion differs therefore quantitatively, but in no way qualitatively, from other ions. With lyophilic colloids it is the same, although in the case of proteins the quantitative difference is more strongly emphasised for certain reasons. In the investigation about to be described, we have tried to make this clear, led by our general theoretical conceptions which we will first indicate briefly.

Theory of Lyophilic Colloids

Investigations by H. R. Kruyt and H. G. de Jong[1] have shown in the case of agar sol that the viscosity of such a lyophilic sol depends only to a very small extent on the actual volume of the disperse substance and to a large extent on the hydration of the particles and also in a similarly important degree, on the electric charge, the so-called electro-viscous effect of Smoluchowski[2]. The charge on the particles is of quite the same nature as that on suspensoids; small quantities of electrolytes exert a great influence on it in the same manner as they do on electro-kinetic processes e.g. on cataphoresis. The lyophilic colloid is protected against flocculation by its electric charge and by its hydration. Sols of agar, gelatine, starch, gum arabic, etc., are only precipitated when both the charge and the hydration are abolished, the former for instance by means of an electrolyte, the latter by means of alcohol or by a high concentration of salt.

In consequence of our experience that the influence of ions on the charge is quite the same with suspensoids and with emulsoids, and because the changes in the viscosity of sols are often electro-viscous changes, we surmised that the role of the hydrogen ion could be played equally well by any other active positively-charged ion, and that the role of the hydroxyl ion could be played equally well by an active negatively-charged ion. We therefore carried out experiments by adding neutral salts and we always ascertained carefully that the pH of the system had not been changed by these additions. For this purpose we selected the trivalent luteo-cobaltichloride $[Co(NH_3)_6]^{\cdots}\ Cl_3$ and the similarly trivalent, but negatively charged ion $[Fe(CN)_6]'''$ of potassium ferricyanide.

Experimental Part

In our investigations we employed gelatin which had been purified according to the directions given by Loeb[3]. As acid we used hydrochloric instead of acetic. In his first papers Loeb worked with HCl or HBr and afterwards substituted acetic acid. For reasons which we will explain in a later paper we preferred the treatment with hydrochloric acid.

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[1] Z. physik. Chem. 100, 250 (1922).

[2] Kolloid-Z. 18, 190 (1916); Smoluchowski speaks of a "quasi-viscous" effect; but to our mind, the term electro-viscous effect is the happier one (cf. Kraut and Eggink).

[3] J. Gen. Physiol. 1, 237 (1918) and numerous other references in his papers.

The gelatin thus prepared had in a 1% solution a pH of 4.65 and a relative viscosity of 1.435. This viscosity of the original solution we call η_{S_0}. A solution was made from the pure gelatin and then a small quantity of hydrochloric acid was added. When this solution was diluted with water to a content of 1% of gelatin, its pH became 3.7. In our experiments various quantities of salt solutions were added to the gelatin sol in such a way that the final concentration of gelatin was again 1%. Since gelatin solutions change in course of time as the result of irreversible hydrolysis, the quantity

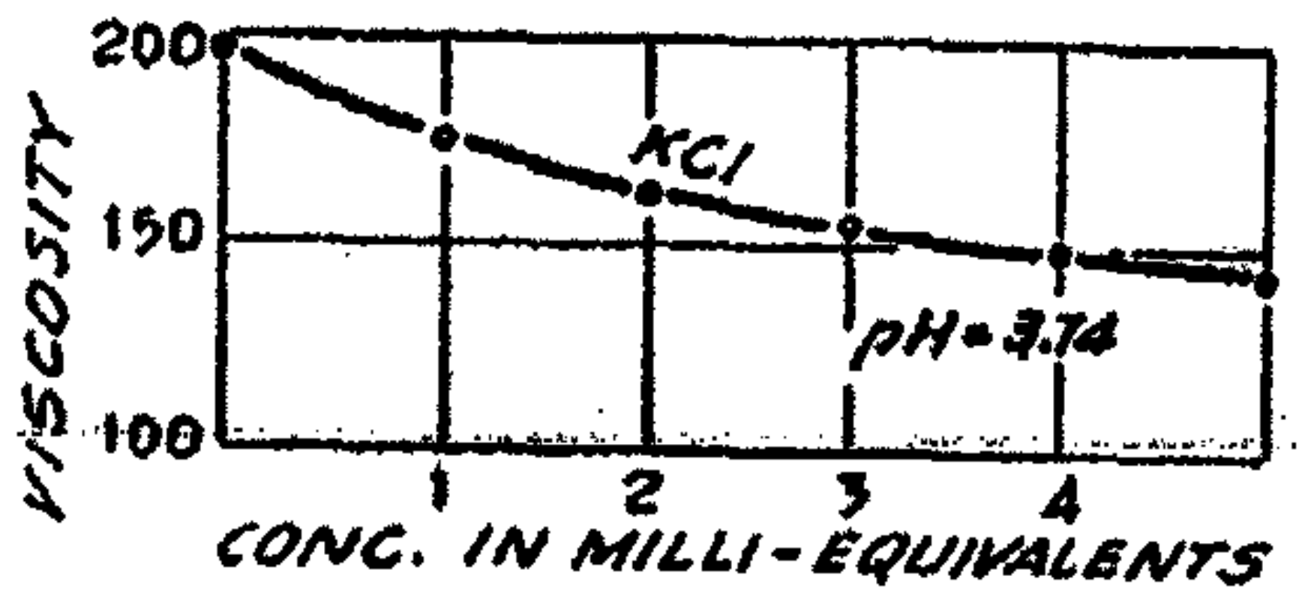

FIG. 1

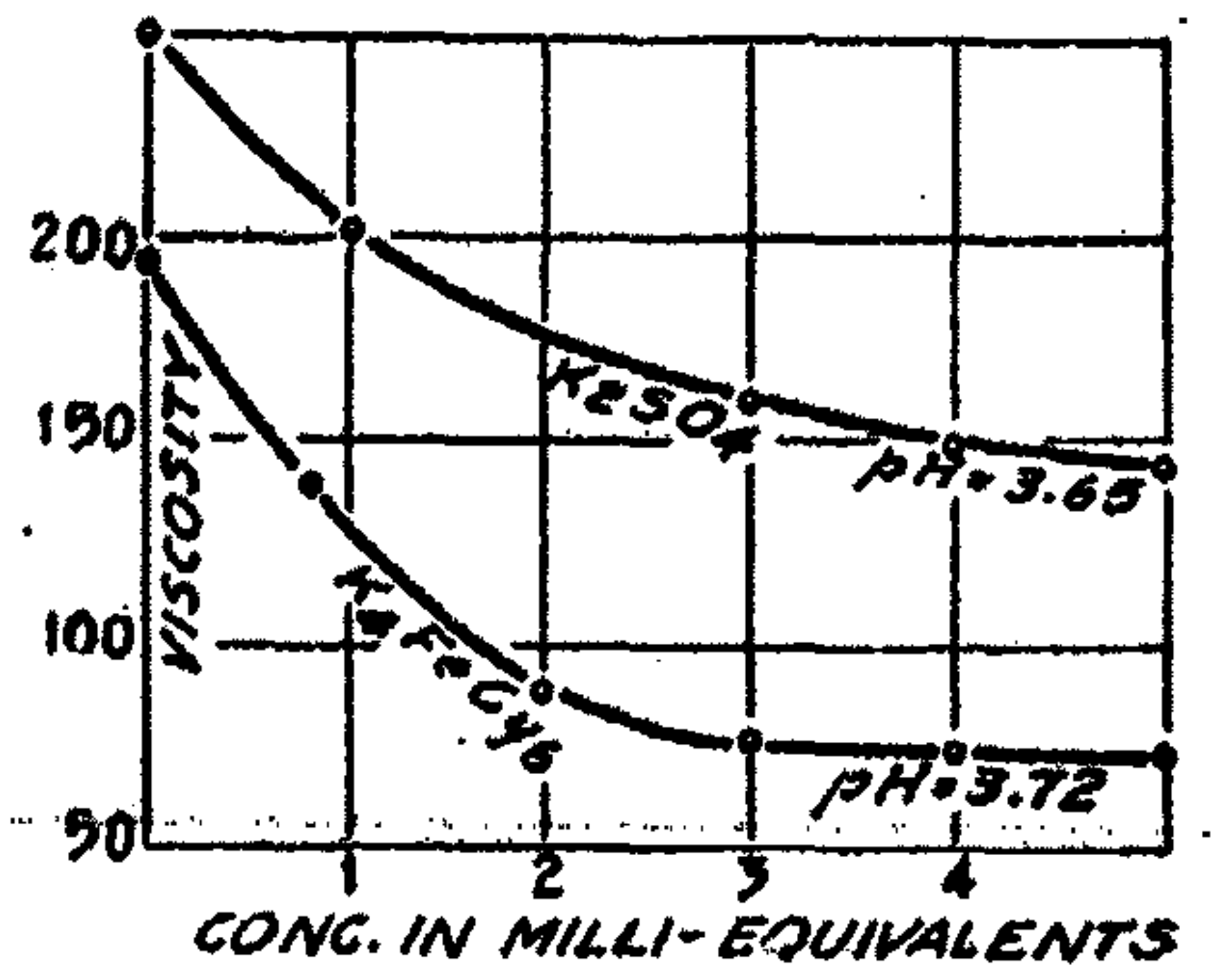

FIG. 2

TABLE I

1% Gelatin-sol.

Original material: gelatin solution without HCl pH = 4.65 η_{s0} = 1.435

Electrolyte	conc. in m. equiv.	η_{s+e}	η_{S_0}	$\eta_{s+e}-1/\eta_{S_0}-1\times100$
K Cl at pH = 3.74	0	1.848	1.435	195
	1	1.740	1.424	174
	2	1.686	1.425	161
	3	1.661	1.426	155
	4	1.635	1.428	148
	5	1.613	1.429	143
K_2SO_4 at pH = 3.65	0	2.079	1.432	256
	1	1.856	1.427	200
	3	1.687	1.428	160
	4	1.634	1.425	149
	5	1.616	1.430	143
$K_4Fe(CN)_6$ at pH = 3.72	0	1.834	1.429	194
	1	1.532	1.423	126
	2	1.378	1.424	89
	3	1.324	1.422	77
	4	1.312	1.421	74
	5	1.310	1.422	73

η_{S_0} was continually controlled by measurement and then the quantity $\eta_{s+e}-1/\eta_{S_0}-1 \times 100$ was calculated where η_{s+e} signifies the relative viscosity of sol + electrolyte. The former quantity so calculated therefore indicates the viscosity of the solution in question referred to a value 100 for a 1% solution of the original gelatin. Table I gives the results of the addition of the salts KCl, K_2 SO_4 and K_4 $Fe(CN)_6$. As is seen from this table, these three solutions differ very little in pH. In Figs. 1 and 2 the results are represented diagramatically.

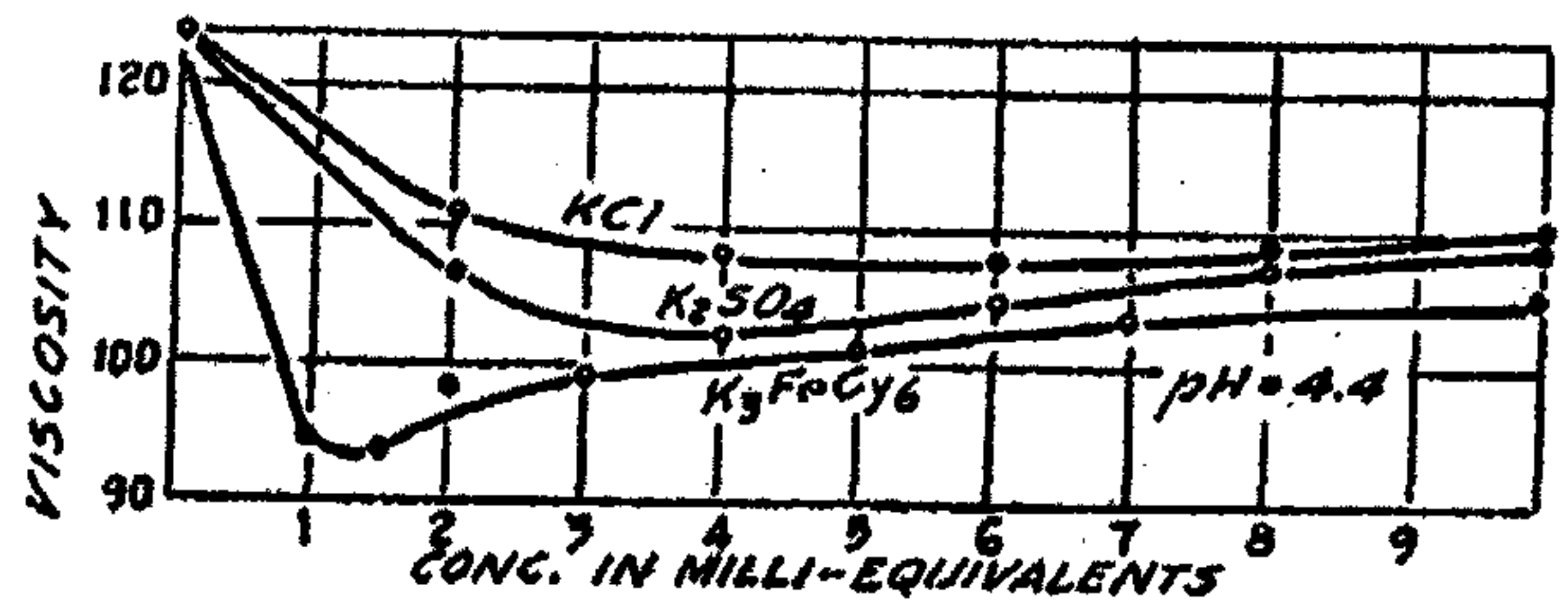

FIG. 3

TABLE II

½ % Gelatin-sol + ¼ M.M. HCl; pH = 4.4

Electrolyte	conc. in m. equiv.	η_{s+e}	η_{S_0}	$\eta_{s+e}-1/\eta_{S_0}-1 \times 100$
Zero experiment	0	—	1.165	100.0
$K_3Fe(CN)_6$	0	1.202	1.165	122
	1.0	1.155	1.165	94
	1.5	1.154	1.164	94
	2.0	1.161	1.164	98
	3.0	1.162	1.164	99
	5.0	1.165	1.163	101
	7.0	1.169	1.163	104
	10.0	1.171	1.162	105
Zero experiment	0	—	1.161	100
K_2SO_4	0	1.198	1.161	123
	2	1.170	1.160	106
	4	1.163	1.160	102
	6	1.166	1.159	104
	8	1.170	1.159	107
	10	1.172	1.158	109
KCl	2	1.175	1.158	111
	4	1.170	1.158	108
	6	1.168	1.157	107
	8	1.170	1.157	108
	10	1.171	1.155	110

These preliminary results show therefore that the viscosity of positively charged gelatin is depressed by the addition of neutral salts and indeed in such a way, that the depressant action depends on the valency of the negatively charged ion. This at once shows the influence of neutral salts and in a way which quite corresponds to our expectations. For the viscosity is a function of the electric charge[1] the latter is influenced by the addition of salt in a manner depending on the valency of the positively charged ion (Hardy, Burton), whilst the hydrogen ion concentration remains unchanged.*

We next carried out similar experiments with gelatin nearer to its isoelectric point. Table II shows the results of experiments carried out with gelatin to which so much HCl had been added that the pH was 4.4. This gelatin is therefore still positively charged. The results are reproduced graphically in Fig. 3. We see once more the depressant action on the viscosity of the solutions in the order of the valency of the anions. Another remarkable difference however appears, viz. that all three curves show a minimum which for the trivalent ion is at about 1 milli-equivalent, for the bivalent ion at about 3 milli-equivalents, and for the univalent ion at about 5 milli-equivalents.

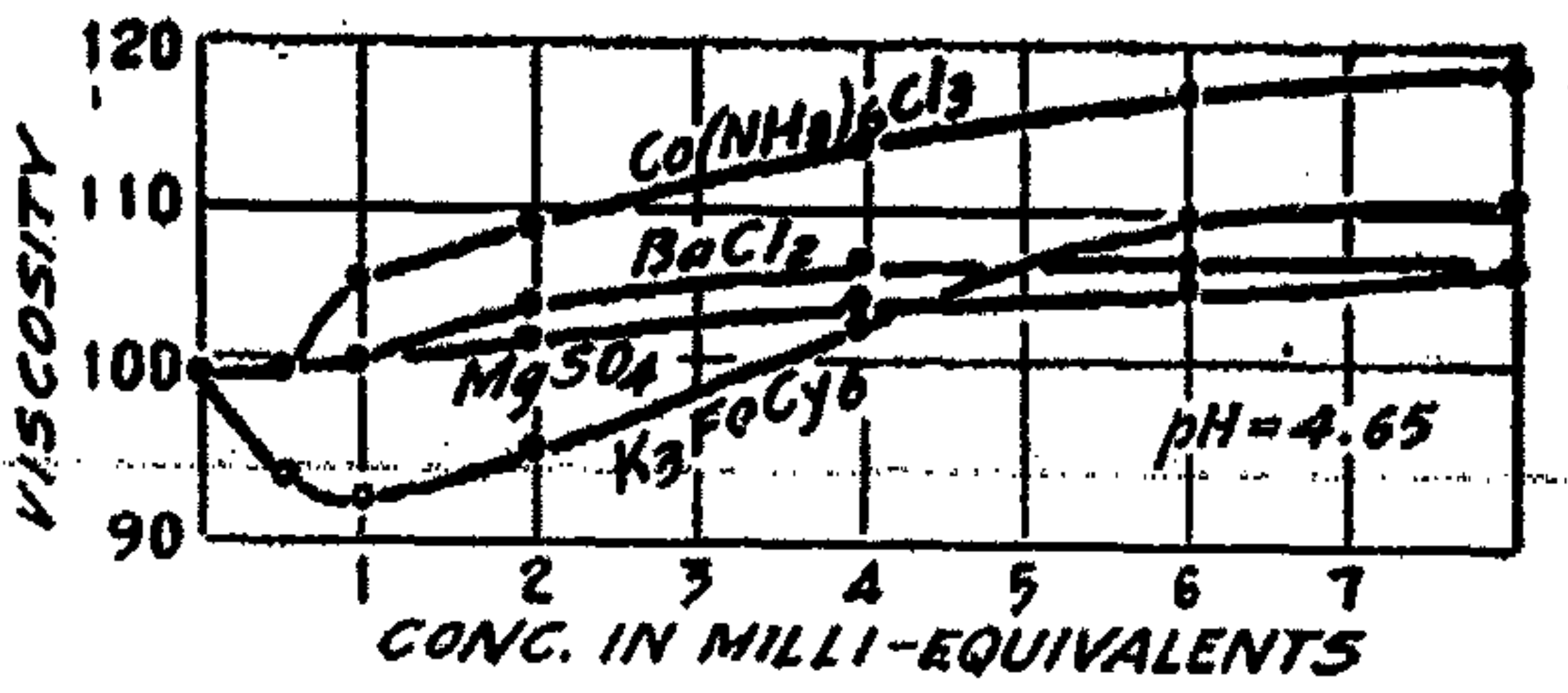

FIG. 4

In Table III the same is shown for a sol of pH = 4.65 also made with gelatin which had been prepared by Loeb's method. Fig. 4 shows the results[1], and we now see that $K_3Fe(CN)_6$ brings about a minimum, but that the salts $MgSO_4$, $BaCl_2$ and $Co(NH_3)_6\,Cl_3$, do not bring about a lowering but an immediate rise of viscostiy. The explanation is as follows:—Bi- and Tri-valent-cations increase the positive charge on the gelatin particles and with it, the viscosity. Only a trivalent anion, combined with a univalent cation, is able to lower the charge, but here also a minimum soon occurs beyond which the viscosity rises.

The explanation is clear. The $Fe(CN)_6'''$ lowers the positive charge to complete discharge, therefore to a condition which in general is determined by hydrogen ions at pH = 4.7; it is the condition of uncharged gelatin. If

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[1] Smoluchowski: Kolloid-Z. **18**, 190 (1916).

* In all experiments we checked continually whether on addition of neutral salts the pH of the system really remained unchanged. This was indeed found to be the case, except for $K_4Fe(CN)_6$, which increases the pH, albeit to a very slight extent. We therefore gave up the use of this salt in the further investigation and preferred the trivalent anion $K_3Fe(CN)_6$, which had no such influence.

TABLE III

½ % Gelatin-sol; pH = 4.65

Electrolyte	conc. in m. equiv.	η_{s+e}	η_{so}	$\eta_{s+e}-1/\eta_{so}-1 \times 100$
$K_3Fe(CN)_3$	0	—	1.162	100
	0.5	1.152	1.162	94
	1	1.150	1.162	93
	2	1.155	1.162	95
	4	1.171	1.162	106
	6	1.178	1.162	110
	8	1.179	1.162	111
$Co(NH_3)_6Cl_3$	0	—	1.159	100
	0.5	1.159	1.159	100
	1	1.167	1.158	106
	2	1.172	1.158	109
	4	1.183	1.161	114
	6	1.188	1.161	117
	8	1.190	1.161	118
$BaCl_2$	1	1.158	1.157	101
	2	1.163	1.157	104
	4	1.167	1.157	106
	6	1.172	1.161	107
	8	1.172	1.161	107
$MgSO_4$	0	—	1.167	100
	2	1.168	1.164	102
	4	1.172	1.164	105
	6	1.175	1.166	105
	8	1.178	1.167	107
	10	1.184	1.167	110

TABLE IV

Gelatin treated with 1/450 n. HCl. ½ % sol. pH = 4.73

Electrolyte	conc. in m. equiv.	η_{s+e}	η_{so}	$\eta_{s+e}-1/\eta_{so}-1 \times 100$
$K_3Fe(CN)_6$	0	—	1.153	100
	0.5	1.155	1.153	101
	1	1.158	1.153	103
	2	1.162	1.153	106
	4	1.167	1.153	109
$Co(NH_3)_6Cl_3$	0.5	1.160	1.155	103
	1	1.166	1.155	107
	2	1.172	1.155	111
	4	1.174	1.155	144

we now add *more* of this salt, then the gelatin is recharged with a negative sign by the multivalent anion and we therefore get negatively charged gelatin.

Experiments of Table IV were carried out with gelatin at pH = 4.73. Both ions, the trivalent cation and anion increase the viscosity (see Fig. 5). This also is quite intelligible. The gelatin is originally uncharged; both the trivalent cation and anion bring about a charge, the one in a positive and the other in a negative sense, just as the hydrogen ion and the OH ion do this.

The final step in this demonstration is given by Table V which was obtained with gelatine of pH = 4.9; therefore negatively charged. Now the complex cobalt salt gives a minimum, whilst the trivalent negative ion brings about an immediate rise (see Fig. 6).

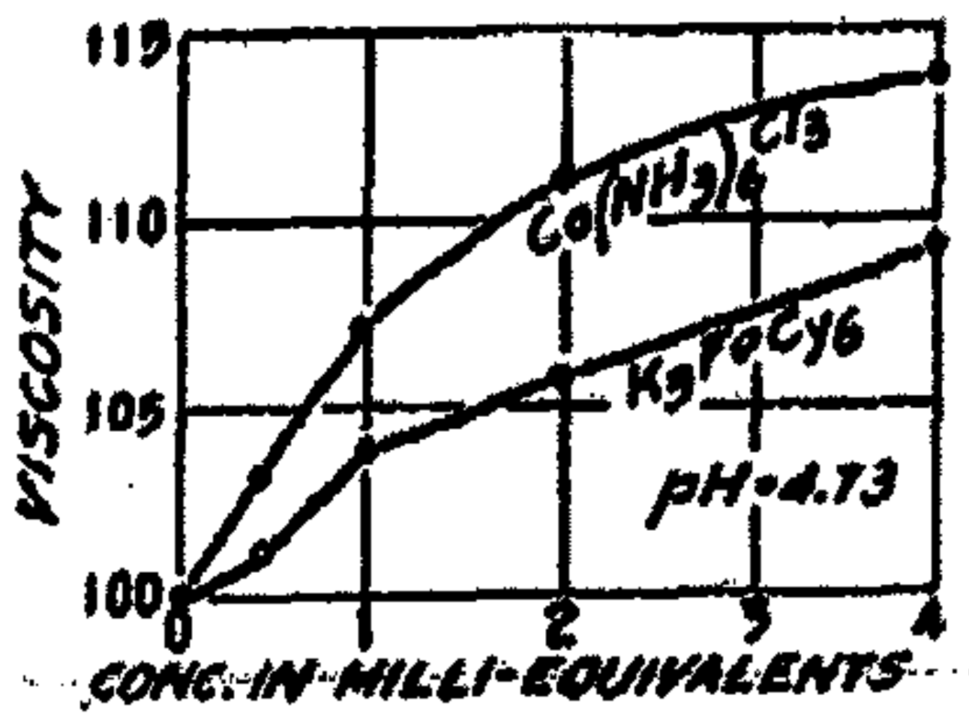

FIG. 5

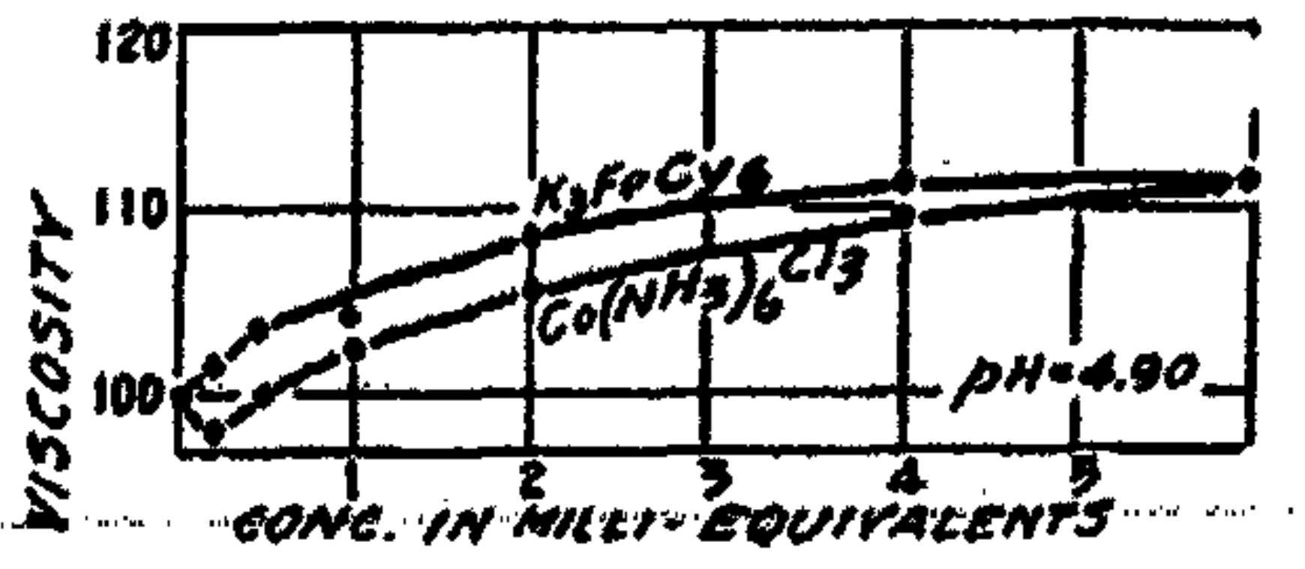

FIG. 6

TABLE V

Gelatine treated with 1/600 n. HCl. ½ % sol. pH = 4.9

Electrolyte	conc. in m. equiv.	η_{s+e}	η_{S_0}	$\eta_{s+e}-1/\eta_{S_0}-1 \times 100$
$K_3Fe(CN)_6$	0	—	1.169	100
	0.2	1.171	1.169	101
	0.5	1.175	1.169	104
	1	1.176	1.169	104
	2	1.182	1.168	108
	4	1.186	1.167	111
	6	1.186	1.167	111
$Co(NH_3)_6Cl_3$	0	—	1.171	100
	0.2	1.167	1.170	98
	0.5	1.171	1.171	100
	1	1.175	1.171	102
	2	1.178	1.170	105
	4	1.186	1.170	109
	6	1.186	1.167	111

Summary and Conclusions

The above experiments therefore show very clearly that the physical properties of gelatin solutions are not determined simply and solely by the hydrogen ion concentration, but that we must say in general that the electrolyte concentration of the medium determines the electrical condition of the colloidal particles and that the action of these electrolytes on lyophilic colloids does not differ in essence from that on lyophobic colloids. The hydrogen ion influences lyophobic colloids in a manner which in general differs very little from the effect of univalent cations. The peculiar matter from which the particles of a protein are built up, brings about that the hydrogen and hydroxyl ions have quantitatively special function. It is, however, a complete misrepresentation of the true relationships if we consider that in contrast to all other ions, the hydrogen ion plays an all-determining part.

This is strikingly shown at the iso-electric point. Whereas the experiments of Loeb in general lead to the conclusion that the iso-electric point depends on a definite hydrogen ion concentration pH = 4.7), our experiments show that this point can be reached at various hydrogen ion concentrations by adding a quantity of another electrolyte just sufficient to produce discharge. Thus it appears from the above tables that the iso-electric point is reached

at p_H = 4.4 with 1.5 milli-equivalent $K_3Fe(CN)_6$
4.65 1. " $K_3Fe(CN)_6$
4.9 0.2 " $Co(NH_3)_6 Cl_3$

It moreover is evident when we can *pass through* the iso-electric point as minimum by means of ions other than H or OH. The passing through the minimum of the curve, i.e.the successive discharge and recharge is therefore also not a prerogative of the H ion but belongs also to other ions.

We have moreover convinced ourselves that the cataphoretic behaviour of the sols is not in conflict with the above conclusions. In the nature of things it is difficult to carry out cataphoretic experiments with gelatin sols; it is especially difficult near the iso-electric point. Unambiguous results are only obtained at a proper distance from this point. We found indeed that the charge at some distance on either side of the minimum was reversed, when this minimum was traversed by means of salt ions. We soon hope to describe in detail the methods employed.

All the above results therefore confirm us in the views stated in our previous communications, namely, that the emulsoid sols must be regarded as hydrated suspensoids and that one of the stability factors, viz. the electrical charge, is influenced by electrolytes in all colloidal solutions in essentially the same manner.

The development of colloidal chemistry must therefore in no way be sought in the direction of a forced falling back on the theory of electrolytic dissociation, but the essence of the problem of electric charge lies in the study of electro-kinetic phenomena which make themselves felt throughout the whole region of colloids, both lyophilic and lyophobic. It is self-evident that since electrolytic dissociation and electro-kinetic processes are all electrical phenomena, both groups of phenomena must in the last resort depend upon a single theory of electricity, but simply to identify electrolytic dissociation and electrical charge of colloids is a retrograde step which has so far not been conducive to a better understanding of colloidal phenomena. We therefore still adhere to the opinion, that the study of electro-kinetic phenomena must bring us to fundamental knowledge of colloidal chemistry. Investigations which have been begun in this laboratory, both in relation to colloids proper and to electro-kinetic phenomena, point in this direction. We hope in due course to refer to them in detail.

Van't Hoff Laboratory, Utrecht.
June 16, 1925.

COLLOID SYSTEMS IN NITROBENZENE

BY FREDERICK STANLEY BROWN AND CHARLES R. BURY

The chief cause of error in the freezing point method of determining molecular weights of substances dissolved in organic solvents is the change of water content of the solvent in the course of the experiment. It has been shown[1] that this error can be eliminated by keeping the solution in contact wth a dehydrating agent such as phosphorus pentoxide, with water, or with a salt hydrate pair such as Na_2SO_4, 0–10 H_2O: these keep the activity of the water constant at a value dependent on their aqueous vapour pressure.

We are investigating the apparent molecular weights in nitrobenzene solution of "associated" substances—alcohols, phenols, and organic acids. No difficulty has been experienced in obtaining consistent results with wet or partially wet solvent, and it has been found that the degree of association depends on the degree of moisture of the solvent. This makes it particularly desirable to continue the work with the dry solvent, but here difficulties are encountered. The following is description of a typical experiment:—

The usual Beckmann freezing point method was used, except that about one gram of anhydrous calcium chloride was placed in contact with the solvent in the inner tube: a current of dry air was used as an additional precaution against moisture. With a solution containing 0.439 grams propionic acid in 20.05 grams of nitrobenzene, the observed depression changed rapidly with time, the following values being obtained successively:— 1.020°, 0.962°, 0.735°, 0.685°, 0.630°, 0.596°, 0.560°, 0.505°, The solution became viscous, and on leaving for an hour, set to an almost solid pasty mass. In other cases the depression does not change with time, but is obviously too small. A solution of 0.365 grams isoamyl alcohol in 19.16 grams of nitrobenzene, for experiments in the moist solvent, should give a depression of about one degree: in the presence of phosphorus pentoxide a value of 0.040° was obtained. Again, the solution became viscous, and on standing an hour set so firm that it showed no sign of flowing when the tube was inverted.

Chemical reaction between the constituents can hardly explain this behaviour, since it occurs with many dehydrating agents (phosphorus pentoxide, calcium chloride, zinc chloride, alumina, and silica.) and with a wide variety of solutes. Also, if a known weight of acid is shaken with calcium chloride and nitrobenzene, allowed to set, then treated with excess water, titration shows that none of the acid has been destroyed. The explanation seems to be that powerful dehydrating agents necessarily have a great attraction for any molecule containing an hydroxyl group, as a result of which the solute is adsorbed.[2] We have shown that the amount of acetic or propionic acid removed from solution by calcium chloride varies continuously with the con-

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[1] Roberts and Bury: J. Chem. Soc. 123, 2037 (1923); Brown and Bury: 125, 2219 (1924).

[2] Calcium chloride forms compounds with many alcohols, but in dilute nitrobenzene solutions, in which it is insoluble, the reaction seems to be limited to the surface, i. e. adsorption takes place.

centration of the acid, in accordance with Freundlich's law of adsorption isotherm. Patrick and Jones[1] have obtained similar results with silica as adsorbent.

This adsorption must lower the surface tension of the dehydrating agent—liquid surface: on vigorous stirring, such as occurs in the freezing point experiments, the dehydrating agents are peptised and pass into solution as colloids. With almost any organic acid, alcohol, or phenol as peptising agent, we have found it possible to prepare colloidal solutions of phosphorus pentoxide, calcium chloride, zinc chloride, or silica, from which these substances cannot be removed by filtration. These filtered solutions show the Tyndall cone phenomenon. The concentration of silica in these solutions is very small, but with calcium chloride concentrations of several grams per 100 grams of nitrobenzene are obtainable: these sols have been observed to display brilliant Christiansen colours. Sufficiently concentrated sols of phosphorus pentoxide and calcium chloride set to gels on standing.

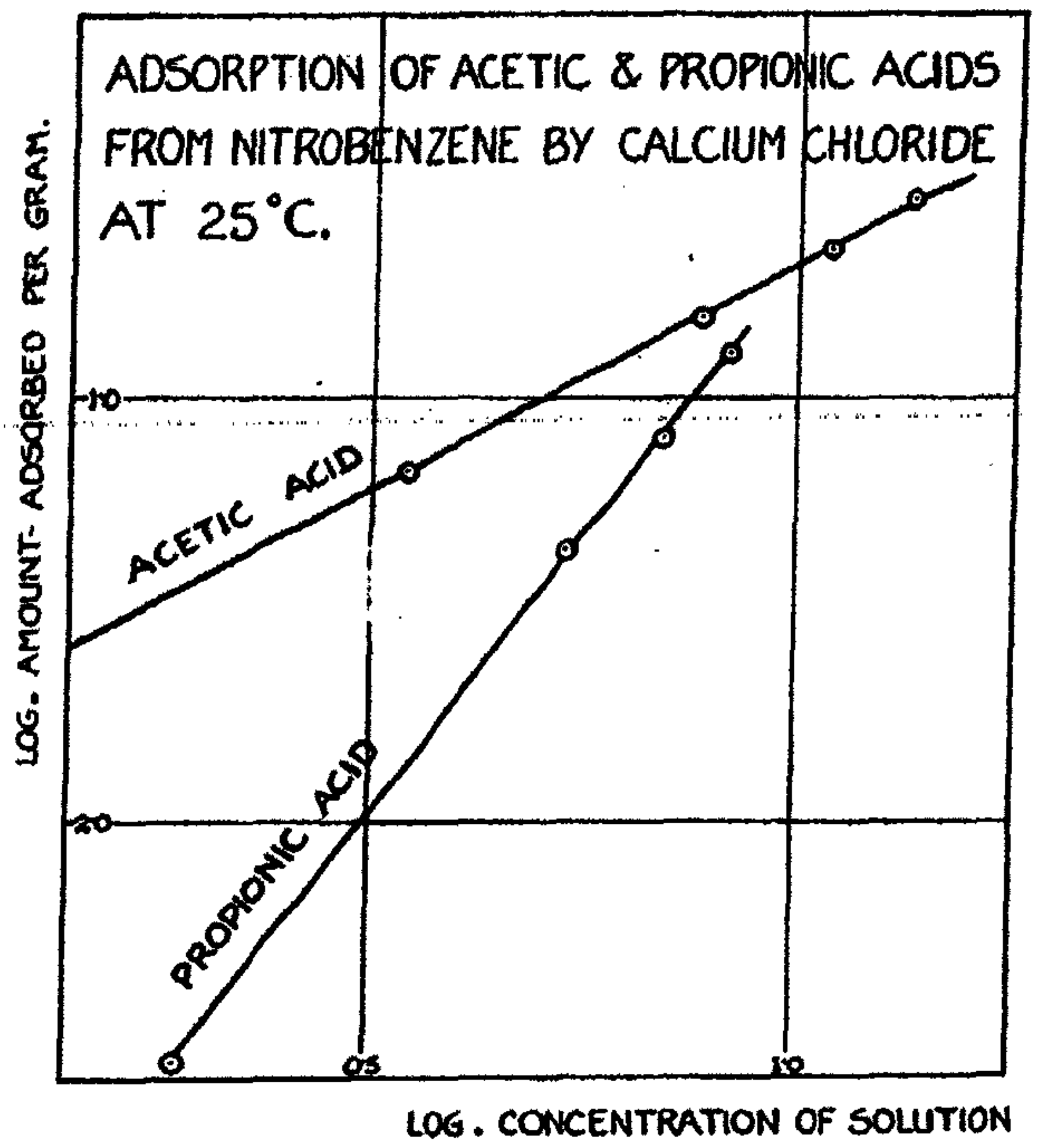

Fig. 1

These sols only exist in the absence of moisture, traces of which cause rapid coagulation: calcium chloride separates out as coarse crystalline needles.

Experimental

Most of the experimental work has been sufficiently described above, but it is desirable to record more fully the experiments of adsorption, and on the

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[1] J. Phys. Chem. 29, 1 (1925).

variation of the concentration of the colloid with the concentration of the peptising agent.

The nitrobenzene used in these experiments was fractionally distilled, fractionally frozen three times, and, immediately before use, distilled in vacuo from phosphorus pentoxide. The anhydrous calcium chloride was prepared from recrystallised hexahydrate by dehydration in a current of hydrochloric acid gas, and was then allowed to cool in a current of pure dry air: it reacted neutral to phenolphthalein and to methyl orange. Acetic acid was twice frozen and then distilled: propionic acid and iso-amyl alcohol were fractionally distilled.

TABLE I

Adsorption of Acetic Acid by Calcium Chloride

Grams acetic acid per 100 grams nitrobenzene.		Grams acetic acid adsorbed per 1 gram calcium chloride. (a)	
Initial	Final. (C)	Observed	Calculated
3.718	3.462	0.0665	0.0667
8.293	7.733	0.153	0.156
11.91	10.99	0.223	0.225
14.76	13.65	0.292	0.284

TABLE II

Adsorption of Propionic Acid by Calcium Chloride

Grams propionic acid per 100 grams nitrobenzene.		Grams propionic acid adsorbed per 1 gram calcium chloride. (a)	
Initial	Final. (C)	Observed.	Calculated.
1.927	1.909	0.0027	0.0027
5.732	5.449	0.0434	0.0423
7.509	6.997	0.0795	0.0810
9.208	8.332	0.1275	0.1277

In the adsorption experiments, closed tubes containing weighed quantities of nitrobenzene, calcium chloride, and acid were kept in a thermostat at 25°C. for five hours, with occasional gentle stirring: after settling, the clear liquid was decanted through a filter, the first portion of the filtrate was neglected and the remainder titrated with alkali. The results are shown in Tables I and II, and are plotted on a logarithmic scale in Fig. 1. The calculated values in the tables are from the adsorption isotherm equation:— $a = kC^{1/n}$, the coefficients used being:—

	k	n
for acetic acid	0.0180	0.949
propionic acid	0.000510	0.384

The unusually low values for n are probably due to the fact that the surface of a given weight of calcium chloride is not constant: the more concentrated solutions have a disintegrating effect on the particles; this is specially noticeable when the tubes are vigorously shaken, as in the following experiments.

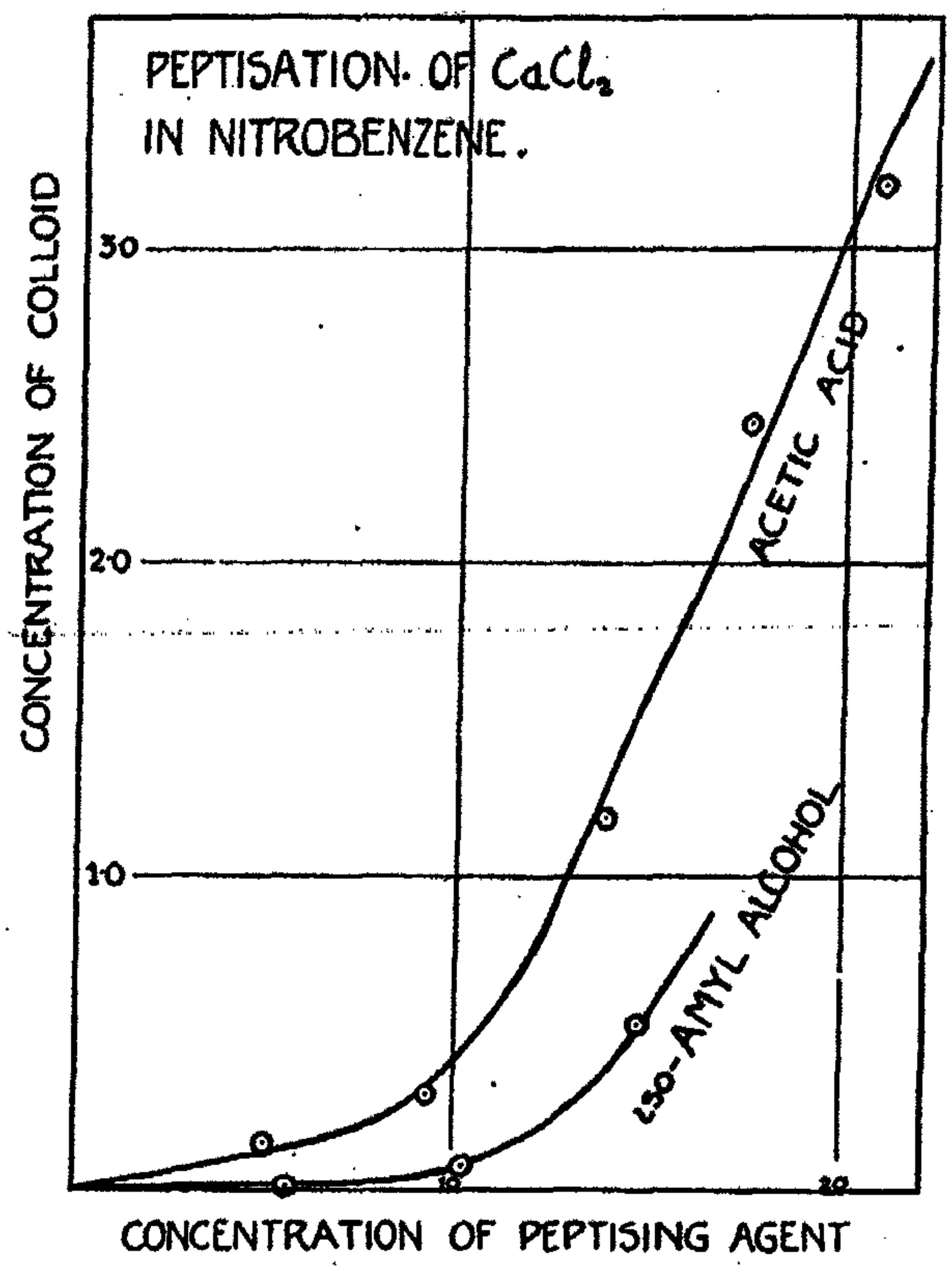

FIG. 2

TABLE III

Variation of the Concentration of Calcium Chloride With the Concentration of Peptising Agent

Peptising agent.	Concentration in grams per 100 grams solution	Grams calcium chloride per 100 grams solution
Acetic acid	0.	0.
	5.126	0.157
	9.260	0.305
	13.80	1.181
	17.28	2.461
	20.82	3.221
Iso-amyl alcohol	5.705	0.012
	10.22	0.082
	14.72	0.526

A number of tubes containing 20 grams nitrobenzene, 4 grams of calcium chloride, and varying quantities of acetic acid were shaken vigorously for about five minutes, allowed to settle over night, then filtered through a No. 40 Whatman filter paper. Calcium chloride was estimated in the filtrate, the results being shown in Table III, and graphically, in Fig. 2. It is clear that the peptising effect of acetic acid is small with low concentrations, but that it increases rapidly with the concentration of the acid. If the logarithm of the concentration of calcium chloride is plotted against the logarithm of the concentration of the peptising agent, an approximately straight line results, which shows that these quantities are connected by an equation of the same form as Freundlich's adsorption isotherm. Similar results were obtained with iso-amyl alcohol as peptising agent.

Edward Davies Chemical Laboratories,
University College of Wales,
Aberystwyth,
May 25, 1925.

SOLUBILITY RELATIONS IN ISOMERIC ORGANIC COMOPUNDS. V. THE CONSTRUCTION OF THE IDEAL TERNARY SOLUBILITY DIAGRAM, AND ITS USE IN ANALYSIS

BY G. T. KOHMAN AND D. H. ANDREWS*

In the course of the investigation of the mutual solubility of *ortho, meta, para* isomers, methods were developed which greatly simplify the construction of the ternary solubility diagram for cases in which the solutions are ideal, or nearly so; which, moreover, put one, with less work, in position to analyze any mixture of the three substances. These methods, which will now be briefly set forth, are not wholly new, but some of the essential points seem not to have been discussed explicitly in the literature;[1] and they have certainly not been made use of by previous authors working in this field.

In view of the evidence presented in previous papers of this series, we shall consider that the solubility follows the ideal law for any one of the three,—say P (*para*)—in O (*ortho*) and in M (*meta*), hence in any mixture of the two. That is, the solubility curve of P in O is identical (except in length) with that in M or in any O—M mixture; its solubility is determined by the temperature (and by its heat of melting) but not by the relative proportion of the other two components except that this latter fixes the eutectic end-point.[2] The solubility-diagram for such a system is sketched in Fig. 1.

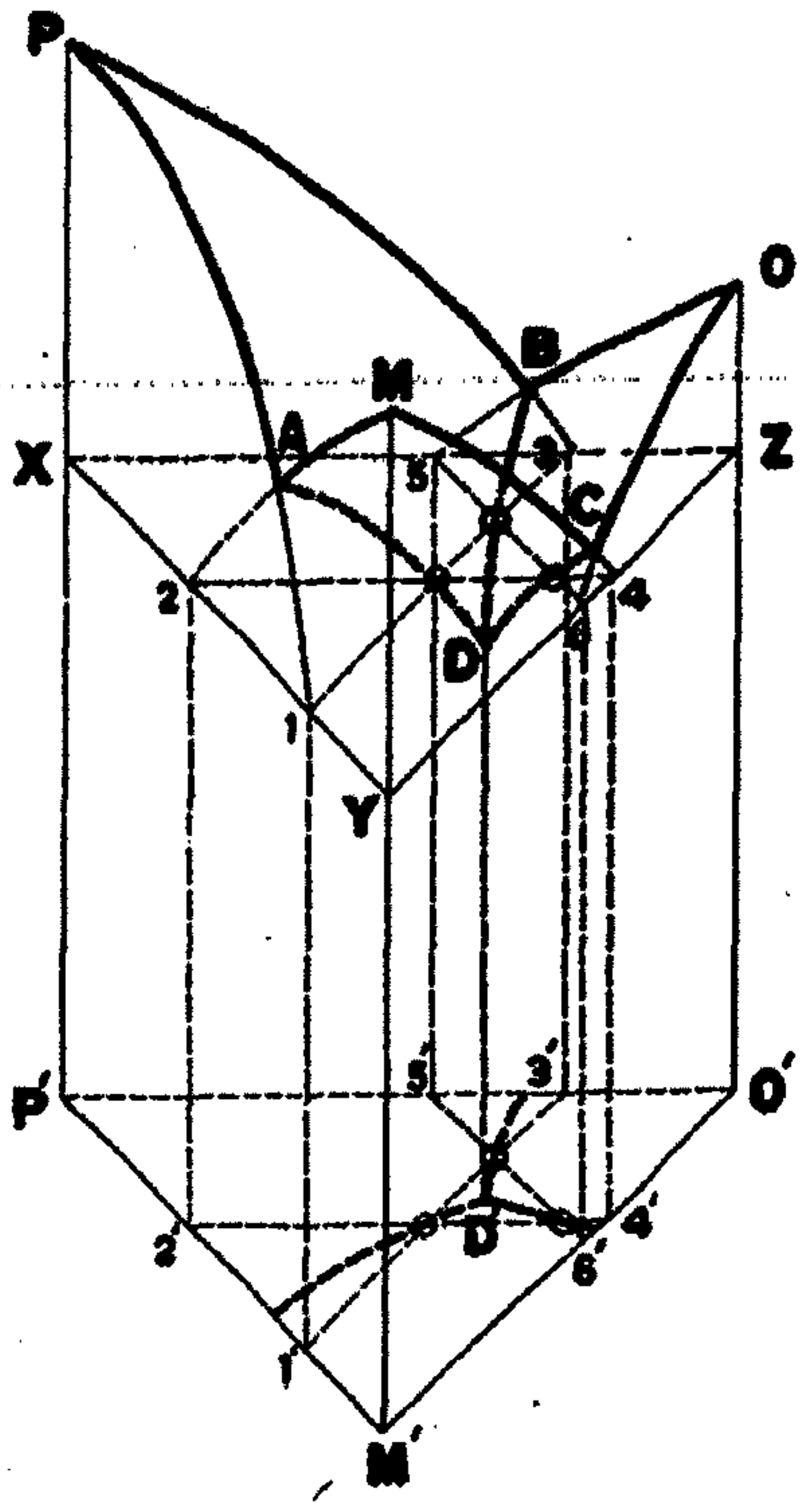

Fig. 1

Projection of the solubility diagram for an ideal ternary system.

The three sides of the prism represent the three binary systems P—M, M—O, O—P. The surface PADB, whose apex is at the melting temperature of pure P, represents the solubility of P in ternary mixtures,—that is, it is the locus of the temperature at which primary crystallization of P begins

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* From the dissertations presented to the Graduate School of Yale University, in June 1923, in candidacy for the Degree of Doctor of Philosophy.

[1] An abstract discussion is given by Van Laar: Z. physik. Chem. 55, 64 (1906).

[2] Our present experience extends only to systems of *o, m, p* XY-benzene, where X and Y are the same for all three; but there is reason to believe that solutions of *o*-XY with *m* and *p*-YZ, or even with *m* and *p*-VZ, would in many cases be ideal or very nearly so.

when any mixture of the three is cooled slowly; and similarly with the similar surfaces MADC and OBDC. Now since at any temperature the proportion of P in the liquid depends only upon the temperature, the locus of points of equal composition of the liquid is an isothermal line upon the surface PADB; and from the property of the plane triangular diagram, according to which the locus of points of equal composition with respect to P is a straight line parallel to the opposite side (O'M'), it is clear that the isothermal on the surface is a straight line parallel to O'M'. It follows therefore that the surface PADB[1] may be generated by sliding a *horizontal straight line* down over the edges PA, PB; and similarly with the other two surfaces. The three lines of intersection AD, BD, CD, of these surfaces are the three eutectic valleys which meet at D, the ternary eutectic point.

For this type of system the solid model may readily be constructed as follows. Draw to scale the three binary diagrams O–M, M–P, P–O side by side upon a sheet of cardboard or metal, cut out along the solubility curves and join them to form an equiangular right prism; the three surfaces, which curve in the vertical but not in the horizontal direction, are made from a sheet of stiff paper or thin metal by appropriate cutting and fitting. For some purposes the solid model is best; for others it may be more convenient to make use of graphical projection. Such a projection is made in the following manner, the angle being chosen as 45° for the sake of simplicity. Draw an isosceles triangle O'M'P', of altitude one-half its base O'P'; and upon this triangle as base draw the projection of the edges of the right prism. The three apices O, M, P are easily fixed. Points on the binary curves are located by the intersection of a line parallel to one of the three sides O'M', M'P', P'O'–i.e. a temperature line e.g. X–1–with the appropriate composition line (as 1–1') parallel to the edge of the prism. To locate the binary eutectic valley—for instance, AD–pass a plane XYZ, parallel to the base of the prism, at a temperature between that of A and that of D. This plane cuts the curves PA and MA extended[2] at points 1 and 2, and intersects the surfaces PADB and MADC along the straight lines 1–3 and 2–4 respectively, each of which moreover is parallel to the side of the triangle opposite the point representing that component which is the stable solid phase on the surface in question. The point of intersection of the two isotherms 1–3 and 2–4 lies in both surfaces and is therefore the point in the eutectic valley AD corresponding to the particular temperature represented by the plane XYZ. Moreover if XYZ is also below B and C, it locates points on the boundaries BD and CD, if the additional line (5–6) of intersection with surface OBDC is drawn. In this way it is possible to locate these boundary curves with an accuracy very nearly equal to that of the binary curves.

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[1] This surface is *not* a surface of revolution, corresponding to a rotation of the curve PA about the axis PP'; the projection of the isothermal on such a surface would be an arc of a circle, which on the basal triangle is not a line of constant composition.

[2] This extension is easily made if points have been determined experimentally in the ternary system at temperatures lower than A, since—as we have seen— the temperature is dependent solely upon the mol fraction in the liquid of the substances crystallizing. It is equally easily derived from the log N—1/T plot, even in absence of experimental points at temperatures lower than A, the binary eutectic.

This method can be used even though there be some divergence form ideality of the solutions. For instance if curve PB is not identical with PA, it is reasonable to suppose that the extent of deviation from PA of the solubility curve of P is a linear function of the amount of M replaced by O in the solution. On this basis, the surfaces and planes intersect again in straight lines, which now however would not be quite parallel to the sides of the prism; apart from this the method is the same.

From the considerations outlined above it is clear that the same result can be attained more simply by means of a diagram such as Fig. 2, which is essentially Fig. 1 as viewed from the XYZ plane. The line of intersection of this plane with the surface PADB is located by projecting 1 to 1′, and drawing 1′–3′ parallel to O′M′, which is now the side of an equilateral triangle; that with the OBDC surface similarly, by projecting 5 to 5′ and drawing 5′–6′ parallel to M′P′ that with the MADC surface by projecting 2 to 7′, drawing 7′–2′ parallel to O′M′ and 2′–4′—the line desired —parallel to O′P′. The intersections of these three lines—1′–3′, 2′–4′, 5′–6′—are the three points on the eutectic valleys, and their coordinates may be determined as before. Two or three such diagrams, with the plane XYZ at different heights (temperatures), suffice to locate the binary curves with as great accuracy as they could be located by observations of the secondary freezing temperature. This method likewise can be used even if there is some deviation from ideality; the only difference is that the two curves (e.g. PA, PB), instead of being coincident, would separate.

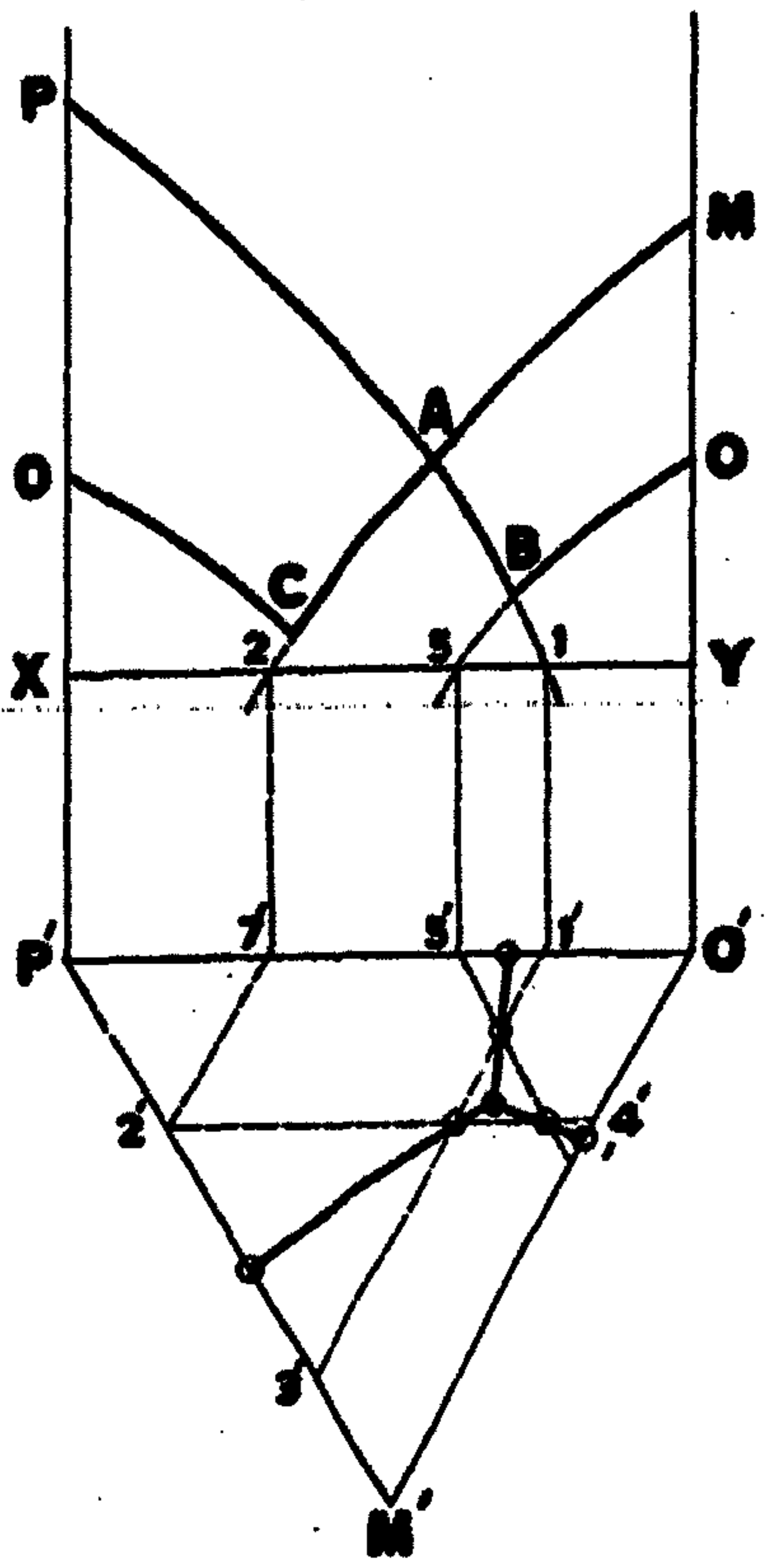

FIG. 2

Fig. 1 in simplified form; essentially as viewed from a point in the XYZ plane.

The use of the log N vs. 1/T plot. For the simple type of ternary system under discussion there is another mode of exhibiting the data which is still easier to follow and utilize. If the solubility curve is ideal, the graph of log N (where N is the mol fraction of the solute in the solution in equilibrium with crystalline solute at T) against 1/T is, as we have seen, linear or very nearly linear; and the position and course of this line depends upon properties (melting temparature, heat of melting, specific heat as solid and as liquid) of the solute itself, and not at all upon the solvent except in so far as the latter determines the eutectic end-point. Consequently the solubility equilibrium in an ideal ternary system can be represented completely, on this mode of plotting, by three lines, one for each component, as in Fig. 3, which was constructed from the data on the *o, m, p* nitroanilines. Each line starts from the point corresponding to the melting temperature of the pure component, and ends at that corresponding to the lowest temperature at which liquid can exist in the system, that of the ternary eutectic composition.

The plot of log N against 1/T, being very nearly straight, affords a better check upon the observations than the N – T plot, which is a curve and hence cannot be extrapolated without uncertainty. The eutectic temperature is easily measured, the corresponding composition is not; but the latter is easily derived from the former with the aid of the log plot, which can be extrapolated with very little error. If this be done for both A and B at the eutectic temperature of the system AB, the sum of the antilogarithms of the abscissa (i.e. of log N_A and log N_B) should be unity, since the eutectic composition is clearly such that the sum of N_A and N_B is unity; otherwise, there must be some systematic error in the data. Alternatively, in order to derive eutectic composition and temperature from pairs of curves such as those in Fig. 3, we have merely to find that value of 1/T at which the sum of the antilogs of log N_A and log N_B is unity[1]). This is readily done by trial, and can be done still more easily by aid of an auxiliary plot of log x against log (1–x), or by making the original diagram upon semi-logarithmic section paper[2]. The ternary eutectic is similarly located from the condition $N_A + N_B + N_C = 1$, or the sum of the antilogarithms of log N_A, log N_B and log N_C shall be unity.

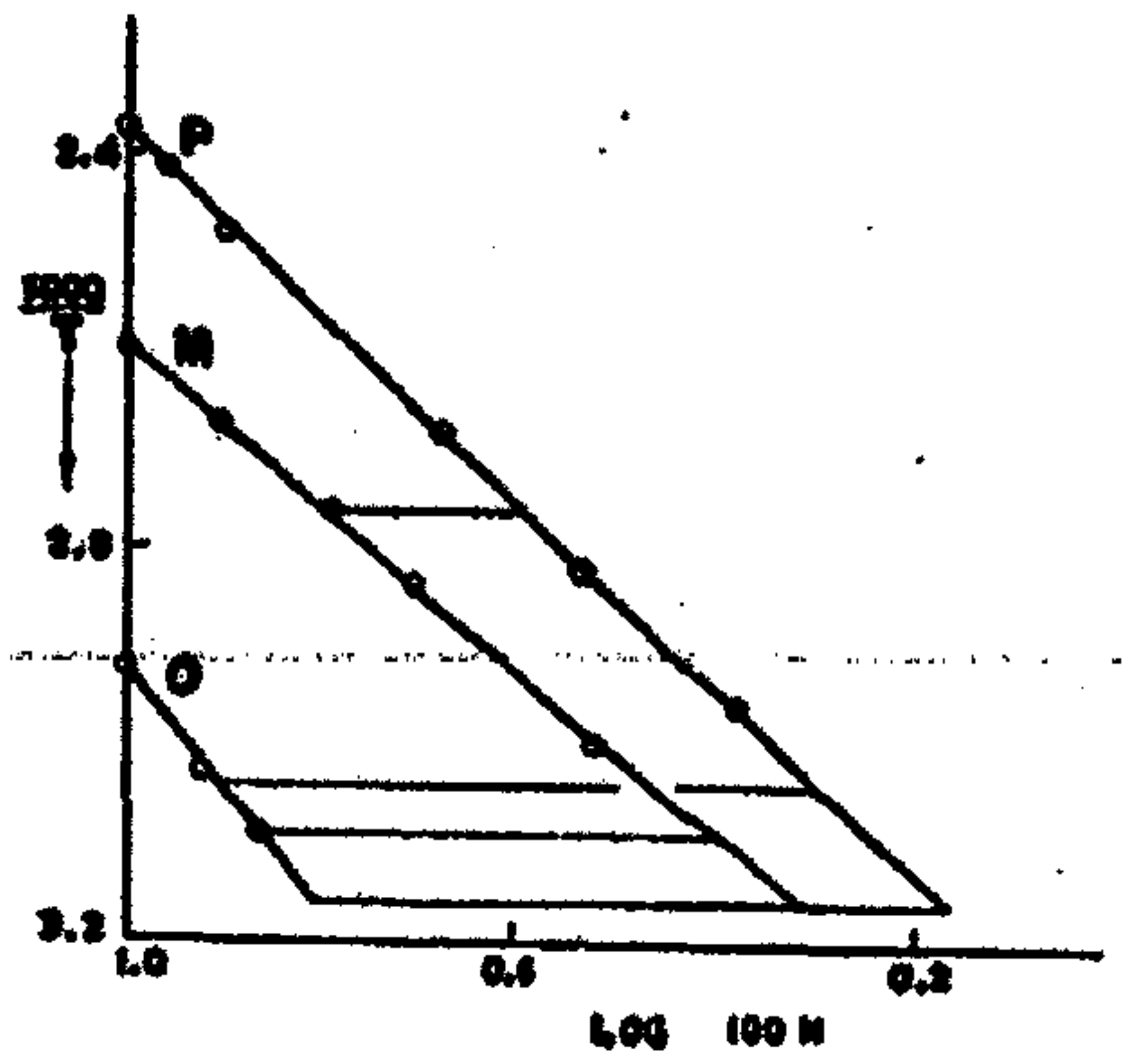

FIG. 3

The plot of log 100 N against 1000/T for the three isomeric nitroanilines, showing the several eutectic temperatures.

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[1] In practice it is more convenient to avoid negative logarithms by plotting log C, where C is the mol percentage (C = 100 N) instead of log N; if this is done the sum of the antilogarithms at the eutectic is 100. It is also preferable to use 1000/T instead of 1/T. But, since the sum log N_A + log N_B is not constant (as $N_A + N_B$ is), there is no advantage in plotting on opposing scales as in the N—T diagram.

[2] In which case one appears to plot N against 1/T, which saves looking up the several values of log N; on the other hand, semi-logarithmic paper may be confusing to one who does not use it regularly.

In this way the three binary eutectics, and the ternary eutectic, in Fig. 3 have been located; and these values we have previously compared with those directly determined[1]. Thus this is a convenient method of predicting eutectic composition and temperature; or conversely, if a eutectic temperature is known, it furnishes a test of the reliability of the pair of solubility curves.

This type of plot moreover affords a convenient method of establishing the binary eutectic lines (valleys); and it yields more certain results than the method, based on an N – T plot, which has been commonly used[2]. To represent the composition of a ternary system at any temperature three points—one for each component—are necessary, and the sum of the three antilogarithms must always be unity; but these points need not lie on the lines. At any temperature the solution is saturated with respect to a component A if the point representing log N_A, the mol fraction of A in the solution, falls upon the solubility curve of A; it is unsaturated with respect to A if the point lies to the right of the curve of A as drawn in Fig. 3; and similarly, of course, for the other two components. Suppose now it is desired to locate a point on the boundary line AD (Fig. 1), along which the solution is saturated with both P and M, and consequently the two points representing the proportion of P and M in the solution must lie on the P and M lines of Fig. 3 respectively. At any temperature T_1 within this range therefore, we can read from Fig. 3 the mol fraction of P and of M and by subtraction get that of O. The latter when plotted lies to the right of the O-curve; the lower the temperature, the more closely does this point approach the O-curve, and it is on this curve at the ternary eutectic end-point. Otherwise, by reading from the P and M curves, for a series of temperatures below the P – M eutectic, pairs of values of the mol fraction, and subtracting their sum from unity, one derives the concentration of O corresponding to temperatures down the eutectic valley, which can therefore be mapped in this way.

The simplicity of this form of diagram for the ideal system enables one to determine the solubility diagram for such a case from a small number of observations. For instance, measure the primary freezing temperature of a known mixture of P and M, and also the eutectic temperature of P and M; these data combined with the melting temperature of pure P and of pure M, enable one to draw the complete curves for P and M. To complete the diagram it is then necessary only to measure the eutectic temperature of O with P, or with M, or with both P and M; for either of these yield a point on the O-curve, which starts form the melting temperature of O. Thus one solubility and two eutectic temperatures suffice on this basis to determine the complete diagram; whereas the usual methods would involve at least four solubility measurements to locate a single point on a eutectic valley. Indeed from the equation to the ideal solubility curve it is clear that, if the heat of melting and heat content of each of the three components is known, one could construct the whole diagram without making any observations of solubility;

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[1] Kohman: J. Phys. Chem. **29**, 1048 (1925).

[2] e. g. by Bell and Herty: J. Ind. Eng. Chem. **11**, 1124 (1919).

but even so, it would be advisable to measure one or two solubilities in order to be assured that the solutions are effectively ideal.

The utility of the graph of log N against 1/T is not confined to the ideal case, but extends to the far larger number of cases in which the divergence from ideality is not too great. In such cases the lines for a pair of binary systems (e.g. PM, PO, Fig. 4) are not superposable, and the P-surface should be represented by a sheaf of lines starting from the melting temperature and bounded by PM and PO[1]. The curvature would usually be slight, so that a small number of observations would suffice to fix each curve, and one could extrapolate with sufficient accuracy as far as the ternary eutectic temperature. From this diagram one reads off the composition of the several binary solutions corresponding to a series of temperatures, plots these points on the sides of an ordinary triangular diagram, and draws in the three sets of isothermals by joining the corresponding pairs of points by straight lines. To make the isothermals straight lines involves of course an assumption, (which we have made on a previous page) but one which is plausible and certainly substantially valid so long as the pair of curves for any one component are similar in form and do not diverge far from one another. These three groups of isothermals are not exactly parallel to the sides of the triangle nor to one another, as in the ideal case; the loci of their intersections are the three boundary curves (projection of the eutectic valleys) which in turn meet in the ternary eutectic composition.

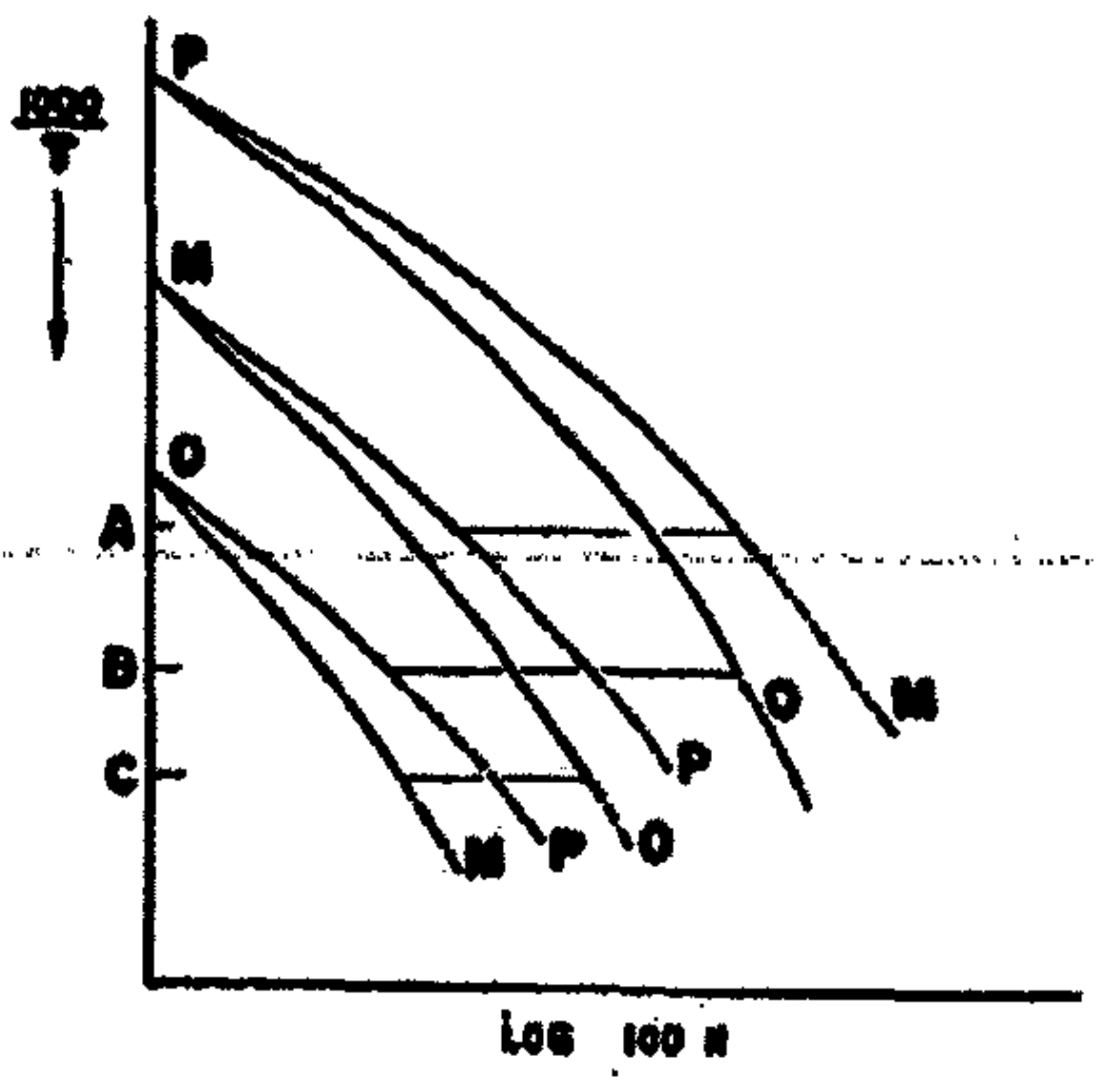

FIG. 4

The plot of log 100 N against 1000/T for a simple ternary system which departs somewhat from ideality.

Use of the Solubility Diagram in the Analysis of Mixtures of the Components

When the complete equilibrium diagram of a three component system, of the general type here discussed, is known, the composition of any mixture of

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[1] The divergence is least between the pair for the lowest melting component, these lines being the shortest.

these components can readily be ascertained with an accuracy of the order of 1 or 2%. Observation of the primary freezing temperature—which should of course be made in the same way as the observations from which the solubility diagram was constructed—of the unknown mixture does not of *itself* inform us as to which component is separating—that is, within which of the three regions PADB, MADC, OBDC the composition lies. But this is readily determined; for if it is, for instance, in the P region, addition of P will *raise*, and addition of M or O will *lower*, the primary freezing temperature. Knowing this, we can read directly from the diagram the proportion of P in the mixture. A weighed amount of M, sufficient to bring the composition into the region MADC, is added, and the primary freezing temperature of this system is observed; from this we know the proportion of M now present, and hence the proportion of M in the original mixture. The proportion of O is obtained by difference, or by proceeding as with M.

In those cases in which the secondary freezing temperature T_2 can be observed with sufficient accuracy, the proportion of M and O can be derived directly from T_2 [1] instead of by the process just outlined. Here again there is ambiguity as to whether the composition is in the valley between P and M or between P and O; but this can readily be ascertained, as before, by adding a little of M or O, when T_2 will be raised or lowered according as the composition is, or is not, on the boundary of the field of the component added.

To those who are unfamiliar with graphical methods of the kind discussed in the preceding pages, this matter may seem very complex; but they will have no difficulty in dealing with any given system on which they have made the necessary observations. In particular the practical application would usually be quite simple because one would be dealing with a quite restricted range of compositions. Moreover the method could be simplified, particularly if used as a control method, by dispensing with the refinements of apparatus or of correction for undercooling, described in a former paper, provided that the particular mode of work be calibrated by observations on a few known mixtures. An analogous calibration is necessary when the mixture to be analysed contains some impurity (e.g.moisture or residual solvent) in fairly constant amount, as would often be the case in actual practice, particularly on an industrial scale. The effect of such impurity is in general to lower the whole ternary surface, though not necessarily by the same amount everywhere; but over a relatively small region this lowering may be considered to be constant, and can be corrected for by suitable calibration with similar mixtures of the pure components to which known amounts of the impurity have been added. This general method when appropriately calibrated is in general more convenient and simpler than any other method of analysis and will yield, we believe, reliable and satisfactory results.

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[1] For this purpose it is convenient to have a plot of T_2 — i. e. the temperature down the valley AD and up DB (of Fig. 1.) — against the proportion of M to O in the solution along these boundary lines; and similarly, *mutatis mutandis*, if the primary solid phase were M or O.

Summary

This paper treats of graphical methods applicable to the construction and interpretation of solubility diagrams of ternary systems which yield ideal, or nearly ideal, solutions—such as those composed of an *o*, *m*, and *p* isomer—a type of case which seems to be less uncommon than had been supposed; and of the usefulness of such diagrams in the analysis of mixtures of these substances.

THE PROMOTER ACTION OF THORIA ON NICKEL CATALYSTS*

BY WILLIAM WALKER RUSSELL AND HUGH STOTT TAYLOR

In view of some recent work[1] in the field of promoter action, it was deemed of importance to obtain information regarding the adsorptive capacities of promoted nickel catalysts for gases reacting at their surfaces. The promoting action of several irreducible oxides on nickel used to catalyze the methanation reaction between carbon monoxide or carbon dioxide and hydrogen has been demonstrated by Medsforth. This author believes that the function of the promoter is to dehydrate the unstable intermediate compound formed in the above reactions, and that, in general, promoters act selectively: (a) to decompose intermediate compounds formed by the catalyst, (b) to form intermediate compounds which are decomposed by the catalyst, (c) to adsorb or combine with one of the reacting substances thereby increasing its concentration on the catalyst. Armstrong and Hilditch, in a study of the hydrogenation of oils in the presence of nickel and nickel plus various irreducible oxides, conclude that the main source of promoter action is a mechanical one, and that it involves simply an increase of the available surface of the nickel. It is of interest to note that alumina which was used as a promoter for supported nickel by each of these authors exerted its maximum effect at approximately the same concentration in each of the two types of reaction studied.

The present investigation, which has been confined to a study of the promoting action of thoria on nickel used to catalyze the interaction of carbon dioxide and hydrogen to form methane and water, was attempted in the hope of somewhat further elucidating the mechanism of promoter action. It is clear that if the function of the promoter is simply to increase the available surface of the catalyst, an increase in catalytic activity due to the presence of a promoter, as shown by reaction velocity measurements, must be accompanied by a corresponding increase in adsorptive capacity. If such a corresponding increase in adsorptive capacity is not found, it is strong evidence for a qualitative rather than a quantitative change in the surface of the catalyst. The experimental work, especially that on supported catalysts, presented in this paper shows that no proportionate increase in adsorption accompanies the increase in activity shown by the promoted catalyst. It appears, therefore, that the promoted catalyst has a much more active surface. Further discussion of this point will be reserved until the evidence is presented.

On account of the known difficulty in reproducing catalysts of desired properties it was considered essential to make both adsorption and reaction velocity measurements on the same sample of catalyst. A method has been devised for doing this, and the same procedure has been followed both for the supported and for the unsupported catalysts.

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*Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] Medsforth: J. Chem. Soc., 123, 1452 (1923); Armstrong and Hilditch: Proc. Roy. Soc., 103 A, 586 (1923).

Experimental

Apparatus.—The apparatus used for the reduction of the catalysts and for the reaction velocity measurements is shown in Figs. 1 and 2. The catalyst tube is seen to be divided into two portions by a constriction. The proper amount of the unreduced oxide was placed in A, Fig. 1, and then a bit of glass wool placed in the lower part of B, which was then filled with a quantity of the same oxide sufficient to give the amounts of catalyst desired for reaction velocity measurements. The constriction was thus kept free from oxide. The thermometer C, was placed well down in the catalyst mass in B and the connection at D was made tight with a piece of rubber tubing. During reduction, the catalyst tube was heated by means of the large furnace E, which was wound with nichrome wire. Hydrogen for reduction was led through the by-pass G, thence through the phosphorus pentoxide tubes and the preheater F, and into the catalyst tube. The effluent hydrogen and water vapor passed out at H through a sulphuric acid trap. When reduction was complete, as shown by weighings of a phosphorus pentoxide tube through which the effluent hydrogen could be passed, the furnace was cooled to room temperature. The hydrogen was replaced by carbon dioxide which could be led into the system through tap I., the three-way tap J being closed. Meanwhile the furnace H was removed, so that the catalyst tube was held suspended only by the furnace cover. The tube A was removed by sealing off at K and quickly sealed in place on the adsorption apparatus by means of the capillary tube H. Keeping the catalyst in B under a positive pressure of carbon dioxide, a short piece of glass tubing was sealed on at K the pressure of the carbon dioxide being used in making the seal. During this operation the tube B was swung into a horizontal position to prevent heating the catalyst mass. Fig. 2 shows the changes made in the furnace in order to make the reaction velocity measure-

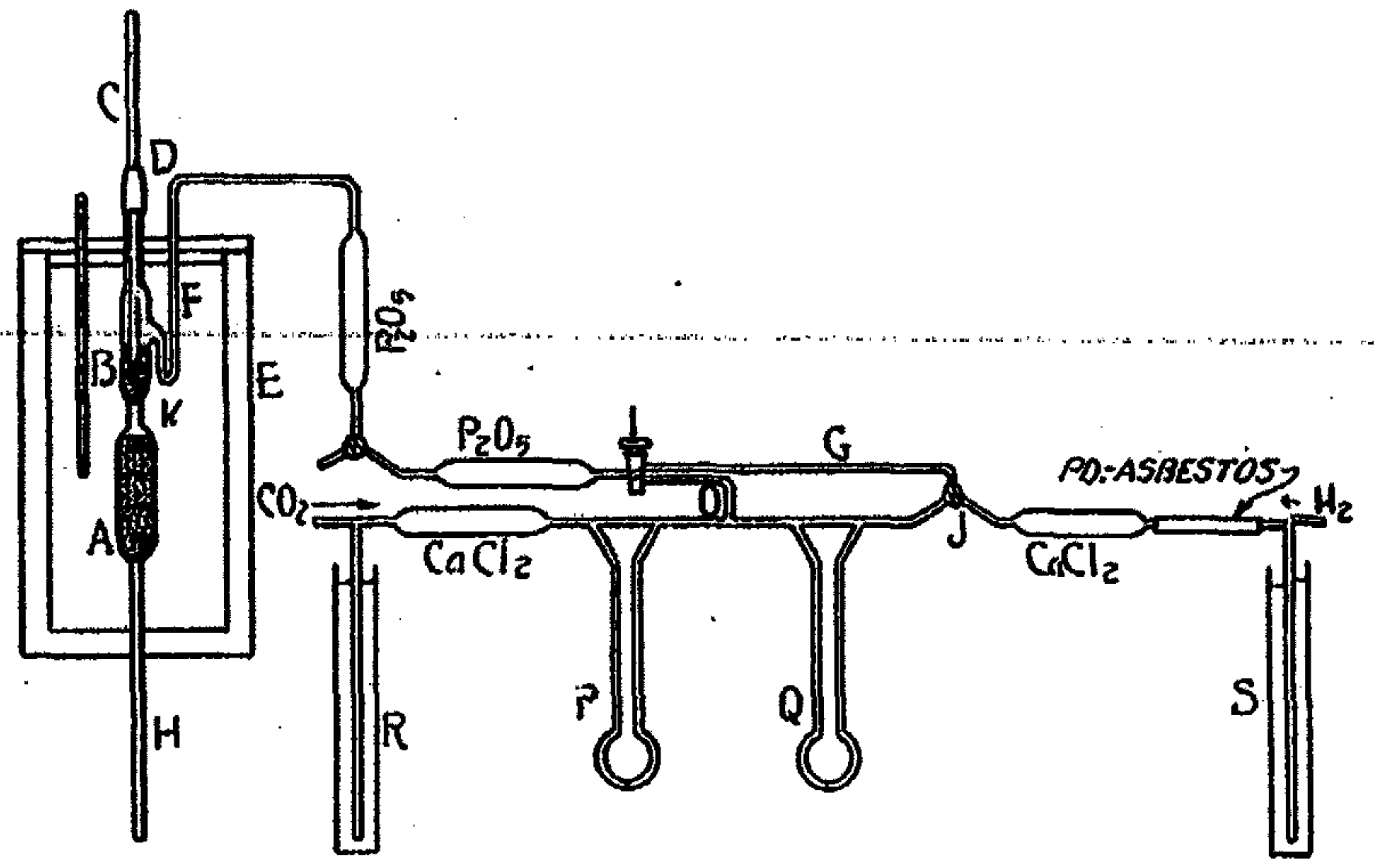

FIG. 1

ments. A shorter furnace L was substituted for E after sealing on the tube M. A small furnace N, which could be raised and lowered, was placed around M to prevent any water from condensing along this tube.

Reaction Velocity Measurements.—In the experiments on reaction velocity, the two interacting gases, carbon dioxide and hydrogen came in contact at O (Fig. 1) and then passed through the two phosphorus pentoxide tubes where they were thoroughly dried and mixed before entering the preheater F and catalyst tube B. The amount of carbon dioxide in the mixture could be controlled by the flow meter P, and the amount of hydrogen by means of its flow meter Q. The traps R and S which contained water served for the regulation of the pressures of the two gases. As shown in Fig. 2, the exit gases were passed through the phosphorus pentoxide weighing tube and then through a sulphuric acid trap to the air. In making a run, hydrogen alone was passed over the catalyst, while the temperature was raised to the maximum to be reached during the run, until weighings of the phosphorus pentoxide tube showed that no water was being evolved. The temperature was then adjusted somewhat below that desired for the first measurements, and carbon dioxide was allowed to enter the system. During all runs, the gas mixture was kept at a ratio of 6 to 1 for hydrogen to carbon dioxide. When the gas mixture was correctly adjusted and the temperature regulated, the reaction was allowed to proceed an hour or more, to insure steady conditions, before measurements were made. During this time the exit gases passed directly from the catalyst tube to the acid trap. Measurements were made by interposing a weighed phosphorus pentoxide tube for 15 minutes, the gain in weight due to the water formed in the reaction being then determined. Determinations were made at a given temperature until several checks were obtained, showing that a steady condition existed. During the periods when the catalyst was not in use, it was maintained at room temperature under a positive pressure of hydrogen. The flow meters were calibrated with the gas with which they were to be used and under the conditions of experiment, the gases being collected and measured over mercury. These meters were frequently checked between runs. Also, during runs, the correctness of the carbon dioxide flow meter could be checked by raising the temperature so as to secure 100% conversion.

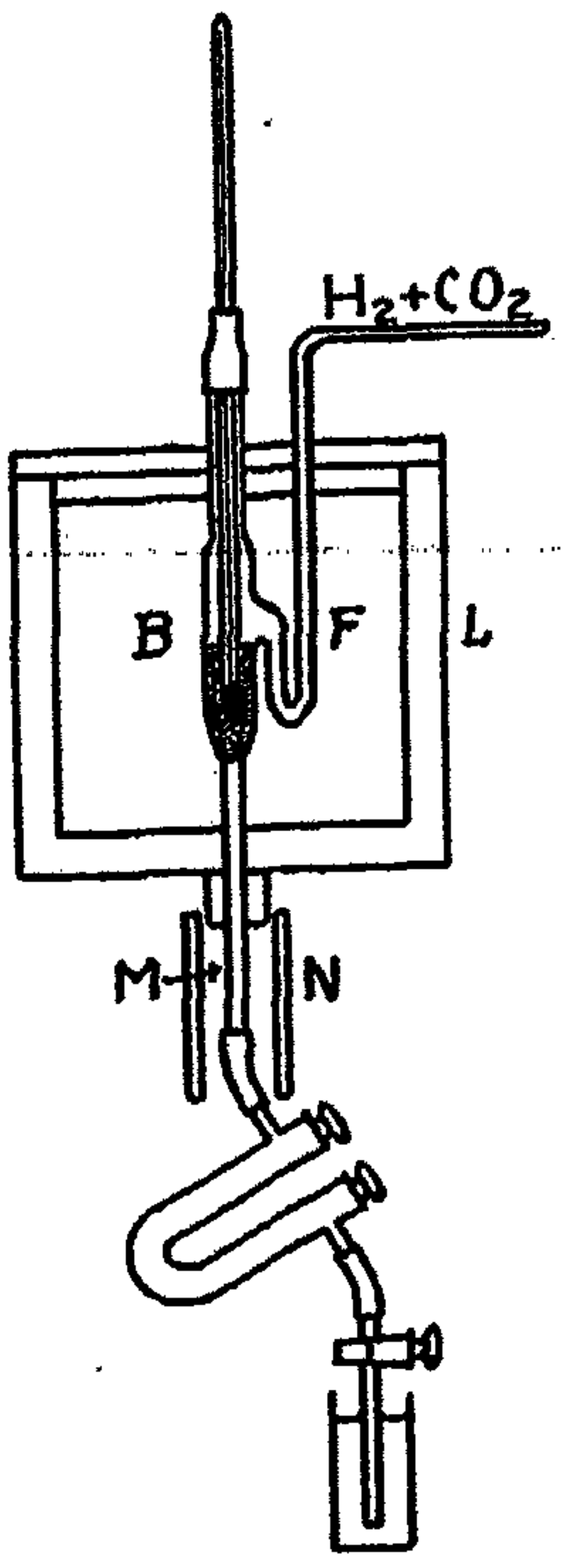

FIG. 2

Adsorption Measurements.—The apparatus used and the technique employed in adsorption was essentially that developed in the Princeton laboratories.[1] All measurements were made at or near atmospheric pressure

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[1] See Pease: J. Am. Chem. Soc., 45, 1197 (1923).

and over a range of temperatures. Temperatures were maintained as follows: 0° with crushed ice and water, 110° with toluene vapor, 218° with naphthalene vapor, and 285° and 345° with an electrically heated air bath.

Preparation and Purification of Gases.—The gases were prepared and purified in the same manner for both the reaction velocity and the adsorption measurements.

Electrolytic hydrogen was passed over heated palladized asbestos, to remove oxygen, and dried over phosphorus pentoxide.

Carbon dioxide was generated in a Kipp generator by the interaction of dilute hydrochloric acid and marble, passed through a solution of sodium bicarbonate, and finally dried over phosphorus pentoxide.

Compressed nitrogen containing only a slight amount of oxygen was purified by passage through ammonium cuprous carbonate solution, washed with dilute sulphuric acid, then with concentrated sodium hydroxide solution, passed over red-hot copper turnings, and finally dried over phosphorus pentoxide.

Preparation of Catalysts.—Pumice ground to 20–40 mesh was used as a supporting material. It was purified by boiling with aqua regia until free from iron. It was then washed free from chlorides and nitrates, dried on a water bath, and finally over a free flame to dusty dryness. It was kept in a tightly stoppered bottle.

Catalyst I was prepared by allowing 16 grams of the prepared pumice, volume 52.44 ccs., to absorb uniformly 10 ccs. of standard nickel nitrate solution equivalent to 1.6 grams of metallic nickel. The standard nickel nitrate solution was made by dissolving 79.29 grams of pure nickel nitrate in water, making up the total volume to 100 ccs. The impregnated pumice was dried for two hours on the water bath. One sixteenth of the total weight of this material, corresponding to one tenth gram of nickel on one gram of pumice, was separated for reaction velocity measurements. The remainder was placed in the lower part of the catalyst tube for use in adsorption measurements while the portion separated was placed in the upper part of the tube and the whole arranged for reduction as previously described. The temperature of the furnace was slowly raised to 200°, during a period of three hours while dry air was sucked through, then more rapidly to 350° and kept there until no more oxides of nitrogen were evolved. The furnace was allowed to cool and the air displaced by hydrogen. The temperature was then raised to 350° and reduction continued at this temperature until less than 1 milligram of water formed per hour as determined by weighing a phosphorus pentoxide tube through which the exit hydrogen passed. The time of reduction was 228 hours. The catalyst was dull black in appearance. Catalyst II was identical in every way with Catalyst I except that it contained in addition 0.16 grams of thoria. The thoria was incorporated by dissolving 0.3338 grams of pure thorium nitrate (this nitrate on analysis had been found to contain 47.93% ThO_2) in the 10 ccs. of the standard nickel nitrate solution used to impregnate the pumice. Reduction at 350° was continued, as with Catalyst I, until less than 1 milligram of water formed per hour. The time of reduction was here, also, 228 hours. This catalyst had a jet-black color.

Catalyst III was unsupported nickel. It was prepared by calcination of pure nickel nitrate to form nickel oxide, which was subsequently reduced in the same apparatus and in the same manner as the supported catalysts. The temperature of reduction was 250°. It required 192 hours to reduce this catalyst to the point where less than 1 milligram of water formed per hour. The catalyst was a dull black, rather dense powder.

Catalyst IV was also unsupported nickel but contained 2% ThO_2 calculated upon the weight of nickel present in the nickel nitrate used. It was prepared by heating nickel nitrate until it dissolved in its water of crystallization and then dissolving the required amount of thorium nitrate in this melt. After thorough mixing, the temperature was raised slowly until oxides of nitrogen were evolved, and calcination was allowed to proceed as in the preparation of Catalyst III. This catalyst was prepared for reaction velocity measurements only. The temperature of reduction was 250° and the time 192 hours. This catalyst was a jet-black powder.

Catalyst V was unsupported nickel and contained 10% thoria calculated upon the weight of nickel. The thoria was incorporated as in Catalyst IV and reduction was carried out as with Catalyst III. The temperature of reduction was 250° but it was necessary to continue reduction for 384 hours before the water content of the effluent hydrogen fell to 1 milligram per hour. This catalyst was a rather light powder of jet-black color.

Heat treatment.—The unsupported catalysts were subjected to a standard heat treatment. The identical treatment was given to catalysts intended for adsorption measurements as was given to catalysts intended for reaction velocity work. It consisted in heating the catalyst in an atmosphere of hydrogen for 1 hour at 400°, the temperature being raised to 400° and lowered again at a given rate. Some reduction occurred during this treatment but it was of slight import as compared to the effect produced by sintering. It was not possible to heat the catalyst in the reaction velocity tube in vacuo, and perhaps it would not have been altogether desirable to heat the catalyst bulb in the adsorption apparatus for any length of time at 400° when evacuated, because of the slow deformation of the glass bulb which might occur.

Supported Catalysts

Adsorption Measurements on Supported Catalysts:—The adsorptive capacities of Catalysts I and II for the reacting gases and nitrogen are shown in Table I. These two catalysts were identical in every way except that II contained 10% thoria.

Both catalysts show a large adsorption of nitrogen at 0°, intermediate between that of hydrogen and that of carbon dioxide. The pumice support is responsible for this large adsorption of both carbon dioxide and nitrogen at this temperature. In the case of the former gas it would seem probable that liquefaction has occurred in the capillaries but in the case of nitrogen the

TABLE I

Adsorption on Catalyst I

Wt. nickel = 1.500 gms; Wt. pumice = 15.000 gms; Apparent vol. = 49.16 cc.

Gas	Vol. of gas N. T. P. to fill bulb at t°, 760 mm.					Vol. of gas N. T. P. adsorbed by sample at t°, 760 mm.				
	0°	110°	218°	285°	345°	0°	110°	128°	285°	345°
N_2	68.5	37.55	28.2	24.45	21.9	18.9	2.2	.65	.2	0
H_2	55.4	41.05	32.45	28.8		5.8	5.7	4.9	4.5	
CO_2		76.05	34.7	27.65	23.75		40.7	7.15	3.4	1.85

Adsorptions on Catalyst II

Wt. nickel = 1.500 gms; Wt. thoria = 0.1500 gms; Wt. pumice = 15.00 gms.
Apparent vol. = 49.16 cc.

Gas	Vol. of gas N. T. P. to fill bulb at t°, 760 mm.					Vol. gas N. T. P. adsorbed by sample at t°, 760 mm.				
	0°	110°	218°	285°	345°	0°	110°	218°	285°	345°
N_2	69.8	38.25	28.8	25.2	22.6	18.65	1.8	.35	.1	0
H_2	57.75	42.95	34.25	30.55		6.6	6.5	5.8	5.45	
CO_2	407.9	78.15	36.25	29.35	25.25	356.8	41.7	7.8	4.3	2.65

Comparison of Adsorptions on Catalysts I and II

Vol. of gas N. T. P. adsorbed by sample at t°, 760 mm.

Catalyst	Gas	0°	110°	218°	285°	345°
II	H_2	6.6	6.5	5.8	5.45	
I	H_2	5.8	5.7	4.9	4.50	
Increase		.8	.8	.9	.95	
Percentage increase		13.8	14.04	18.37	21.1	
II	CO_2		41.7	7.8	4.3	2.65
I	CO_2		40.7	7.15	3.4	1.85
Increase			1.0	.65	.90	.80
Percentage increase			2.46	9.09	26.47	43.24
II Ratio	$\frac{CO_2}{H_2}$		6.4	1.3	.8	
I Ratio			7.1	1.5	.8	

temperature is far above that of the critical temperature (−146°C) of this gas[1]. Previous work in the Princeton laboratories has shown no appreciable adsorption of nitrogen when diatomite brick was used as a support, and little or none has apparently occurred with unsupported nickel catalysts dealt with later in this paper.

In calculating the amounts of the gases adsorbed, it has been assumed that the nitrogen adsorption occurring at 345°, the highest temperature at which measurements were made, was negligible. This assumption gives values for nitrogen adsorption at 285° which are very small e.g. 0.1 and 0.2 cc., and for the comparative purposes for which these adsorption values are useful can involve no appreciable error.

The hydrogen adsorption on either catalyst shows comparatively little change with temperature as has been previously observed in the case of supported nickel alone[2]. The promoted catalyst shows an increased adsorption

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[1] Landolt-Börnstein-Roth-Scheel.

[2] Gauger and Taylor: J. Am. Chem. Soc., 45, 920 (1923).

at all temperatures investigated. The actual increase varies from 0.8 to 0.95 cc. over the range 0°—285°. The percentage gain in hydrogen adsorption of the promoted catalyst over the unpromoted in the range 110°–285° shows a linear increase with temperature. This is shown graphically in Fig. 3.

The carbon dioxide adsorptions at 0° are doubtless largely due to liquefaction, a value of 356 ccs. having been obtained at 0° for this gas on Catalyst II. Even at 110° adsorption is also without doubt largely of the secondary or unreactive type. At all temperatures, however, the promoted catalyst shows the greater adsorptive capacity. The actual increase in carbon dioxide adsorption which Catalyst II shows over Catalyst I varies from 0.65 to 1.0 cc. in the range 0°—345°. As may be seen in Fig. 3, the percentage increase in the assorption of this gas becomes nearly linear in the temperature range 220°–345°.

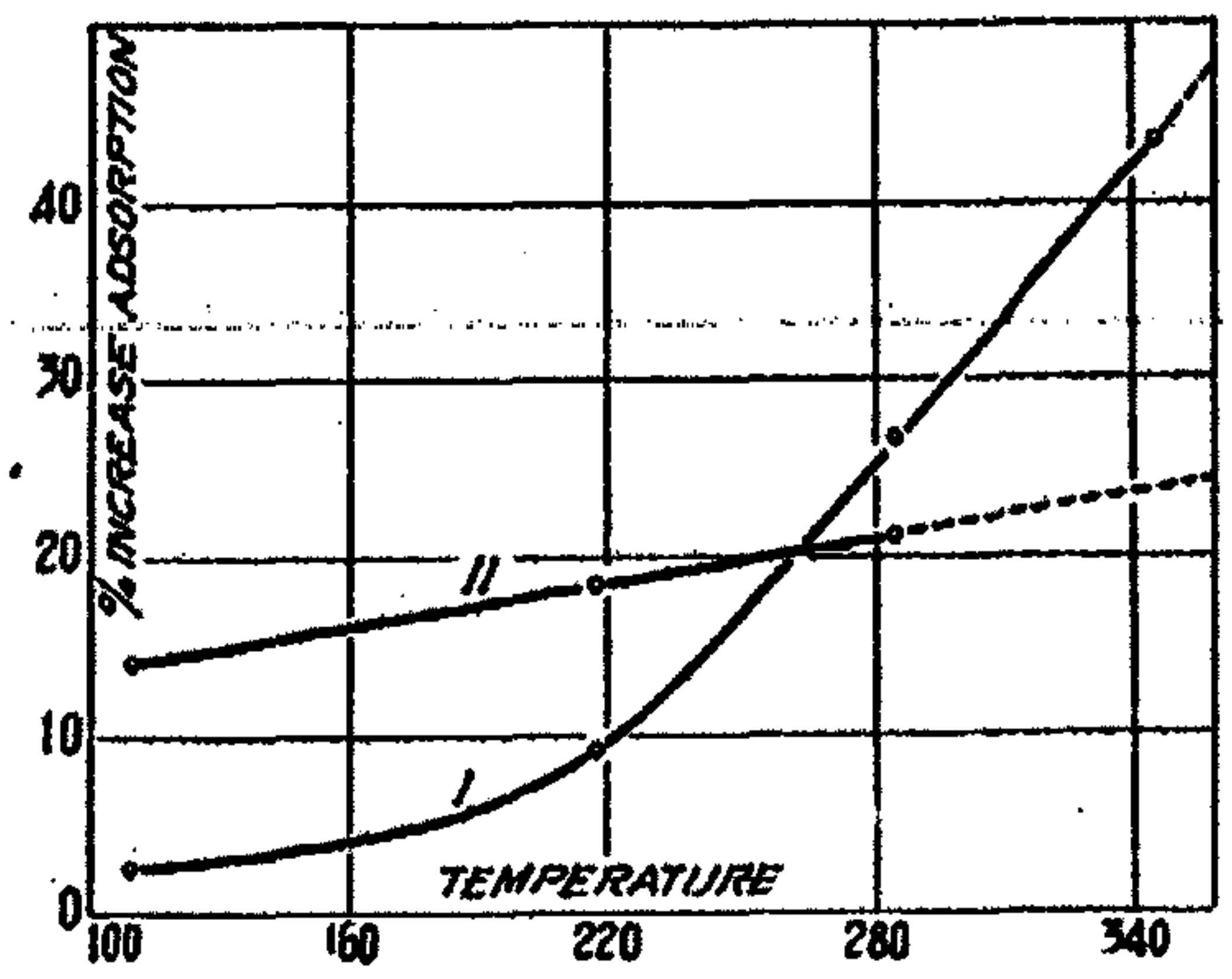

FIG. 3

The percentage increases in adsorption shown by Catalyst II over Catalyst I. Curve I-hydrogen. Curve II-carbon dioxide.

The nitrogen adsorptions are somewhat less on the promoted catalyst. This may be due, as Armstrong and Hilditch suggest, to the plugging of some of the pores of the pumice support by the thoria.

Reaction Velocity Measurements on Supported Catalysts.—The activities of Catalyst I and II, as shown by their capacities for catalyzing the interaction of hydrogen with carbon dioxide, are shown graphically in Fig. 4. Temperature has been plotted horizontally and percentage conversion vertically. The same amount of each catalyst was used, and conditions of experiment were identical for both, so that the results should be completely comparable. With both catalysts, the rate of reaction increases linearly with the temperature at rates of conversion between 20 and 75%. Curve 1 in Fig 4 shows the steady behavior of Catalyst I, and curve 2 that of Catalyst II, both at the same rate of flow, 35 ccs. per minute. The promoted catalyst shows the same activity 55°–60° lower than the unpromoted one.[1] The temperature coefficient of the

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[1] In this connection it is interesting to note that adsorption measurements of hydrogen on Catalyst II when it already held some adsorbed carbon dioxide showed that these two gases interacted even at 110°C., although very slowly.

reaction on the more active catalyst appears somewhat greater when rates of flow are the same for both catalysts. When, however, the rate of flow on Catalyst II is increased until its rate of conversion is practically the same as for Catalyst I at a flow rate of 35 cc. per minute, the temperature coefficients become the same. The slope of curve 3, which shows the behavior of Catalyst I at a rate of flow of 49 ccs. per minute after the catalyst had been somewhat deactivated by allowing the reaction to proceed at 400°, indicates that the reaction now has a somewhat smaller temperature coefficient. It may be noted here, and it will be shown more strikingly in the case of unsupported nickel catalysts, that the more active the catalyst the greater the temperature coefficient of the reaction catalyzed.

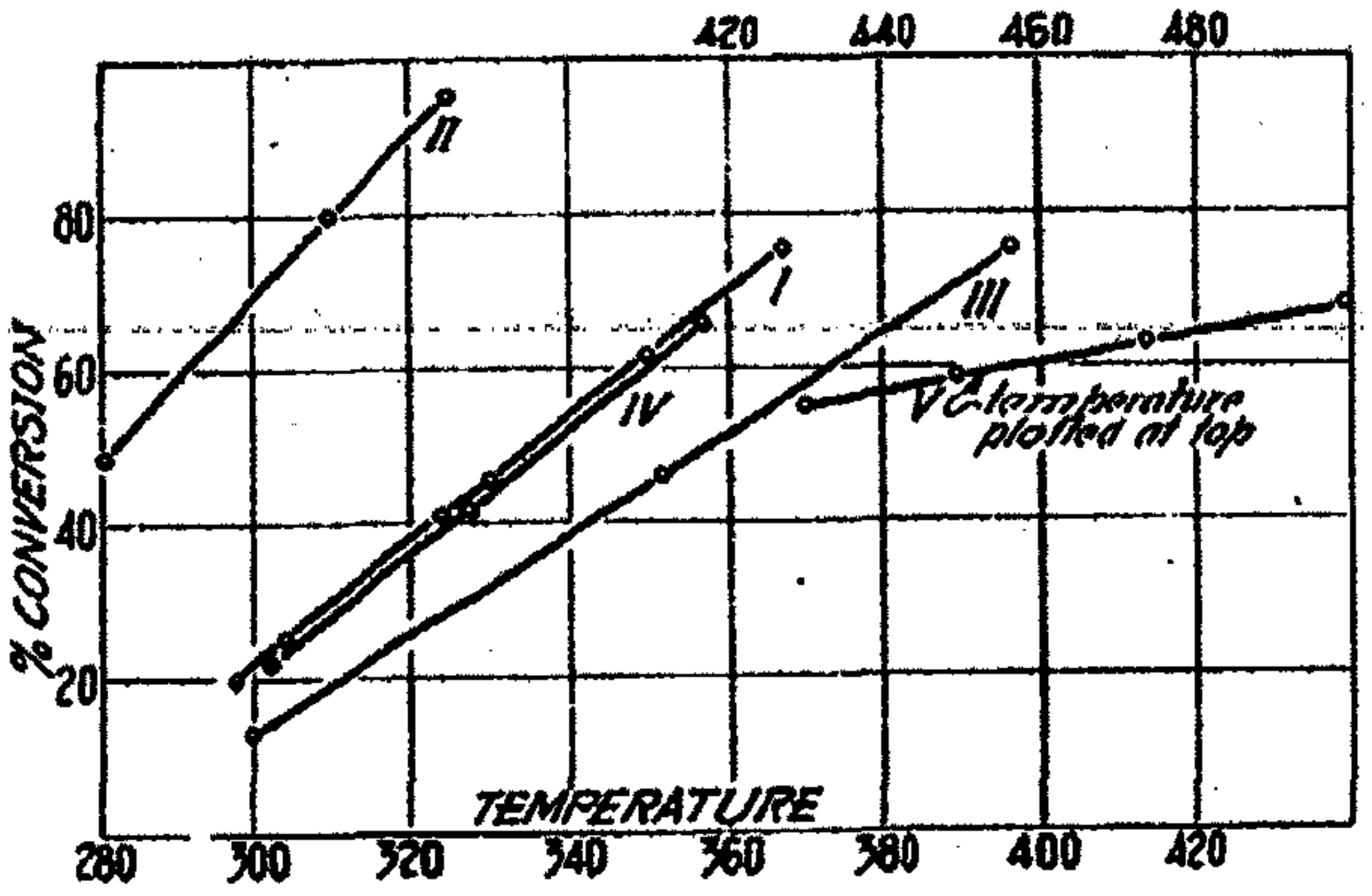

Fig. 4

Reaction velocities on supported catalysts. Curve I-Catalyst I with rate of flow 35 ccs; Curve II-Catalyst II with rate of flow 35 ccs; Curve III-Catalyst I with rate of flow 49 ccs; Curve IV-Catalyst II with rate of flow 350 ccs. Curve V-Catalyst II with rate of flow 23 ccs.

Discussion of Results on Supported Catalysts.—From a comparison of curves 1 and 4 in Fig. 4 it is apparent that the gas mixture may be passed nearly ten times as rapidly over Catalyst II as over I with the same conversion. This is interpreted to mean that the presence of 10% thoria has increased the efficiency of the nickel ten times. It is clear that the increased adsorptions of the reacting gases by the promoted catalyst will not account for the ten fold increase in activity shown by this catalyst, on any basis of quantitative extension of surface alone. Instead of an increase of 900% as would be demanded by such a theory we find actually much less. Upon extrapolation of the curves shown in Fig. 3 it appears that, at 360°, where reaction is 70% complete, the increase in hydrogen adsorption is only about 24% and that of carbon dioxide only about 48%. These facts argue that the change in surface in the case of supported promoted catalysts must be largely qualitative in character.

The possibility of explaining promoter action on a basis of a change in the ratio in which the reacting gases are adsorbed seems, also, unlikely. For, although the value of the ratio CO_2/H_2 appears larger for Catalyst I than for

TABLE II

Adsorptions on Catalyst III (Nickel alone)
Wt. of nickel = 37.98 gms; Density 8.892

Gas	Vol. of gas N. T. P. to fill bulb at t°, 760 mm.			Vol. of gas N. T. P. adsorbed by sample at t°, 760 mm.		
	0°	110°	218°	0°	110°	218°
N_2	27.7	19.55	15.45			
H_2	52.8	50.55		25.1	31.0	
CO_2	43.15	28.9	25.3	15.45	9.35	9.85
$H_2 = 6$ $CO_2 = 1$	52.85			25.2		
After heating to 400° C. for 1 hour.						
N_2	27.1	19.35	15.4			
H_2	37.05	33.9	28.1	9.95	14.55	12.7
CO_2	34.15	22.9	20.4	7.05	3.55	5.0
$H_2 = 6$ $CO_2 = 1$	38.5			11.4		
Percentage decrease in adsorptions due to heat treatment.						
H_2				60.4	53.1	
CO_2				54.4	62.0	49.2
$H_2 = 6$ $CO_2 = 1$				54.8		

Adsorptions on Catalyst V (nickel plus 10% thoria)
Wt. of catalyst = 20.42 gms; Density = 8.899

Gas	Vol. of gas N. T. P. to fill bulb at t°, 760 mm.			Vol. of gas N. T. P. adsorbed by sample at t°, 760 mm.		
	0°	110°	218°	0°	110°	218°
N_2	32.2	22.2	17.4			
H_2	58.25	53.45		26.05	31.25	
CO_2	67.9	44.45	33.65	35.7	22.25	16.25
$H_2 = 6$ $CO_2 = 1$	61.5			29.3		
After heating to 400°C. for 1 hour.						
N_2	32.05	22.2	17.4			
H_2	45.9	38.75	34.4	13.85	16.55	17.0
CO_2	62.15	40.9	30.85	30.1	18.7	13.45
$H_2 = 6$ $CO_2 = 1$	52.75			20.7		
Percentage decrease in adsorption due to heat treatment.						
H_2				46.8	47.0	
CO_2				15.7	16.0	17.2
$H_2 = 6$ $CO_2 = 1$				29.4		

Comparisons of adsorptions on Catalysts III and V.

Catalyst	Gas	Vol. of gas N. T. P. adsorbed per vol. of catalyst at t°, 760 mm.			After heating to 400°C. for 1 hour Vol. gas N. T. P. adsorbed per vol. of catalyst at t°, 760 mm.		
		0°	110°	218°	0°	110°	218°
V	H_2	11.35	13.6		6.05	7.2	7.4
III	H_2	5.8	7.2		2.3	3.35	2.95
Increase		5.55	6.4		3.75	3.85	4.45
Percentage inc.		95.7	88.9		163.0	114.9	150.9
V	CO_2	15.55	9.7	7.1	13.1	8.15	5.85
III	CO_2	3.6	2.15	2.3	1.65	.8	1.15
Increase		11.95	7.55	4.8	11.45	7.35	4.7
Percentage inc.		332.0	351.2	208.7	694.0	906.3	408.7
V III	$H_2 = 6$ $CO_2 = 1$	12.75 5.85			9.0 2.65		
Increase		6.90			6.35		
Percentage inc.		117.95			239.6		
V Ratio $\frac{CO_2}{H_2}$		1.37	.71		2.17	1.13	
III " "		.62	.30		.72	.24	

Catalyst II at lower temperatures, the difference between these ratios decreases as the temperature increases and, at 285°, where the reaction is still slow, this ratio is practically the same for both catalysts. Therefore, it appears impossible to explain the action of the promoter either by a quantitative extension of surface, or by a change in the relative concentrations of the adsorbed reactants. It seems most probable, however, that the surface of the promoted catalyst is such that it holds adsorbed in a reactive condition a larger fraction of the total amount of gas adsorbed than does the unpromoted catalyst.

If the whole adsorbing surface of the promoted catalyst were actually active catalytically, it is evident that not more than 10 per cent of the unpromoted catalyst surface could possibly be active. Actually the percentage of active surface must be much smaller than this.

Unsupported Catalysts

Adsorption Measurements on Unsupported Catalysts.—In order to prepare unsupported catalysts of high activity, reduction was carried out at as low a temperature as was deemed possible, namely 250°. This procedure had the advantage of making the pure nickel catalyst, used as a basis of comparison, as active as possible, but the disadvantage of making entirely consistent adsorption measurements impossible. Some irregularities were anticipated in working with such active catalysts produced by low temperature reduction, but it is believed that these are small enough as compared to the effects observed to render the conclusions valid. Hydrogen values at 110° and 218° are obviously increased by a slow reduction still occurring at these temperatures. Carbon dioxide values are also large at 218° probably because of a tendency toward carbonate formation at this temperature. However, all values presented are the averages of reproducible check determinations.

In Table II adsorption measurements on Catalyst III, composed of nickel alone, and on Catalyst V composed of nickel plus 10% thoria are given, both before and after the standard heat treatment of 1 hour at 400°. The values for hydrogen adsorption at 0° are somewhat higher than those obtained by either Gauger[1] or Burns[2] for nickel reduced at 300°.

The effect of heat treatment on Catalyst III has been to decrease the adsorption of hydrogen, carbon dioxide and the reaction mixture of these gases about 55%. Catalyst V shows as a result of the heat treatment a reduction in hydrogen adsorption amounting to 47%, in carbon dioxide of only about 16% and in the adsorption of the mixture of an intermediate value of 29%.

From a comparison of the adsorptions of the two catalysts under investigation, the wide difference between the increases in the adsorptions of the two reacting gases on the promoted catalyst is at once apparent. An increase of about 92% for hydrogen but of nearly 342% for carbon dioxide occurs on the promoted catalyst in the temperature range 0°–110°. After the heat treat-

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[1] Gauger and Taylor: loc. cit.

[2] Taylor and Burns: J. Am. Chem., 43, 1273 (1921).

ment the values for hydrogen become about 139% and those for carbon dioxide average 800% over the same temperature range. The promoted catalyst thus shows a greater resistance to heating than does nickel alone. The promoter evidently acts as a support. However, the further function of the thoria in selectively adsorbing carbon dioxide here becomes apparent. The relatively larger adsorptions of carbon dioxide by the promoted catalyst become still larger after heating. The actual increase in ccs. of carbon dioxide adsorbed by Catalyst V as compared to Catalyst III remains practically the same after the heat treatment, while there is a considerable decrease in the corresponding hydrogen values. This means that the relation between the CO_2/H_2 ratios on Catalysts III and V becomes considerably changed due to heating. Between 0° and 110° these ratios are about 1:2 before heating but, afterwards, they are nearer as 1:4. The adsorptions of the reaction mixture show about the same effect. In the case of Catalyst III the adsorption of hydrogen and that of the mixture have the same value. After heat treatment there is a relatively larger adsorption of the mixture than of hydrogen. This relative decrease in hydrogen adsorption may be attributed to a qualitative change in surface due to sintering which has rendered some of the surface formerly capable of adsorbing hydrogen now capable only of holding carbon dioxide. On Catalyst V the adsorption of the mixture is larger than that of hydrogen alone and increasingly so after heating. This must be attributed in part to a specific action on the part of thoria in adsorbing carbon dioxide due perhaps to a tendency for carbonate formation.

In connection with the adsorption of the gaseous mixture it is of interest to note that Hurst and Rideal[1] found for a mixture of carbon monoxide and hydrogen on copper and copper plus palladium surfaces, that the volume of the mixture adsorbed was much less than would be calculated from the adsorption of the two gases separately. This phenomenon is explained by them, on the basis of the polarity of the carbon monoxide molecule. Since carbon dioxide is a non-polar gas, however, we should expect to find more or less additive relations or simple replacements involved in the behavior of mixtures of carbon dioxide and hydrogen on finely divided metal surfaces. Such seems to be the case with nickel.

Reaction Velocity Measurements on Unsupported Catalysts.—Three unsupported catalysts were investigated: Catalyst III composed of nickel alone, weight 4.7961 grams; Catalyst IV composed of nickel plus 2% thoria, weight 4.5565 grams; and Catalyst V composed of nickel plus 10% thoria, weight 4.8059 grams. The behavior of these catalysts both before and after heat treatment is shown in Fig. 5. The results are treated in the same manner as were those of the supported catalysts. The rate of gas flow is in all cases the same, 49 ccs. per minute.

When compared with the supported catalysts the difference in the temperature range at which comparable conversions are occurring is apparent. The difference in the temperature of reduction of these two types of catalysts is

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[1] Hurst and Rideal: J. Chem. Soc., **125**, 694 (1924).

probably one of the chief factors causing this phenomenon. Taking comparable conditions, we have 50% conversion shown by Catalyst IV at 196°, by Catalyst V at 200°, by Catalyst III at 223°, but by Catalyst I at 358°. The first in order were reduced at 250° while the last was reduced at 350°. One of the effects of the standard heat treatment has been to raise considerably the temperature at which equivalent conversion occurs.

The slopes of the reaction velocity curves are somewhat steeper for the unsupported catalysts and steepest for Catalyst IV which shows the greatest promotion at the lowest temperature. This is more strikingly illustrated by Curve 5 in Fig. 4 which shows the course of the reaction at 430-500°.

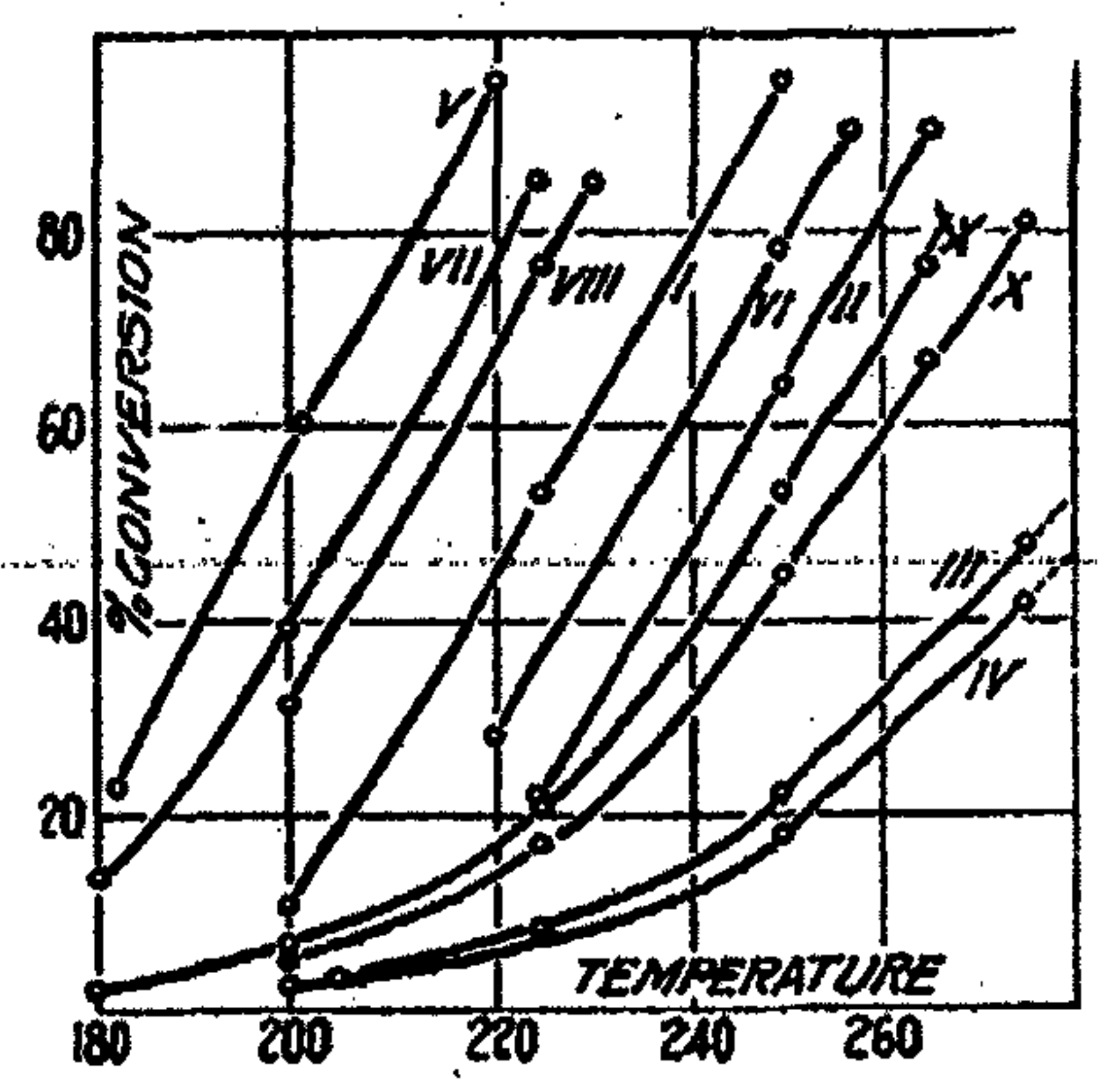

Fig. 5

Reaction velocities on unsupported catalysts. Rate of flow 49 ccs. Catalyst III: Curve I initial rate; Curve II rate after 25 hours' run; Curve III rate after 1 hour at 400°; Curve IV rate after 2 hours at 400°. Catalyst IV; Curve V initial rate; Curve VI rate after 1 hour at 400°. Catalyst V: Curve VII initial rate; Curve VIII rate after 25 hours' run; Curve IX rate after 1 hour at 400°; Curve X rate after 2 hours at 400°.

It will be noted that for Catalysts III and V curves are shown designated as "initial rate" and "rate after 25 hours use." The "initial rate" curves represent the activity on the catalyst as determined by the first 4-5 hours run. Catalyst III showed a continuous decrease in activity with use, and after 25 hours, a slow depreciation still occurred. At the end of this interval this catalyst showed its initial activity 18° higher than at the beginning. Catalyst V after 25 hours use had acquired a steady rate, with a change in initial reaction temperature of only 5°. Catalyst IV maintained its initial activity with continued use. This catalyst, also, contained nearer the optimum amount of thoria as determined by Medsforth than did V. These facts would indicate that the optimum amount of promoter not only gives the greatest activity but also creates the surface of greatest permanence and durability. The marked depreciation which Catalyst III suffered with use is in all probability due to the exothermicity of the reaction (40,500 cals.) occurring on the active surface of the catalyst. The heat of reaction is great enough to cause a slow sintering of this surface and the consequent loss in activity. That the promoted catalysts did not depreciate thus, is an indication as to the function of the thoria as a support material.

At 50% conversion Catalyst IV has the same activity 27° lower than Catalyst III while Catalyst V is 17° lower than nickel alone. If the rates after 25 hours use were to be compared, the promoted catalysts would appear somewhat more favorably still. Of the promoted catalysts we are more interested in V because of the adsorption measurements made upon it, and also because it contains the same ratio of nickel to thoria as did Catalyst II. Catalyst V has the same activity as Catalyst III at a temperature 17° lower. To obtain an idea of the relative activities of these two catalysts we will assume that the ratio of the temperature coefficients on Catalysts II and V is also the ratio between the increases in activity which these catalysts show with rising temperature. Since it was found that a 55° difference in temperature between Catalysts I and II corresponded to a ten-fold increase in activity for II, and since the slopes of the curves for Catalysts II and V are 1:1.9, we find that a 17° difference in temperature between Catalysts III and V should correspond to approximately a six-fold increase in activity for V. By the same reasoning Catalyst IV would show about a 9.5-fold increase in activity over Catalyst III.

As a result of the standard heat treatment a loss in activity at 50% conversion equal to 54° occurs with Catalyst III while under similar treatment Catalyst V suffers a loss equivalent to but 42°. This may be interpreted to mean that Catalyst III showed approximately a 28.5% larger decrease in activity than did Catalyst V.

Physical Effects of Heat Treatment.—When pure nickel oxides are reduced by hydrogen the resulting product is usually a dense, dull black powder, or a substance easily reducible to powder form. If irreducible impurities such as oxides are present even in small amounts, a jet black powder of a much less apparent density results. When a promoter of the thoria type is present it acts as an impurity to prevent sintering and, therefore, to maintain a greater surface.

As a result of work done in 1899 on the occlusion of hydrogen by metallic cobalt and other metals including nickel, Baxter[1] showed that the adsorptive capacity of metals for hydrogen depended upon the temperature at which their oxides were reduced or the temperature to which they were subsequently heated. He also observed that, "Metal reduced from the impure oxide at low temperatures is not coherent but powdery, while pure metal shows a decided tendency to cling together. This sintering can be nothing more or less than incipient fusion. When the minute particles of metal are in close contact with one another the contraction takes place very readily, while impurities keep apart the particles of metal and necessitate the application of higher temperatures to produce the same effect." The results of the present work are in agreement with these ideas.

At a temperature as low as 250° the volume of the pure nickel catalyst was only about three-quarters of that of the original oxide before reduction,

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[1] Baxter: Am. Chem. J., **22**, 351 (1899).

while the promoted catalyst reduced at the same temperature showed little shrinkage. Some data on the apparent densities of the unsupported catalysts are given in the following table.

Catalyst	Apparent Density	Apparent Volume
III	1.44	0.69
III (heat treated)	1.81	0.55
V	0.90	1.11
V (heat treated)	1.20	0.83

The effect of a second similar heating on catalysts used for reaction velocity measurements produced much less effect. This is evident from the relation of the positions of curves 9 and 10, also 3 and 4 in Fig. 5.

It appears evident from the preceding data and from the adsorption and reaction velocity measurements on unsupported catalysts before and after heat treatment that the nature, extent, and catalytic activity of a surface are dependent upon (a) the purity of the metal, that is, the presence or absence of foreign substances which may act as promoters. (b) the highest temperature at which the surface has been allowed to equilibrate itself. These conclusions are in line with Baxter's work and that of Pease[1] with copper.

Discussion of Results on Unsupported Catalysts.—The proportionately larger increases in the adsorption of the reacting gases on the promoted, unsupported catalyst will more nearly account for the increase in activity found than was the case with the supported nickel. Catalyst V showed only a six-fold increase in reaction velocity over that of Catalyst III, but an average increase in hydrogen adsorption of some 92% and in carbon dioxide adsorption of some 342% occurred in the temperature range 0°-110°. A quantitative extension of surface must therefore in part account for the increased activity. The thoria here is acting partly as a support. This view is substantiated first by the increased apparent volume of the catalyst and second by the longer time necessary to obtain equivalent reduction, e.g. 384 hours for Catalyst V as compared to 192 hours for Catalyst III. That supported nickel cannot be reduced at as low a temperature as the unsupported material is well known.

Catalyst V did not contain the optimum concentration of thoria although the ratio of thoria to nickel was theoretically the same as in Catalyst II. Catalyst IV with only 2% thoria was more active. Aside from a possible blanketing effect[2] it is believed that thoria, in amounts above the optimum, causes a retardation in the reaction due to a disproportionately large adsorption of carbon dioxide. The CO_2/H_2 ratio on Catalyst V is more than twice that on Catalyst III and after heat treatment becomes more nearly four times as much. The hydrogen adsorption is dependent upon the extent of surface, whereas the carbon dioxide is being adsorbed in two ways, first by the nickel surface and second specifically by the thoria. This latter type of adsorption is apparently little altered by heat. The effect of heat treatment on the promoted nickel is, therefore, two-fold, first a disappearance of surface due to

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[1] Pease: J. Am. Chem. Soc., 45, 2296 (1923).

[2] Armstrong and Hilditch: loc. cit.

sintering, and second an unfavorable change of the CO_2/H_2 ratio. These two factors would make high temperatures especially disastrous to nickel promoted by thoria were it not for the action of the thoria in decreasing materially the amount of sintering.

As was previously noted, the standard heat treatment has caused approximately a 28.5% larger decrease in the activity of Catalyst III than it has in that of Catalyst V. The decrease in hydrogen adsorption at 0° due to this heat treatment was 60.4% on Catalyst III and 46.8% on Catalyst V. This gives approximately a 29% larger decrease for hydrogen adsorption for Catalyst III than for V. This points to a dependence of the reaction on the hydrogen adsorption. It is also of interest to note that the ratio of the increase in density of Catalyst III over V due to heating is 1.23 while the ratio of the displacements of the reaction velocity curves due to heating is 1.28 at 50% conversion.

Conclusions

It is believed that the results obtained from the work presented in this paper can best be explained in terms of the following theory.

The nature of the surface of a nickel catalyst produced by the reduction of the oxide is determined (a) by the nature and amount of foreign substances present, and (b) by the temperature of reduction. The most active catalyst imaginable would be one consisting of single atoms of the metal sufficiently isolated from each other so that all their valence forces would be available for adsorbing the reactants, and in certain cases the resultants. A most inactive catalyst, on the other hand, would be one whose atoms were regularly arranged in their stable crystal lattice with the consequent almost complete mutual saturation of valence forces. This latter type is easily realizable with metals in the massive state, when adsorptions are immeasurably small and catalytic power negligible. The former extreme type would not be experimentally realizable nor would it be an effective catalyst for many reactions because it would enter into true chemical combination with adsorbates. Catalysts actually realizable will have their atoms only partly unsaturated and will, therefore, hold the adsorbate with only part of the whole valence force. It, therefore, follows that the greater the irregularity of the metal atoms, e.g. the further they are removed from their regular crystal lattice the greater the force by which they can hold molecules by adsorption. The force which a catalytic surface exerts in adsorption will be equal to the sum of the total valence forces of the atoms concerned multiplied by a factor expressing the average degree of unsaturation of the component atoms.

The lower the temperatures of reduction the more unsaturated the resultant metal atoms. Other things equal the lowest temperature at which reduction will proceed will give the greatest realizable unsaturation, because, here, mobility of the metal atoms is least and, therefore, their tendency to mutual saturation a minimum. With rising temperature, a surface adjusts itself by an irreversible mutual saturation, or as is usually said "sinters." The function of a promoter of the thoria type is to prevent this saturation or sintering. The presence of the saturated molecules of thoria, which are more or less neutral electrically and which act as insulators between the charged metal atoms, prevent coalescence and consequent saturation. Foreign oxides which undergo reduction (preliminary work on mixtures of nickel and copper showed no promoter action) are not effective as promoters as they do not prevent saturation and may even assist it. The promoter, therefore, makes possible the production of a surface containing atoms of a more unsaturated character than it is possible to produce from the pure metal oxide under similar conditions of reduction. The efficiency of a promoter in preventing coalescence must, therefore, depend upon (a) the amount present (b) its distribution (c) its chemical and consequent electrical properties.

It is believed that the promoting action of thoria on nickel supported by pumice is largely due to such an increase in the unsaturation or activity of the surface. This increase in the activity of the surface of the promoted catalyst manifests itself (a) by a disproportionately large increase in reaction velocity as compared to the increase in extent of surface (b) by manifesting an equivalent activity at a lower temperature (c) by showing the higher temperature coefficient of the surface reaction. Other factors also become of importance in the case of unsupported nickel promoted by thoria. Here, the thoria acts also as a support to increase the extent of surface. This increase in extent of surface on the part of the unsupported promoted catalyst is shown (a) by its increased adsorption values (b) by the greater apparent volume of the catalyst (c) by the increased time necessary for reduction.

That the optimum ratio of thoria to nickel should be less for the unsupported nickel catalyst even though the thoria acts as a support is explained by the fact that much of the nickel present is also acting as a support and has little or no catalytic significance. The specific action of thoria in adsorbing carbon dioxide, aside from considerations of surface as shown by the effects of heat treatments, demonstrates the influence which the promoter may exert on the ratio in which the reacting gases are adsorbed. The behavior of the unsupported catalysts after heat treatment indicates that this last factor has become a retarding influence but is still more than compensated by the other factors still operating in a positive direction. Substances which cause the reactants to be adsorbed in an unfavorable ratio or lead to stable compound formation will act as poisons rather than promoters.

Summary

1. The reaction between carbon dioxide and hydrogen to form methane and water is a surface reaction, markedly so at low temperatures, and strongly affected by the adsorbing power for the reactants, of the surface catalyzing this reaction.

2. The activity of nickel alone, supported or unsupported, is dependent mainly upon the temperature at which it is reduced. Other things being equal, the lower the temperature of reduction the greater is the number of highly unsaturated nickel atoms which can exist per volume of catalyst.

These atoms are assumed mainly responsible for catalytic activity. A surface stable at the temperature of reduction or lower is profoundly modified when subjected to higher temperatures. The change consists in the coalescence of these unsaturated atoms due to valence force attraction, when their mobilities are increased with temperature, and their consequent saturation, whole of partial, and loss of effective adsorption power.

3. The primary function of the promoter, thoria, with supported nickel is to make possible, through the creation of thoria-nickel interfaces, the existence of a greater number of nickel atoms of a more highly unsaturated character per unit of catalyst than can exist in nickel alone, reduced under similar conditions.

4. Thoria may function in at least three ways in promoting catalysts of unsupported nickel (a) by the creation of a more active surface through the interface mechanism as in the case of supported catalysts (b) by an increase in the extent of surface in as much as the promoter acts as a support (c) by a favorable alteration in the ratio in which the reacting substances and possibly the products of reaction are adsorbed. A catalyst of maximum reactivity for a given reaction will, therefore, be produced when the nature, amount, and distribution of the promoter is such as to give the proper balance between these effects.

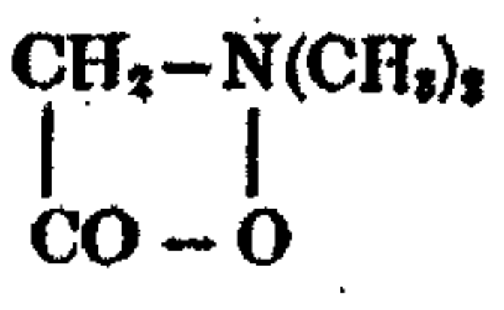
5. These conclusions have been based upon the results of both adsorption and reaction velocity measurements on samples of promoted and unpromoted, supported and unsupported nickel catalysts.

Princeton, N. J.

NEW BOOKS

Theorien der organischen Chemie. *Fifth edition. By Ferdinand Henrich. 23 × 16 cm; pp. viii+616. Braunschweig. Friedr. Vieweg und Sohn, 1924. Price: 17.50 marks, bound 19.50 marks.* Only a brief notice is needed to direct attention to the appearance of a fifth edition of a book which is already well established as an essential guide to the study of organic chemistry. In no branch of chemistry is such a guide more urgently necessary, since the preparation of new organic compounds and the study of old ones is proceeding so fast that there is very serious danger of being unable to see the forest on account of the innumerable trees and the unceasing development of young and vigorous seedlings. Under these conditions, it is essential that the books which deal with preparative methods should be supplemented by one in which all the experimental details are omitted and only the theoretical significance of the observations is expounded. The assertion that Dr. Henrich's book supplies this urgent need is proved by the fact that three German editions have now appeared since the last year of the war, that an American translation of the last German edition was issued in 1922, and that a French translation is in course of preparation. The American translation was noteworthy in that two additional chapters on "Recent Theories in regard to Valency" and "The Electron Conception of Valency" were interpolated between the chapters dealing with "The Theory of Alfred Werner" and "The so-called Negative Nature of Atomic Groups or Radicals". This scheme has not been taken over in its entirety in the new German edition, but the chapters dealing with Werner's Theory has been replaced by two chapters dealing with the Distribution of Affinity, and with Recent Views on the Nature of Valency. In the former of these chapters the question of strong and weak bonds is considered, whilst the latter chapter is mainly devoted to an exposition of the views of Stark, (which were described in the final chapter of an earlier German edition), of Falk and Nelson, and of H. S. Fry. Only brief references are made to the later work of G. N. Lewis and those who have followed him, since much of this work "was not accessible in the original" to the author when the present edition of his work was prepared. Of special interest, however, is a short section devoted to Pfeiffer's argument (1922) that since *o*, *m*, and *p* animobenzoic acids yield betaines with equal readiness, it is wrong to represent the betaines as containing a complete ring of real bonds I, and that they ought to be written as internally ionised salts II.

I.



$$\begin{array}{ccc}\mathrm{CH_2} & - & \mathrm{N(CH_3)_3} \\ | & & | \\ \mathrm{CO} & - & \mathrm{O}\end{array}$$

II

$$\overset{-}{\mathrm{O}}.\mathrm{CO_2}.\mathrm{N}\overset{+}{\mathrm{Me_3}}$$

Some of the later chapters of the book have also called for heavy revision in order to keep them up to date, but the principal addition is a chapter on Theories of Biochemistry in which new ground is broken, and old and new views on the chemistry of vital processes are described.

In conclusion, it may be said that in its present form Dr. Henrich's book has more than maintained its usefulness, and that readers who are not in the first instance organic chemists, as well as those who have every right to claim that title, may be grateful to the author for bringing to their attention so many of the most fascinating aspects of this branch of chemistry.

T. M. Lowry

The Principles of Applied Electrochemistry. *By A. J. Allmand. Second edition, revised and enlarged by the author and H. J. T. Ellingham. 23×16 cm; pp. xi+727. London and New York: Edward Arnold and Co; Longmans, Green and Co., 1924. Price: 35 shillings; $10.50.* The first edition of this very useful and valuable book appeared in 1912. In its present form it has been very completely revised and brought up to date. As in the first edition, the book is divided into two parts, of which Part I, entitled GENERAL AND THEORETICAL, embraces the following subjects:—Power; Faraday's Laws and Current Efficiency;

Electrolytic Dissociation; Energy Relations (including thermodynamics); Electromotive Force; Electrolysis, Polarisation, and Energy Efficiency; Electrode Processes in Detail; the Electrolysis Bath; Molten Electrolytes; General Principles of Electrothermics; Electrical Discharges in Gases. Part II, entitled SPECIAL AND TECHNICAL, which forms the major portion of the book, gives a very full account of all known electrolytic and electrothermal processes and includes chapters on Primary Cells, Secondary Cells, the Oxidation of Atmospheric Nitrogen, and Ozone.

As the title of the book implies, the authors, whilst sufficiently detailed in their descriptions of technical processes and plant, lay stress on the application of scientific principles and methods, and in this they have been eminently successful. The book is in every respect a model of what a scientific treatise on a technical subject should be. It shows how scientific principles and data can be employed in *calculating* the design, operation, and control of electrochemical processes and plant. Without the understanding and knowledge to think quantitatively and to make correct calculations, there can exist no science and no good practice in industry. The point is worth some emphasis, for, when Professor Allmand's book appeared in 1912, there existed extremely few works in the English language which dealt with any part of technical chemistry in a quantitative and scientific manner.

The present work will certainly appeal to many. The serious University student of physical chemistry will learn from a careful study of it how the science which he is studying can be applied to a great and important branch of industry, and in so doing cannot fail to find that his knowledge of scientific principles will become much more real and secure. For those intending to specialise in electrochemistry, the book is indispensable, and the same may confidently be said of those who are already engaged in electrochemical industries or in any industries which make some use of electrochemical or electrothermal processes. As an instance of that, the reviewer remembers that during the late war a great commercial corporation was searching in two Continents for a copy of Professor Allmand's book. Great was its chagrin to learn that the work was out of print and unobtainable!

F. G. Donnan.

The Theory of Quantitative Analysis and its Practical Application. *By Henry Bassett. 14 × 22 cm; pp. vii + 308. London: George Routledge and Sons. Price: 15 shillings.* As the title suggests, this book deals with quantitative analysis from the physico-chemical standpoint and so is, in a sense, the lineal descendant of Ostwald's "Scientific Foundations of Analytical Chemistry"; but it is nevertheless an entirely fresh and individual exposition of the subject. Most teaching of chemistry is founded on the belief that a practical study of analytical chemistry affords the best introduction to the study of chemistry as a whole; it is an important merit of the book that it must facilitate all such teaching and make it more effective. While it is not intended to be either a complete treatise on quantitative analysis or a textbook of physical chemistry, it presents the physico-chemical *principles* of quantitative analysis in a most thorough and satisfactory manner, and illustrates them by examples drawn from ordinary analytical practice. For these selected determinations precise practical directions are given, together with the reasons for them. The book is not intended for the beginner, but will be most valuable to the serious student and may well afford interest and inspiration to many of us who teach or practice analytical chemistry.

An introductory chapter deals with the essential details of analytical manipulation and is really very good indeed: though quite brief, it should suffice to guide any student of ordinary intelligence into sound and cleanly methods of work. Succeeding chapters deal in turn with: double decomposition; the solubility product; acidimetry and alkalimetry; the theory of indicators; the connection between the solubility of electrolytes and "electro-affinity" or ionic strength; the solubility of salts in acids; the condition of ammonia in aqueous solution; determinations involving precipitation with ammonium phosphate; the significance of colloidal chemistry in quantitative analysis; crystalline, amorphous, and colloidal states of "solid" matter; amphoteric compounds; quantitative precipitations and separations as oxide or hydroxide; hydrolysis; quantitative precipitations by means of hydrogen sulphide; quantitative separations by means of hydrogen sulphide in acid solution; co-ordination and solubility; other analytical aspects of complexion formation; oxidation and reduction. Though these titles give a general idea of the scope of the work, the excellence of their detailed treatment can be appreciated on reading the book; the argument is so closely woven that it is useless to quote from it, and it is everywhere sound and full of inspiration. Though it has adequate author and subject indexes, the book is rather for reading than for reference and being eminently readable should be read as a whole. On every substantial point reference is made to the original literature, but these references are so well chosen that they do not overburden the text and will be most valuable to the student. The text is singularly free from errors and misprints.

Thus it will be clear that the book has two outstanding merits (or are they really one?): that it is an admirable practical statement of the principles of analytical chemistry, and that it gives life and reality to may of the chief principles of physical chemistry. It should be read and re-read by every serious student of chemistry, and it is therefore a pity that the comparatively high price must tend to hinder that general *purchase* of the book by individual students which would so greatly assist their studies. It is true that the paper, printing and binding are good, but they can hardly justify so high a price for a book which merits and should command a wide sale.

H. V. A. Briscoe

The Production and Measurement of Low Pressures. *By F. H. Newman. 23 × 14 cm; pp. 192. London: Ernest Benn, 1925. Price: 16 shillings.* In response to technical demands arising in connexion with incandescent electric lamps, thermionic valves, and X-ray tubes, as well as to the requirements of research laboratories, there has been during recent years an extraordinarily rapid development in the methods available for producing and measuring high vacua. The present excellent and authoritative volume will supply a want which many workers have felt, and will be found of great interest on its theoretical as well as its practical side. After all, the rational basis of many of the devices for the production and measurement of low pressures is to be found in the kinetic theory, and the "mean free path" keeps turning up in all sorts of unexpected directions.

In setting out the methods for the production of low pressures the author deals in succession with oil pumps, mercury pumps, high-speed molecular pumps, and particularly with mercury vapour pumps, which are doubtless the pumps of the future. Subsidiary processes for the removal of gases, such as adsorption by cooled charcoal, and the "clean up" by means of electric discharge or the incandescent filament, also receive attention.

The manometers available for measuring low gas pressures, notably the McLeod and Knudsen gauges, are discussed at length, and the conditions under which each may best be used are set forth. Of importance, especially from the practical point of view, are (1) the chapter dealing with exhaust procedure and the difficult problem of occluded gases and vapours, (2) the appendices, which contain data referring to the vapour pressures of mercury, tungsten, etc, the speeds of various pumps at different pressures, the lowest pressures attained with various processes, and the pressure ranges for different manometers.

One novel feature in the printing of the book, which, in the opinion of the reviewer, is not an improvement, is the commencement of each chapter close to the top of a page. The result is that the eye misses the blank space which usually marks the opening of a new chapter, and there is some difficulty in finding one's whereabouts.

In connexion with the question of units of pressure it is unfortunate that no agreement has been reached as to the definition of the "bar", According to some, the bar is one dyne per sq. cm., and this is the definition adopted by the author, but on the other hand, according to the practice of the British Meteorological Office the bar is 10^6 dynes per sq cm.

J. C. Philip

CALORIFIC VALUE AND CONSTITUTION*

BY MATTHEW FELIX BARKER

The heat of combustion of an organic compound is the algebraic sum of a number of thermal changes accompanying the transformation of the carbon to gaseous carbon dioxide and the hydrogen to gaseous or liquid water, according to the experimental conditions. One of the simplest of combustions is that of solid carbon to gaseous carbon dioxide. The general chemical equation for this change is $[C]_n + nO_2 = nCO_2$ (1)
where $[C]_n$ represents the solid carbon complex.

According to general opinion, before the combustion can take place, the carbon and the oxygen must become dissociated. Both processes require a definite amount of heat, so that in the first instance the combustion is preceded by the two endothermic reactions

$$[C]_n \longrightarrow nC - nq_c \qquad (2)$$

$$nO_2 \longrightarrow 2nO - nq_o \qquad (3)$$

If Q_c denotes the absolute heat of combustion of one gramme atom of carbon to carbon dioxide, then $nC + 2nO = nCO_2 + nQ_c$ (4)
and thus $[C]_n + nO_2 = nCO_2 + n[Q_c - q_c - q_o] = nCO_2 + nQ$
where Q is the observed calorific value of 12 grammes of solid carbon.

Further, if we consider the combustion of the hydrocarbon $[C_aH_b]_n$, where *n* indicates association of the simpler molecules to form a larger unit, it is seen that the process consists of a series of changes with specific thermal values. The first of these is the dissociation of the complex into simpler molecules and then the atomisation of these elementary units. Both processes are endothermic and may be represented as in equations (6) and (7).

$[C_aH_b]_n = nC_aH_b - nq_1$ (6): $nC_aH_b = naC + nbH - nq_2$ (7)

The combustion of (a) atoms of carbon and (b) atoms of hydrogen require $2a + b/2$ atoms of oxygen. Thus $a + b/4$ molecules of oxygen have to become dissociated

$$(a + b/4)\,O_2 = (2a + b/2)\,O - (a + b/4)q_3 \qquad (8)$$

and if

$$C + 2\,O = CO_2 + q_4 \qquad (9)$$

$$2H + O = H_2O + q_5 \qquad (10)$$

then the whole process of the combustion may be stated thus

$$\left.\begin{aligned} [C_aH_b]_n &= nC_aH_b - nq_1 \\ nC_aH_b &= naC + nbH - n(b + a - 1)q_2 \\ n(a + b/4)O_2 &= n(2a + b/2)O - n(a + b/4)q_3 \\ anC + 2anO &= anCO_2 + anq_4 \\ bnH + bn/2\,O &= 1/2\,bnH_2O + bnq_5 \end{aligned}\right\} \qquad (11)$$

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* Thesis approved for the degree of Doctor of Philosophy in the University of London—External.

so that the thermal equation representing the complete combustion of the molecule $[C_aH_b]_n$ is $[C_aH_b]_n + n(a + b/4)O_2 = naCO_2 + 1/2\ bn\ H_2O + anq_4 + bnq_5 - nq_1 - n(b + a - 1)q_2 - n(a+b/4)q_3$ (12) where q_1 is the heat necessary to release one simple molecule from the more complex unit; q_2 the heat necessary to produce a scission of any two atoms in the molecule C_aH_b, and q_3 the heat required to dissociate one molecule of oxygen into its atoms. q_4 and q_5 are respectively the thermal effects due to the combination of an atom of carbon with two atoms of oxygen and of two atoms of hydrogen with one atom of oxygen to form gaseous carbon dioxide and liquid water at the temperature of observation.

Since equation (12) is a true energy relationship, then the total amount of heat represented on the left hand side is the difference between the total energies of equal quantities of matter, and consequently it follows that the heat of combustion is an additive function of the chemical and physical constitution of the molecule undergoing the combustion. For simplification of the argument the value of the heats of combustion of like atoms has been taken as being equal to each other. Actual experimental results point to the contrary. This does not affect the above generalisation but rather emphasises the connection between the heat of combustion and the constitution of the molecule. From this consideration it appears that a much better interpretation of results may be effected, if, instead of endeavouring to obtain a mathematical formula to express results, the contributions of the various atoms are calculated and their variations correlated with differences in constitution.

The study of the heats of combustion of members of homologous series has shown that the contribution of the additional CH_2 group varies only between narrow limits. The variations are larger than those which would arise solely from experimental error, yet in spite of this, the contribution of the CH_2 group has been considered by various workers as a constant. Notably with regard to the aliphatic hydrocarbons various formulae have been put forward consisting of simple linear functions. Upon this basis, Gomez[1] deduced the following expressions for the various series as indicated below

Paraffin Hydrocarbons	$157\,n + 55$
Olefine ”	$157\,n + 28$
Acetylene ”	$157\,n + 2$
Di-olefine ”	$157\,n - 39$
Di-acetylene ”	$157\,n - 91$

The number 157 is apparently the value assigned to the contribution of each CH_2 group. The purely numerical term may be calculated from the equation $H = 157\,n + A$ where H is the molecular heat of combustion and n the number of carbon atoms in the hydrocarbon. According to these expressions the molecular calorific values are simple functions of the value for the CH_2 group. If the hydrocarbon is unsaturated, H is not, however, entirely a function of the value for the CH_2 group but of $(x - 2n)CH_2 + 2nC$ where 2n is

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[1] Anal. Fis. Quim. **10**, 153-166 (1912).

the number of carbon atoms concerned in the formation of multiple bonds. Lemoult[1] deduces similar formulae for the calculation of the heats of combustion of saturated acids, their esters and anhydrides. He concludes from his calculations that the calorific values for the substances considered may be connected by the equation $\gamma = 157x + A$ where γ = the heat of combustion of the compound; x = the number of carbon atoms present in the compound and A is a constant. This is obviously the same as $H = 157n + A$ previously uqoted in connection with the results arrived at by Gomez. In the second paper, by Lemoult, the heat of combustion of a hydrocarbon C_xH_y, is assumed to be given by the expression $Ax + By$ and from the heats of combustion of the saturated hydrocarbons $A = 102$ and $B = 27.5$. Hence the expression becomes $102x + 27.5y$ and this equals the γ of the equation $\gamma = 157x + A$. For saturated hydrocarbons $y = 2x + 2$, so that $\gamma = 102x + 27.5(2x + 2) = 156x + 54$ which is almost identical with the relationship put forward by Gomez.

Although, these expressions give calculated values agreeing satisfactorily with the observed results, yet as regards the correlation between calorific value and constitution they are of little importance since they have been deduced mainly statistically.

Thomsen[2] puts forward an expression derived from more detailed considerations than those of Gomez and Lemoult. The different heat effects of the various carbon to carbon linkages are taken into account. He does not, however, consider the possibility that like atoms may have different contributions to the heat of combustion in consequence of their different relative positions in the molecule, as for instance in straight chain compounds. The constants in Thomsen's relationship are arrived at by interpolation of the observed values of the molecular heats of combustion and the expression for the paraffin series reduces to $105.9x + 26.2y$ (cf. Lemoult: loc. cit.).

Prior to these deductions by Gomez, Lemoult and Thomsen, there appeared, in a paper entitled "A Thermochemical Constant" by F. W. Clarke[3] a deduction which at first appears to be of importance but unfortunately it was arrived at by the assumption of a number of numerical and purely arbitrary constants. The relationship put forward was the following

$$\frac{4K}{12a + 6b - c - 8n} = \text{constant} \qquad (13)$$

where K is the molecular heat of combustion; *a* is the number of molecules of carbon dioxide produced; *b* is the number of molecules of water produced; c is the number of molecules of oxygen dissociated and *n* equals the number of atomic unions in the compound burnt.

The average value of the constant for a number of hydro-carbons including several containing the double link is 13873. This number approximates to

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[1] Compt. rend. 137, 656-658, 979-982 (1903).
[2] Z. physik. Chem. 51, 657 (1905).
[3] J. Am. Chem. Soc. 24, 882 (1902).

the value for the heats of neutralisation of strong acids and bases and the round figure, 13800 is brought forward as a unit quantity of heat and termed the henotherm.

The "law" has been severely criticised by Noyes[1] and Thomsen[2]. The scepticism regarding this relationship is well illustrated by the following extract from the review by Noyes; "Whether these empirical formulae are merely mathematical fictions or whether the author has succeeded in bringing to light real theoretical relationships can be fully established only by an exhaustive study of the question, whether the close agreement between calculated and observed heat effects could have arisen solely through the arbitrariness of the choice of even integral numbers of henotherms to represent the various elementary heat effects." In the above paper by Thomsen, it is shown that the relationship is by no means general and he emphatically declares that this empirical law is of no value.

A similar conclusion may be arrived at by a detailed examination of the relationship as expressed in equation 13. The divisor $12a + 6b + c - 8n$ is obviously a simple linear function of composition, for if we consider the case of the saturated hydrocarbons C_xH_{2x+2} then

$$a = 4X$$
$$b = 4X + 4$$
$$c = 6X + 2$$
$$n = 3X + 1 \quad \text{so that}$$

$12a + 6b + c - 8n = 42X + 14$ and thus $\frac{4K}{42X + 14} = \text{const.}$

For any series, X increases in arithmetical progression and the difference between any two consecutive values is one. If K_1 and K_2 be the calorific values of two consecutive members of a series then $\frac{K1}{42X+14} = \frac{K2}{42(X+1)+14}$ and therefore $K_2 - K_1 = 42 \times \text{constant}$. Hence to fulfill Clarke's "Law" $K_2 - K_1$ must be constant. For any homologous series the expression formulated by Clarke may be written $\frac{4K}{mx + n} = \text{constant}$, from which it follows that $K_2 - K_1 = \{m(x + 1) + n - mx - n\} \times \text{const.}$

$$= m \times \text{const.}$$

Whatever values be given to the coefficients in the original expression from which this is derived, *m* will have a specific value. Since $K_2 - K_1$ approximates to constancy, the quotient $\frac{K_2 - K_1}{m}$ will also be correspondingly constant but its value will be entirely dependent upon the arbitrary values given to the coefficients of *a*, *b*, *c* and *n* in the original expression. Thus the significance of the value 13800 for the constant disappears. Further, the relationship necessitates that $K_2 - K_1$ is constant for all series, which is contrary to experimental fact.

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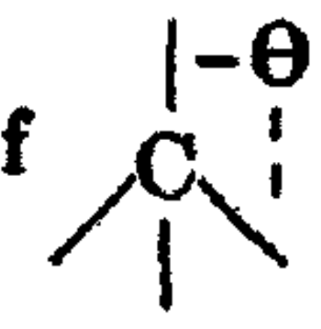
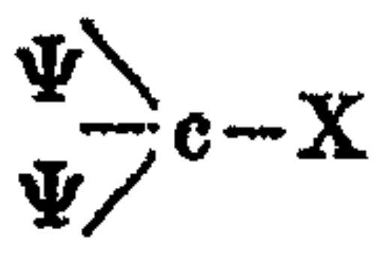
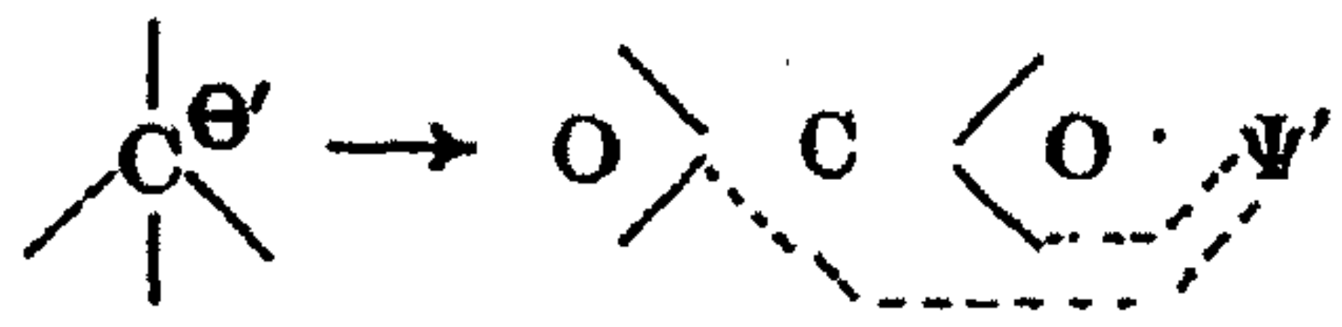
[1] J. Am. Chem. Soc. 25, 156r (1903).

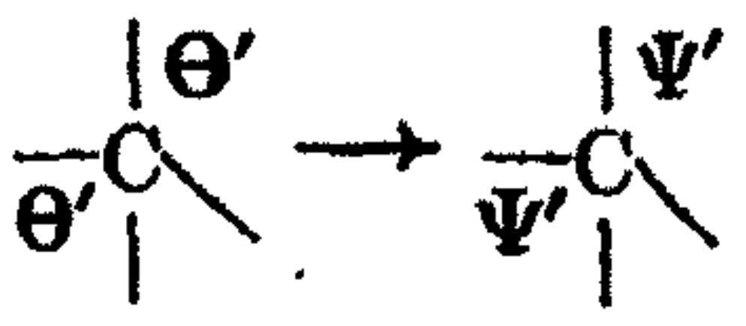
[2] Z. physik. Chem. 47, 487-493 (1903).

The formulae derived by Thomsen for the calculation of the heats of combustion are based upon more detailed considerations than those of the investigators previously considered. For the hydrocarbons the fundamental equation used is $C_aH_{2b} = ax + 2by - \Sigma v$ where x is the contribution of each carbon atom, y the contribution of each hydrogen atom and Σv indicates the summation of the heat effects due to the carbon to carbon unions. When the carbon atoms are united by only single bonds, the number of these linkages is $2a - b$ and if the thermal effect due to one single bond is v_1 then

$$C_aH_{2b} = a(x - 2v_1) + b(2y + v_1) = aA + bB$$

In this equation the contribution for each carbon atom as well as for each hydrogen atom has been assumed to be constant. It will be shown later that the contribution of each hydrogen atom may be taken as constant, but from the following considerations this is not so with respect to the carbon atom. Ethane may be considered as the product obtained by the substitution of the CH_3 group for one hydrogen atom in methane. This means that a group of relatively large atomic volume is introduced into the hitherto perfectly symmetrical methane molecule. This introduction will necessitate a rearrangement of the relative positions of the hydrogen atoms. Since for perfect symmetry the angle between the directions of the bonds in the normal tetrahedral position is a maximum, any distortion will result in the valencies being separated by a less angle than hitherto. Thus if  represents Methane, then after substitution the three remaining valencies will be inclined to each other at an angle Ψ thus  where Ψ is less than Θ. The heat of combustion of a carbon atom in an organic compound is partly dependent upon the angles Θ′ and Ψ′ as designated below.



Thus the heat absorbed during the transformation  will be a function of $\Theta' - \Psi'$ and since Θ is greater than Ψ, the heat lost from this cause in the case of methane is greater than that due to the same cause with respect to the calorific value of ethane. It follows therefore, that the contribution of each of the carbon atoms in ethane is greater than the calorific value of the carbon atom in methane. Further it would appear that the nearer Θ′ approaches to Ψ′ the greater is the calorific value of the carbon atom. This variability of the contribution of the carbon atom to the molecular calorific value is emphatically indicated by the observed values for the cyclic hydrocarbons of the paraffin series and also for the benzenoid hydrocarbons and it will be shown later that the calorific value of the carbon atom increases as the angle Θ' diminishes. Obviously this is of the utmost importance regarding the correlation of the calculated values with the observed results and it is the neglect of such theoretical possibilities as these that has given rise to the numerous mathematical relationships that have been formulated from time to time purporting to connect calorific values and the constitution of organic compounds.

The apparatus employed, was the Mahler-Kroeker modification of the Berthelot bomb. The combustions were carried out with pure oxygen at pressures varying between twenty and thirty atmospheres. For comparison, the results of other observers are quoted side by side with those obtained for the purposes of this investigation. Determinations were made mainly for those compounds the calorific values of which are relevant to the subsequent discussion.

Benzene	783.4	782.3	(Auwers and Roth.)
		781.1	(Davis and Richards.)
Toluene	941.3	934.2	(Davis and Richards.)
		935.2	(Auwers and Roth.)
Xylene	1091.3	1084.0	(Auwers and Roth.)
		1089.5	(" ")
Naphthalene	1238.0	1230.6	(Davis and Richards.)
		1235.2	(Auwers and Roth.)
Di-phenyl	1500.0	1492.	(Auwers, Roth and Eisenlohr.)
Phenol	733.0	732.3	(Stohmann and Langbein.)
		734.6	(Berthelot and Luginin.)
Cresol (ortho)	883.7	883.5	(Stohmann, Rodatz and Herzberg.)
Cresol (para)	885.0	883.4	(" " ")
Cresol (meta)	883.0	880.5	(" " ")
Benzyl Alcohol	890.0	895.8	(" " ")
Pyrogallol	618.1		
Di-hydroxy benzene (ortho)	684.9	685.5	(Stohmann and Langbein.)
Di-hydroxy benzene (meta)	683.9	683.7	(" ")
Di-hydroxy benzene (para)	684.7	685.9	(Berthelot and Luginin.)
		683.6	(Stohmann and Langbein.)
Benzoin	1670.8	1672.0	(Stohmann, Kleber and Langbein.)
Benzil	1621.6	1625.3	(" " ")
Furoin	1114.0	1097.7	(Wrede.)
Furil	1064.4		
Lepidene	3288.4		
p-Nitro acetyl Benzoin	1864.3		
p-Nitro Benzil	1600.9		
p-Nitro benzoyl Benzoin	2443.4		

Calorific Values of the Carbonyl and Hydroxyl Groups

The values of these groups were deduced from the determinations of the calorific values for (1) Di-phenyl, (2) Benzil and (3) Benzoin. The subtraction of the value for (1) from the value for (2) gives 121400 calories which should be equal to the heat given out during the oxidation of the portion of the benzil molecule represented by $\begin{array}{c}-\mathrm{CO}\\ |\\ -\mathrm{CO}\end{array}$ so that one half of this figure should approximate to the thermal effect accompanying the oxidation of the carbonyl group in an organic compound. Thus $CO + O = CO_2 + 60.7$ kilogramme calories. By using this result in conjunction with the calorific value for di-phenyl and substituting in the equation for the combustion of benzoin, the value for the hydroxyl group is deduced, taking into account that in this case one hydrogen atom will unite with one hydroxyl group. This gives the number 12.9 kilogramme for the thermal effect of the combination of one hydrogen atom with one hydroxyl group to form one molecule of water. This result is, approximately, numerically equal to the value obtained for the heat of neutralisation of strong acids and bases.

Calorific Value of Aliphatic Hydrocarbons

(a) *Saturated Hydrocarbons.*

Referring to equation 12, when $n = 1$ then $q_1 = O$, so that $C_aH_b + (a+b/4)O_2 = aCO_2+b/2\ H_2O+aq_4+bq_5-(b+a-1)q_2-(a+b/4)q_3$ where according to the view previously expressed with regard to the variability of the contribution of the carbon atom, q_4 is the mean absolute heat of combustion of the carbon atoms set free from the compound. For the total of 'a' atoms the actual contribution will be $aq_4-aq_3-2aq_2$ and for 'b' hydrogen atoms the contribution will be $bq_5 - \frac{bq_2}{2} - \frac{bq_3}{4}$. Thus if C is the mean nett heat given out by the combustion of a carbon atom in the above compound and H the heat given out by one hydrogen atom, then the heat of combustion may be written as $a\,C + bH$. From X-ray determinations the structure of the free carbon molecule appears to be similar to that of the benzoid carbon complex hence the value of C will be quite different from that for the molecular calorific value of elementary carbon. On the other hand the mode of the combustion of diatomic hydrogen to water exhibits a similarity to the combustion of the hydrogen in a hydrocarbon. The process in both instances is preceded by the scission of an elementary bond equivalent to a unit of valency and hence should be thermally equal to each other. The value of H therefore in the equation $aC + bH = K$ is that of one gramme of gaseous hydrogen burning to water. Further, it implies that the calorific value of the hydrogen in an organic compound is constant and the same for all compounds. In the above equation K (observed calorific value), H, *a* and *b* are known; thus the value of C may be calculated. This assumption regarding the contribution of the hydrogen atom is upheld by the figure for the molecular calorific value of formaldehyde, (130000 calories). The value already deduced for the carbonyl group is 60700, hence the value for the two hydrogen atoms in formaldehyde should be the difference of these two figures which equals 69300. The usually accepted value is that of 68920 (by Thomsen). It would appear then that there is adequate foundation for the assumption that the heat of combustion of a hydrogen atom in situ is the same as, or very nearly so, as that of gaseous hydrogen and that it may be taken as a satisfactory basis for the calculation of the molecular heats of combustion of organic compounds or their component atoms.

According to Thomsen, the molecular calorific value of methane is 210.9. This appears to be the generally accepted value and the one used by various investigators when considering methods for the calculation of molecular calorific values. Determinations carried out by Berthelot gave the figure 213.5. Putting these values in the equation $aC + b34460 = K$ the values deduced for C are 73.9 and 75.5 kilogramme calories per gramme molecule of carbon, respectively. The higher figure is, probably more correct, so that this latter value may be taken as the heat of combustion of a normal carbon atom the valencies of which are directed towards the corners of a regular tetrahedron. The substitution of the CH_3 group for one hydrogen atom in methane causes an increase in the molecular calorific value of 159.6 kilogramme calories. The theoretical contribution of the carbon atom of this group is therefore $159.6 - 68.9 = 90.7$. Since there is no reason for doubting that ethane has a symmetrical structure, the two carbon atoms in the ethane molecule have the same calorific value. Thus the contribution of the original methane carbon has increased and is equal to $\frac{(90.7 + 75.5)}{2}$ i. e., 83.1. Calculated direct from ethane it is 82.6. Allowing for the lower number of hydrogen atoms the molecule of a cyclic hydrocarbon of the paraffin series has a higher calorific value than that of the straight chain compound of an equal number of carbon atoms. It seems therefore highly probable that the angle between the valency bonds has a considerable effect upon the calorific value of the atom. A decrease in this angle causes, apparently, an increase in the calorific value of the atom. Thus in ascending from methane to ethane the bonds of the carbon have become displaced and do not point exactly towards the corners of a regular tetrahedron. As the number of carbon atoms increases, the effect of the additional CH_3 group diminishes. This is shown by the following results for straight chain and cyclic paraffins. The calorific values for the carbon atoms have been calculated as already indicated. It is noteworthy that the two series of values appear to converge to the same figure. This would also follow from the fact that as the number of the carbon atoms in the cyclic molecule increases, the disposition of any two consecutive atoms approaches more nearly to that existing in a straight chain molecule.

Hydrocarbon	Calorific value of the Carbon	Hydrocarbon	Calorific value of the Carbon.
Methane	75.5	Cyclo-propane	97.8
Ethane	82.6	Cyclo-pentane	88.6
Propane	84.2	Cyclo-hexane	88.2
Butane	85.5	Cyclo-heptane	87.6
Hexane	85.8		
Heptane	85.8		

From the previous argument it should follow that when the four hydrogen atoms of methane have all become replaced by the same kind of group then the central atom should have the same contribution to the calorific value as the original methane carbon, for, presumably, the molecule is again perfectly symmetrical and hence the direction of the four bonds of the central carbon atom are the same as those indicated by the tetrahedral representation. That this is so is shown by the value for tetra-methyl methane (847.1 Thomsen.) The mean increment for each additional CH_2 group is 158.8 so that the contribution of the central carbon atom is given by $847.1 - 4 \times 158.8 - 4 \times 34.46 = 75.1$ (cf. calculated value in the preceding table).

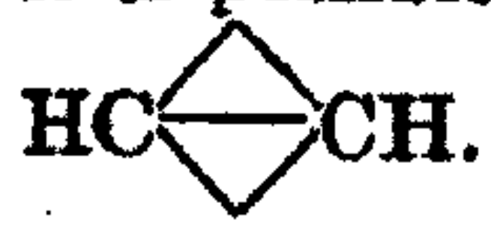
(b) *Aliphatic Hydrocarbons containing doubly linked Carbon Atoms.*

Although the ethylene molecule contains two hydrogen atoms less than the ethane molecule, yet the calorific value is only diminished by approximately 37 kilo-gramme calories. The increase in the molecular calorific value for the additional CH_2 group is of the same order of magnitude for this series as for the saturated hydrocarbons and for homologous series in general. These facts suggest that the carbon atoms concerned with the ethenoid linkage have a considerably higher contribution to the calorific value than the saturated atom. The molecular calorific value of ethylene has been determined by various investigators. The result are surprisingly discordant; there is nearly 4% difference between the highest and the lowest figures. The principle values are 333.4 (Thomsen), 341.1 (Berthelot) and 345.8 (Mixter). Merely upon the grounds that in any heat determination the higher results are most probably the more accurate, provided that the necessary precautions have been taken against radiation, the result of Mixter has the premier claim to correctness. On the other hand this high result and also the lower one of Berthelot causes an abnormality in the increment for the CH_2 group for the series ethylene, propylene and iso-butylene and iso-amylene.

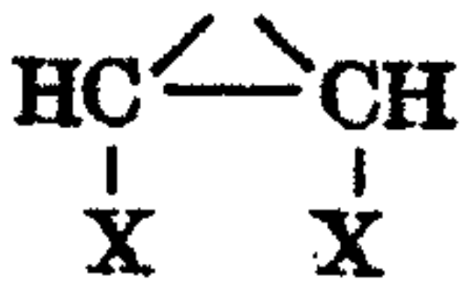
Proceeding on similar lines as in the case of the saturated hydrocarbons, the contribution of the 'ethylene' carbon is obtained from the equation $2\,C + 4\,H = 333.4$. Thus $(\text{—C : C—}) \longrightarrow CO_2 + 97.7$ kilo-gramme calories. Using the highest value for ethylene the number is 103.9. It is noteworthy that these results are of the same order of magnitude as the value obtained for the combustion of elementary carbon. Further, considering the hydrocarbon trimethylene, which presumably consists of three carbon atoms in a ring and united by valency bonds inclined to each other at an angle of 60°, it is significant that the value obtained for one carbon atom of this ring is 97.5.

This suggests that the valency directions in an unsaturated doubly linked atom are inclined to each other at an angle of 60° also, or at any rate approximating thereto. Thus ethylene would be represented by $H_2C\triangle CH_2$ which indicates that the unsaturated affinities form a closed triangle of force. The reactivity of such an arrangement is readily accounted for by the opening of this triangle thus H_2CCH_2 and hence the ability to combine with a further quantity of matter through the medium of these two freed valencies. For the series ethylene to iso-amylene the calculated value for the unsaturated carbon atom varies only between the following values 97.7 and 98.3 kilogramme calories per gramme molecule. The mean increment for the CH_2 group for this series is 157.4. The calculated value for ethylene from the molecular calorific value of propylene is therefore 335.3, which is in good agreement with the value found by Thomsen. Since the increment for CH_2 is, although not constant, yet always of the same order of magnitude, the acceptance of the higher value found by Mixter would provide an interesting abnormality. This latter value would give 146.9 for the increment ethylene —propylene, which is 11.0 kilo-gramme calories below the mean value of the increment for thirteen different series. It is obvious that Thomsen's value has much in its favour and must be credited with the greater accuracy until substantial evidence is brought forward to the contrary.

(c). *Aliphatic Hydrocarbons containing trebly linked Carbon Atoms.*

The molecular calorific value of acetylene is 310.0 (Thomsen). Here again the figure is higher than the value which would result if the allowance is made merely for the decrease in the hydrogen content of the molecule. Thus it appears that trebly linked carbon has a still higher molecular calorific value than even 'ethenoid' carbon. The value calculated from acetylene is 120.5, and from allylene it is 120.3. From di-propargyl the value deduced is somewhat higher; i. e., 124.5. Although the results for the contribution of trebly linked carbon are rather limited in numbers, yet there is sufficient evidence that such an atom has quite a large molecular calorific value. Further, with regard to the disposition of the three bonds forming the treble link, it is possible that it is made up of two closed triangles of valency, thus . The reactivity, would, by similar argument to that for the ethylenes, be occasioned by the opening of the triangles of force giving successive pairs of freed valencies as indicated by the following

(a) 

(b) 

Aromatic Hydrocarbons

(1) *No Side Chains.*

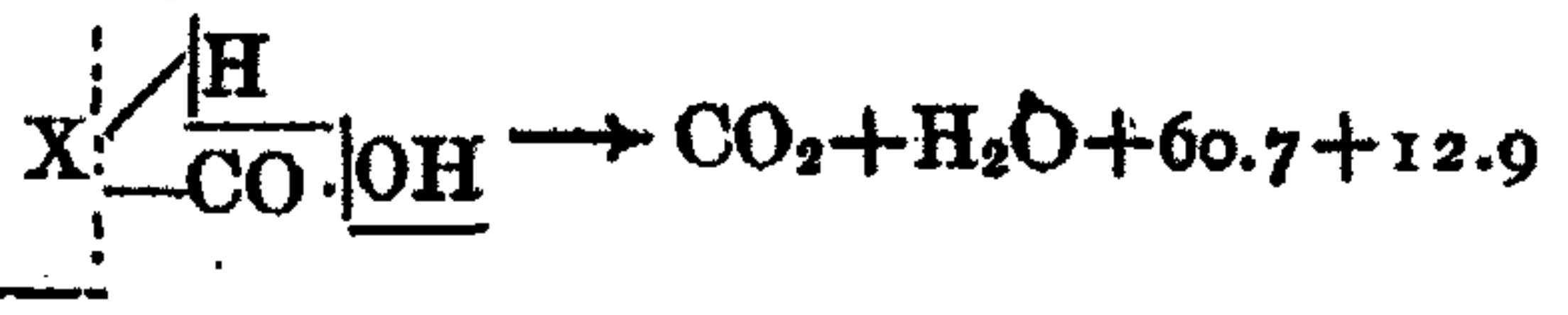
The values for the calorific value of the carbon were obtained by subtracting the contribution of the hydrogen atoms from the observed calorific values and dividing by the number of carbon atoms in the compound. The figures are satisfactorily constant and show a favourable agreement with the result for elementary carbon. This indicates a similarity between the carbon skeletons of the hydrocarbons under discussion and that of the carbon complex in graphite. This similarity has been pointed out by Debye and Scherrer[1] and Hull[2], who have shown by X-ray analysis that the structure of the graphite molecule is similar to that of the benzenoid carbon complex. The values of the carbon deduced by the method indicated above were benzene (96.1); naphthalene (96.2); anthracene (96.3); phenanthracene (96.3) and di-phenyl (96.3) from which it follows that the calorific values of these hydrocarbons may be expressed with fair accuracy by the simple formula 96.96 X + 34.46 Y, where 96.96 is the molecular calorific value of carbon and 34.46 is the heat given out by the combustion of one gramme of hydrogen to liquid water. X is the number of carbon atoms in the molecule and Y the number of hydrogen atoms in the compound. The result will be given in kilo-gramme calories.

(2) *Saturated Side Chains.*

Similar calculations for toluene and xylene gave large discrepancies. It is significant that the difference in the case of xylene, which has two side chains, is approximately twice that in the case of toluene which has only one side chain. The values of these differences are 29.0 and 13.7 respectively. This suggests that the discrepancy is due to the contribution of the side chain carbon. It would appear that this carbon has a contribution of (13.7 + 29.0)/3 = 14.1 kilo-gramme calories less than that of the benzene carbon. Further, the results for these homologues afford evidence of the similarity of the carbon to carbon linkage, and the carbon to hydrogen linkage. The value for di-benzyl given by Auwers, Roth and Eisenlohr[3] is 1809.3. Using the value for the side chain deduced above, (viz. 96.96 - 14.1 = 82.9) the calculated value is 1812.3. One half of this figure is 906.1. Thus the group $C_6H_5CH_2$—has a calorific value of 906.1 kilo-gramme calories when united to carbon. If the linkage of carbon to carbon is equal to that of carbon to hydrogen, then the calorific value of toluene should be given by the summation of the heats of combustion of the benzyl group and one equivalent of hydrogen, that is 906.1 + 34.5 = 940.6 (observed value, 941.3). This equality is also shown by the values for benzene and di-phenyl. The calculated value for di-phenyl using the observed result for benzene is 2(783.4 − 34.5) = 1497.8 (observed value 1500.0).

Carboxylic Acids

Considering the accepted constitution of the carboxylic acids it would appear that the carboxyl group would burn in conjunction with an atom of hydrogen from the hydrocarbon residue.



$$X\left\langle\begin{matrix}H\\ CO\cdot OH\end{matrix}\right. \longrightarrow CO_2+H_2O+60.7+12.9$$

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[1] Physik. Z. 17, 277 (1916).

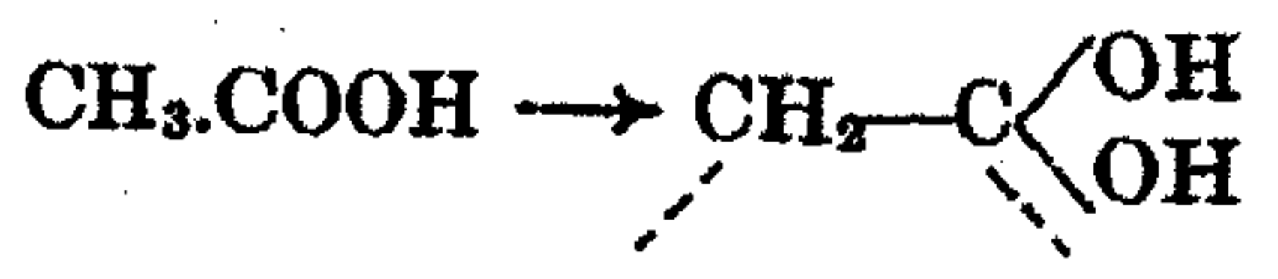
[2] Phys. Rev. (2) 10, 661 (1917).

[3] Liebig's Ann. 378, 278 (1910).

The molecular calorific value of various acids were calculated according to this scheme. To arrive at the contribution of the carbon of the hydrocarbon residue, the value for the carbon in the hydro-carbon of an equal number of carbon atoms was used. Thus for acetic acid the value used for the carbon in the expression $C + H_3 + (H + OH) + (CO + O)$ is that for ethane. The differences between the observed and the calculated are very large and suggest that the constitution of the molecules of these compounds are not represented by the usual simple formulae.

Acid	Molecular Calorific Values Observed	Calculated	Differences.
Formic	59.0	73.6	14.6
Acetic	206.7	225.2	18.5
Propionic	364.0	380.0	16.0
Butyric	520.4	537.4	17.0
Valeric	677.4	692.8	15.4
Malonic	207.5	231.4	23.9
Succinic	360.3	387.2	26.9
Glutaric	515.0	542.6	27.6
Adipic	668.9	697.4	28.5
Benzoic	771.7	788.0	16.3
Phthalic	771.6	792.6	21.0

These differences seem to have a definite significance. They are approximately twice the value for the di-carboxylic acids than for the mono-basic acids. It is likely therefore that these differences are due to some abnormality connected with the carboxyl group. It must be borne in mind that whereas the hydrocarbons have practically normal molecular weights the carboxylic acids show varying degrees of association. If we assume that such complexes depend for their existence upon some diverted valency energy, then a possible arrangement which suggests itself and which gives rise to the necessary conditions would result from a transference of hydrogen from the hydrocarbon residue to the carboxyl group thus



$$CH_3.COOH \longrightarrow CH_2{-}C\begin{matrix}OH\\OH\end{matrix}$$

If a similar unit becomes so placed that these freed valencies may cooperate, then contact between molecule and molecule will be established. For acetic acid the association number given by Ramsay and Shields[1] is 3.6. Since any such figure is merely a mean complexity number for a mass of the substance under the conditions of observation we will consider the molecule of complexity 4. This will be made up of four units of the type shown above,

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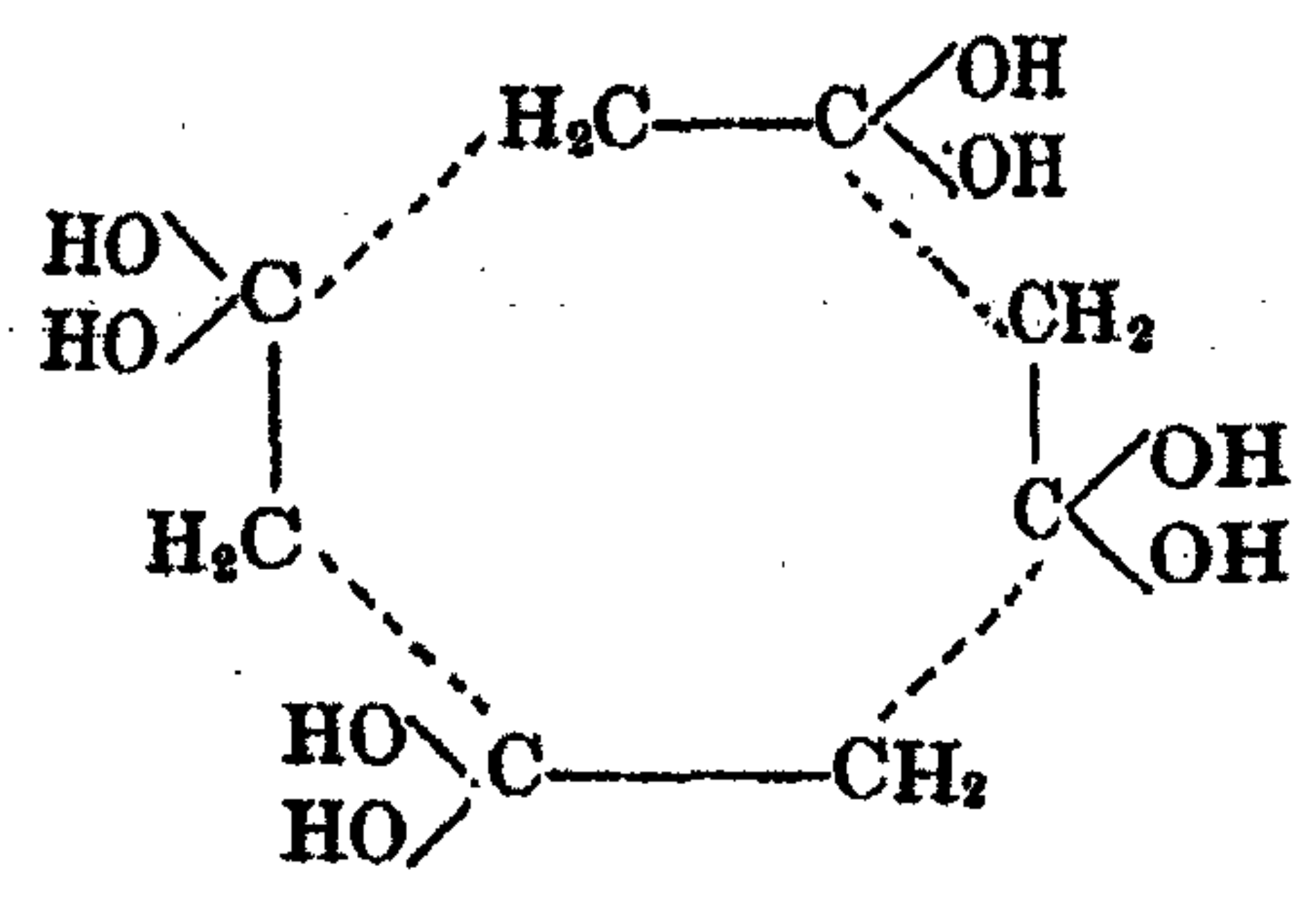
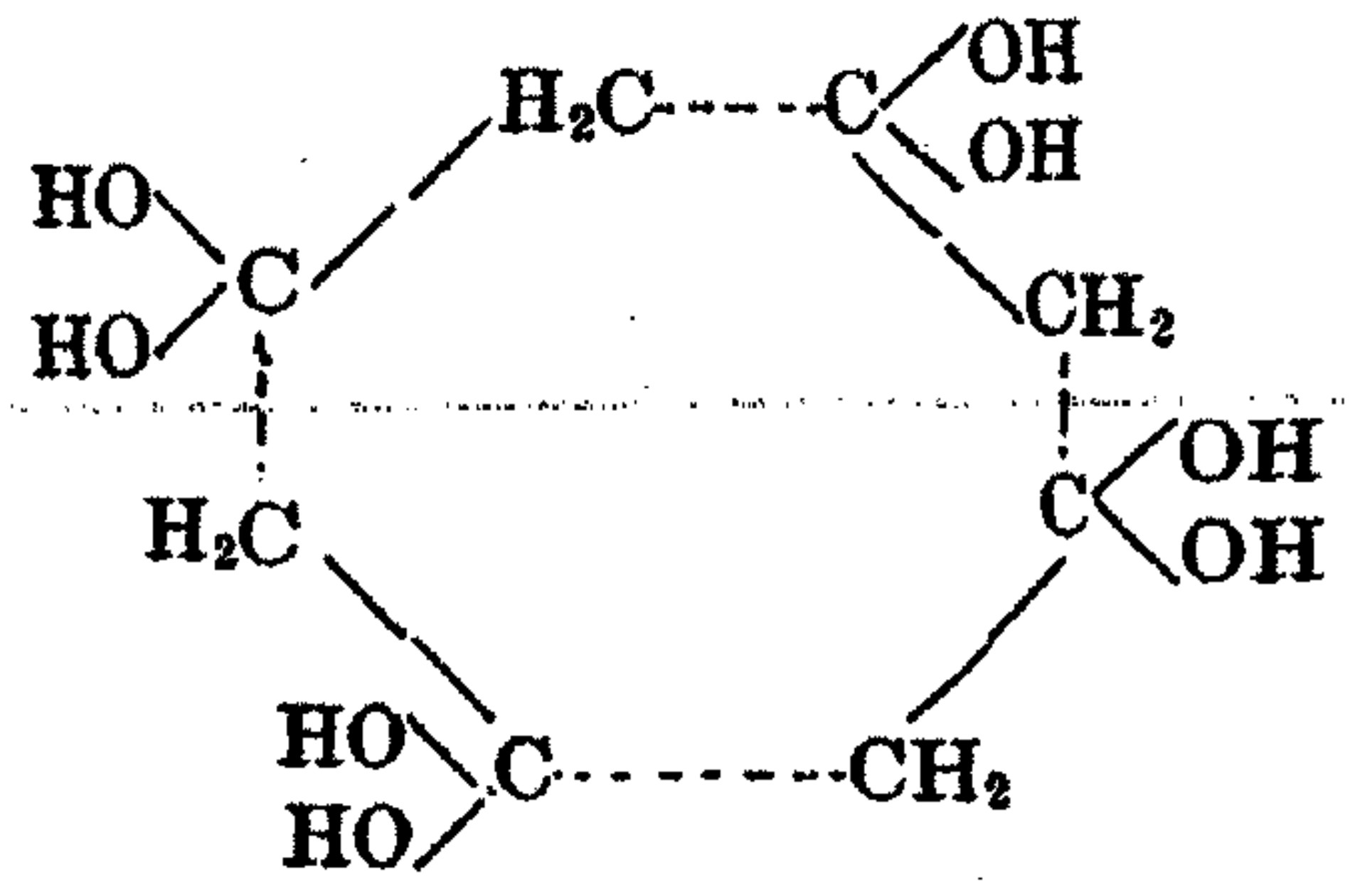
[1] J. Chem. Soc. 63, 1089 (1893).

(A)



the carbons forming an eight membered ring. If this is considered as an oscillatory system the next phase would be

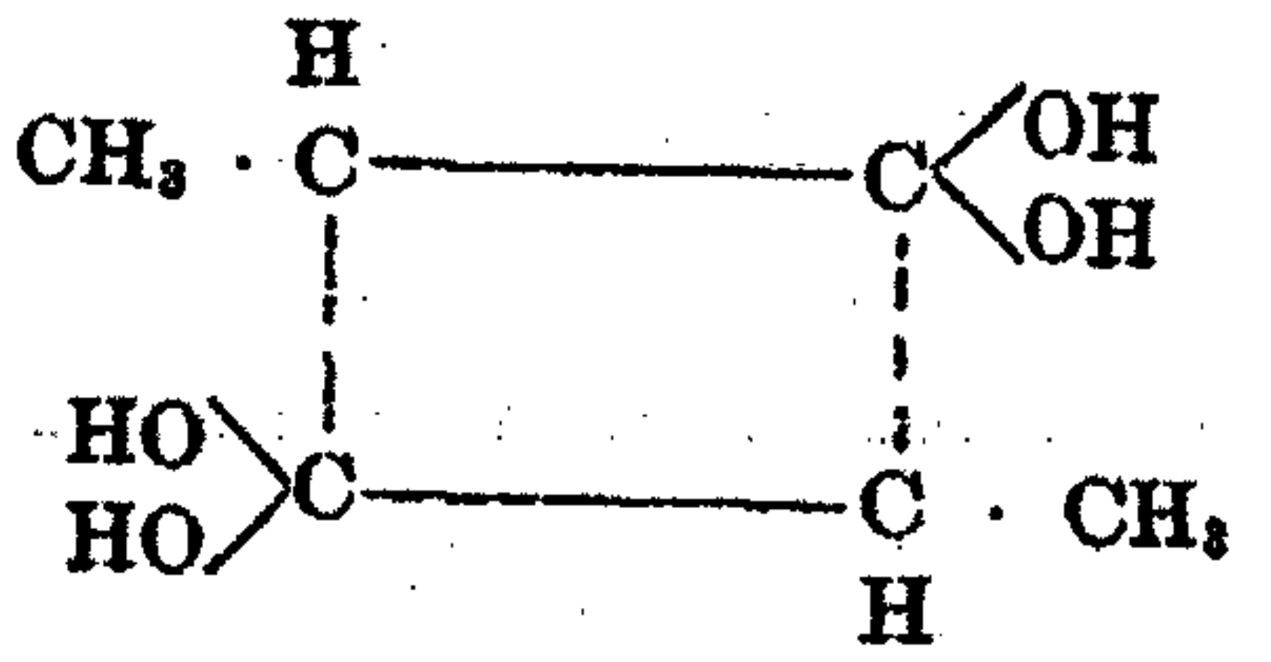


This is identical with that shown in (A). Any carbon atom in the above arrangements is attached to mono-valent groups and is to a great extent comparable to the carbons in the cyclo-paraffins. Thus the calorific value of such a carbon in the acetic acid complex would approximate to 87.6, and for one molecular proportion of acetic acid the calorific value calculated upon these assumptions is 201.0. For the association of three molecules the calculated result is 202.3. These figures are 5.6 and 4.4 kilogramme calories less than the observed value, but nevertheless are much nearer the actual result than that obtained by the original method of calculation.

A fact that supports this view that the association of the molecules is responsible for the discrepancies between the observed and the calculated values obtained from the ordinary formulae, is, that the calorific values of the vapour of the acids agree fairly satisfactorily with the calculated results obtained in the first instance.

Acid	Molecular Calorific Values		
	Vapour at B. Pt.	Gas at 18°C	Calculated
Formic	70.75	69.4	73.6
Acetic	227.6	225.3	225.2
Propionic	390.1	386.5	380.0

In the case of propionic acid the association number is 1.77. Thus suggests that a large proportion of the molecules consist of the di-complex

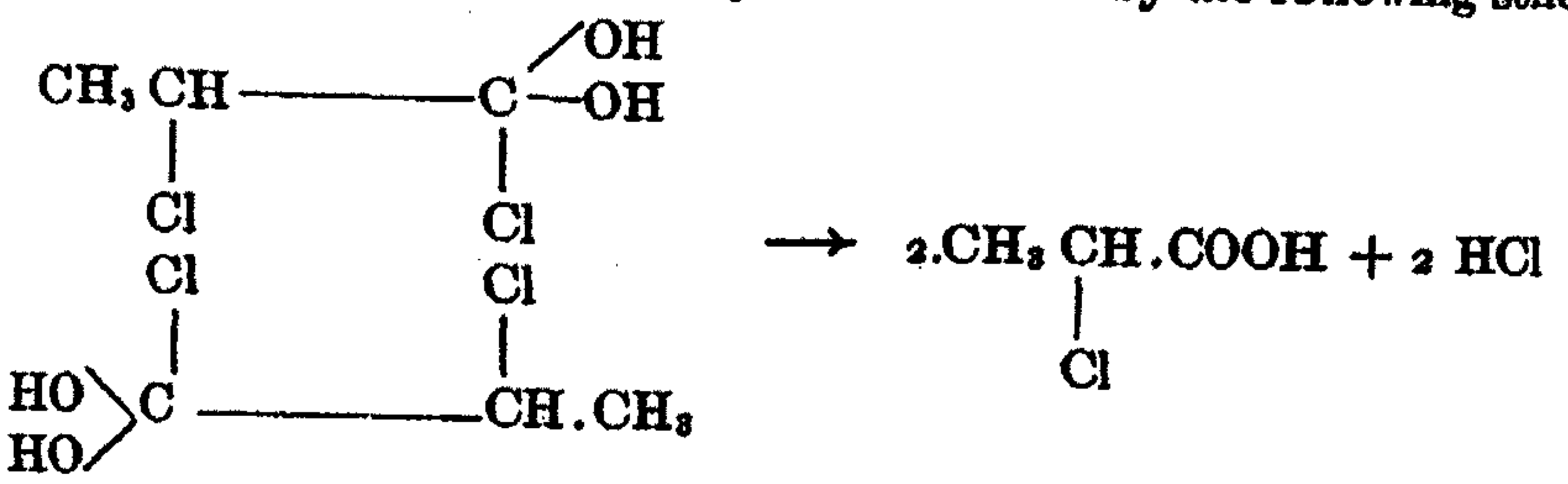


The calculated value is therefore given by the expression $2C + (CH_2) + 2(H + OH)$ which should be equal to 364.1, the observed value. The calculated value of the carbon atom in the four membered ring was calculated from the relationship between the calorific value of a carbon atom and the number of carbon atom in a cyclo-paraffin. This relationship is given by the equation $Y = 166.45 - 39.45x + 6.65x^2 - 0.375x^3$ where Y is the calorific value of the carbon, and x the number of the carbon atoms in the cyclo-paraffin. When $x = 4$, $Y = 91.0$, so that the calculated value for heat of combustion of one gramme molecular quantity of propionic acid is 360.9 (c. f. with the observed value quoted above). Butyric acid has the association number 1.71. The calculated value for the double molecule is 516.6 and the observed value is 520.4.

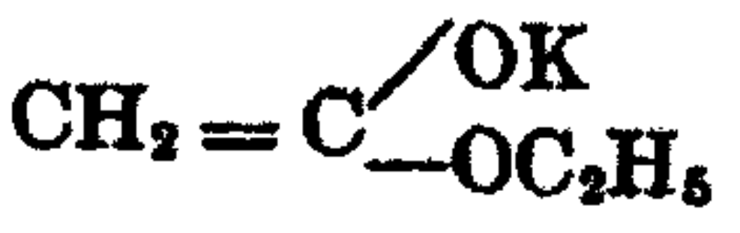
This idea regarding association is not in opposition to the well known fact that substitution takes place initially in the carbon next to the 'carboxylic' group. Also the formation of a mono-halogenated derivative takes place much more readily than the formation of the higher halogenated acids. In the case of acetic acid the attack of the halogen, for instance chlorine, on the complex, results in the formation of four molecules of the unstable di-chloro compound

$\mathrm{Cl.CH_2 - C \begin{matrix} \diagup OH \\ -OH \\ \diagdown Cl. \end{matrix}}$

From this, hydrochloric acid readily splits off leaving mono-chloracetic acid. Similarly, in the case of propionic acid the chlorination would take place as indicted by the following scheme.



The existence of the di-hydroxylic molecule is also indicated by the production of a potassium derivative of ethyl acetate. In a recent communication, Scheibler, Zeigner and Peffer[1] show that the action of potassium on ethyl acetate in ethereal solution leads to the formation of



$\mathrm{CH_2 = C \begin{matrix} \diagup OK \\ \diagdown OC_2H_5 \end{matrix}}$

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[1] Ber. 55B, 3921-3931 (1922).

The Calorific Value of the Aldehyde Group

The calorific values of the aldehydes show that the contribution of the aldehyde group to the calorific value is what would be expected from a group consisting of one hydrogen atom and one CO group. Thus the characteristic group of these compounds is, thermally, equivalent to a carbonyl group (value already deduced) and one hydrogen atom, and the combustion of this part of the molecule may be represented by the equation

$$(CO + O) + \frac{1}{2}(2H + O) = CO_2 + \frac{1}{2}H_2O + 60.7 + 34.5$$

Thus the complete combustion of an aldehyde group to carbon-dioxide and water (liquid) is accompanied by the evolution of 95.2 kilo-gramme calories per gramme molecular weight.

Substance	Molecular Calorific Values.	
	Found.	Calculated.
Formaldehyde	130.0	129.6
Acetaldehyde	281.9	281.2
Propionaldehyde	441.5	437.1
Benzaldehyde	848.3	849.4
Salicylaldehyde	795.8	793.2

The Calorific Value of the Hydroxyl Group in Connection with the Simpler Hydroxy Aromatic Compounds

With the exception of the di-hydroxybenzenes, there is satisfactory agreement between the calculated and the observed values. The phenol and cresols were the same as those employed for the work on freezing points[1] and were of an exceptionally high degree of purity.

Substance	Molecular Calorific Values.	
	Found.	Calculated.
Phenol	733.0	732.7
Cresol (ortho-)	883.7	884.0
Cresol (meta-)	883.0	
Cresol (para-)	885.0	
Pyrogallol	618.1	620.7
Di-hydroxybenzene (ortho)	684.9	676.8
Di-hydroxybenzene (meta)	683.9	
Di-hydroxybenzene (para)	684.7	

The calculated value for the cresols was arrived at as follows; side chain carbon—82.9, equivalent to that of toluene; benzenoid carbon—96.96; Hydroxyl—12.9 as deduced.

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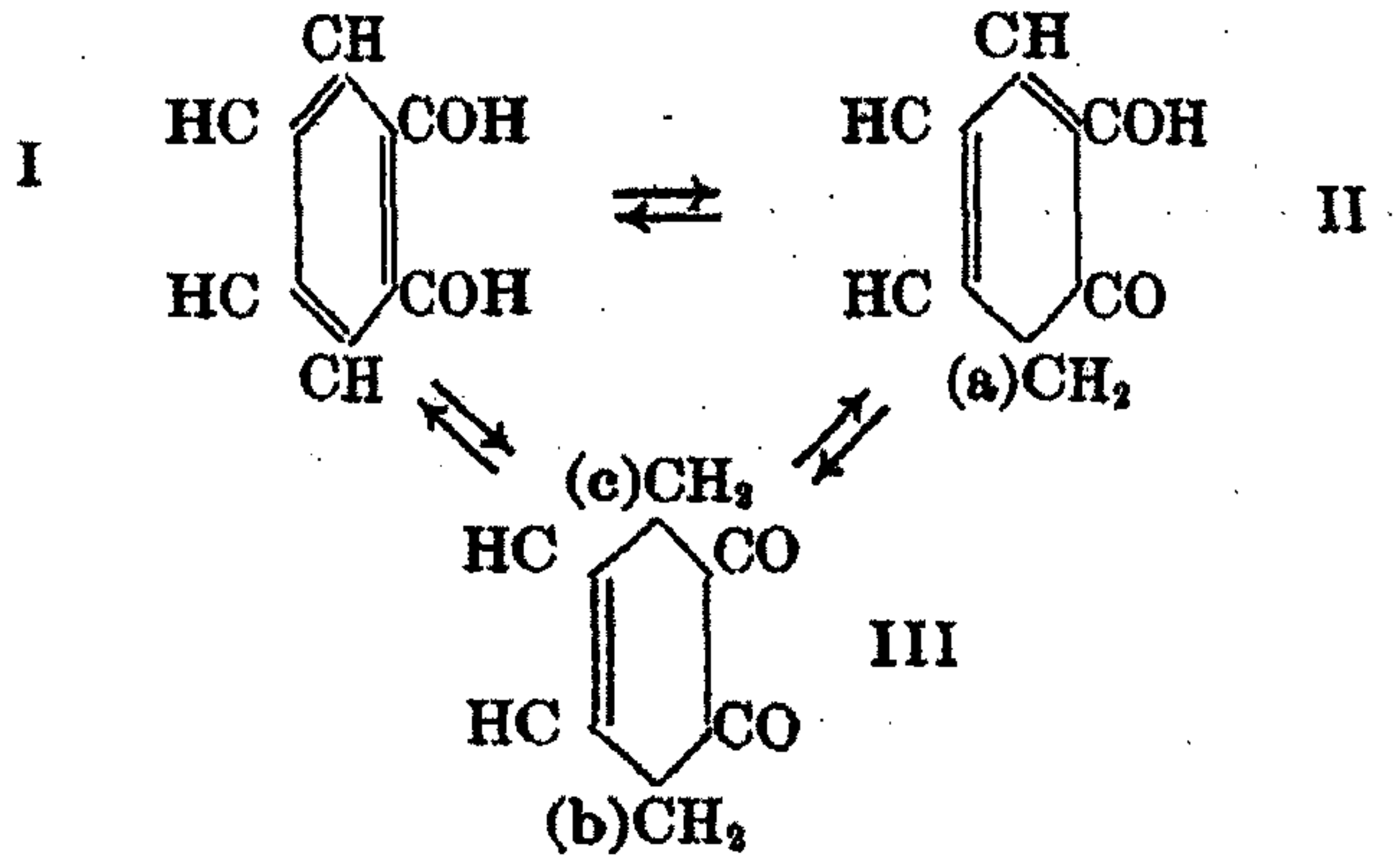
[1] Fox and Barker: J. Soc. Chem. Ind. 38, 265-272T (1918).

The discrepancies in the case of the di-hydroxybenzenes may be due to the existence of tautomeric forms in equilibrium with each other as represented below for the ortho compound.



The carbon atoms (a), (b) and (c) are to a great extent comparable with the carbon in a cyclohexane which has a calorific value of 88.2. Thus the calculated calorific values of II and III are 687.6 and 698.7 respectively. Since, according to the previous calculation I has a molecular calorific value of 676.8, mixtures of I, II and III may have the intermediate values found by observation.

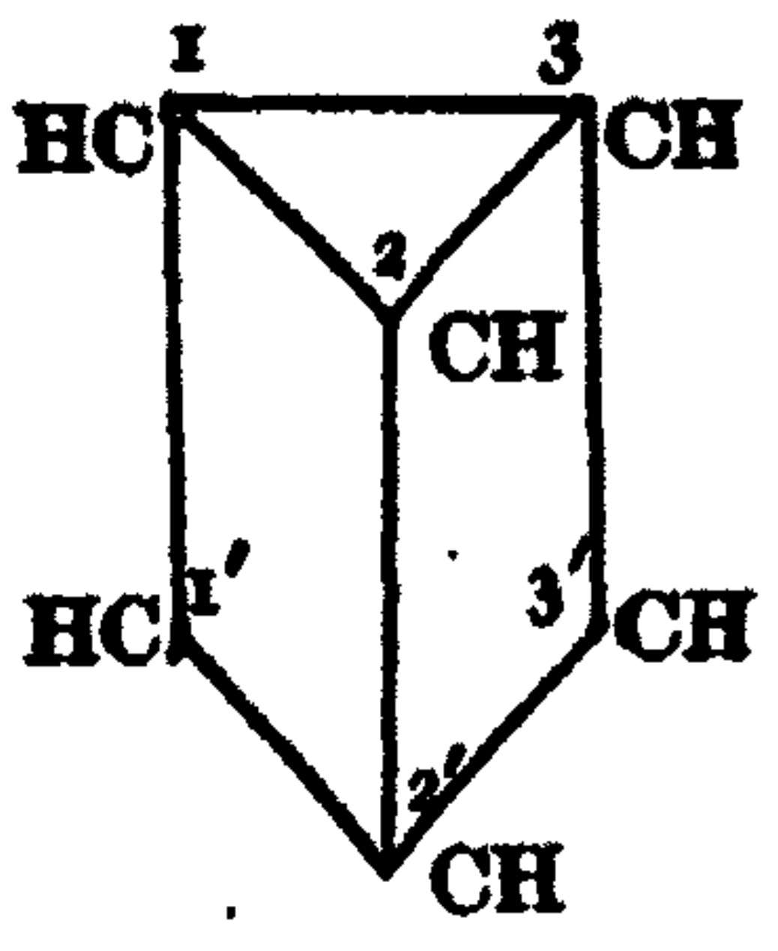
The Calorific Value and the Constitution of Benzene

Earlier in this paper, it was shown that the carbon in benzene and naphthalene and the ring carbons in toluene and xylene had a molecular calorific value of 96.96. It was then pointed out that the heat given out by a carbon atom in cyclo-propane was also very nearly equal to this value. This fact appears to throw light upon the constitution of benzene and to afford an explanation of the results of Stohmann, Roth and Auwers concerning the calorific values of benzene and some of its derivatives and their products of hydrogenation. In 1915, Roth and Auwers repeated the earlier observations of Stohmann relating to the increase in the calorific value due to hydrogenation, and although in some instances there were appreciable differences between the two sets of values, yet the same general conclusions were indicated by both. It is therefore quite beyond cavil that the successive addition of two hydrogen atoms to the benzene ring causes widely different incremenets in the molecular calorific values of the hydrogenated compounds. This is true not only for benzene but for the terephthalic acids and esters and naphthalene.

The results necessary for a further discussion of this subject are given in the following table.

		Stohmann		*Roth and Auwers*	
Benzene		779.8		782.3	
			68.2		
Di-hydrobenzene		848.0			
			44.0		
Tetra-hydrobenzene		892.0		893.7	
			41.2		44.8
Hexa-hydrobenzene		933.2		938.5	
Naphthalene				1235.2	
Di-hydronaphthalene				1297.8	62.6
				1299.8	64.6
				1302.7	67.5
Tetra-hydronaphthalene				1341.2	41.1
Terephthalic Acid		770.9			
Di-hydro " "	1 4	836.8			
	1 5	842.7	70.6		
	2 5	845.8			
Tetra-hydro "			41.3		
		882.5			
			45.8		
Hexa-hydro "		928.6			

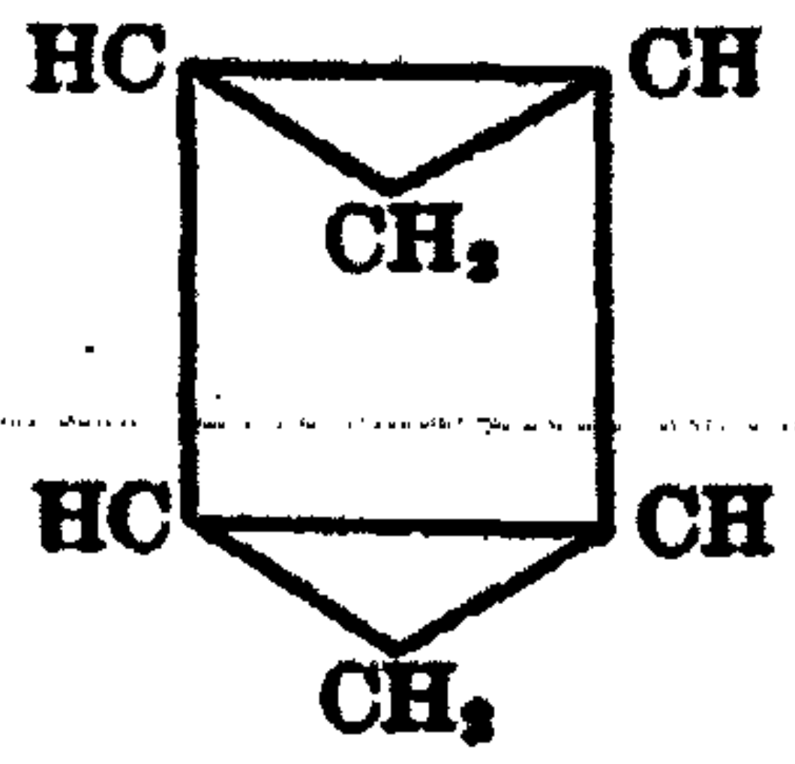
According to the Kekulé formula, as hydrogenation proceeds, the carbon approaches more nearly to the condition of the carbon atom in a fully hydrogenised six membered ring. The calorific value, in consequence, drops from 96.96 to 87.4 so that the increase in the heat of combustion due to the addition of two hydrogen atoms, can never be equal to the heat of combustion of two hydrogen atoms. For the Kekulé formula the increment for the first two hydrogen atoms should be given by $2 \times 34.5 - 2(96.96 - 87.4) = 49.9$. This is not in agreement with the observed results. Assume now that the carbon atoms are arranged in two sets of three, and each carbon atom is situated at a corner of an equilateral-triangular prism. Since the hexa hydrogenated molecule consists of six fully hydrogenated carbon atoms united together in a six membered ring, it is necessary to assume that the di-hydrogenation may occur by addition either to 1, 3; 1′, 3′ or 2, 2′. The addition of the first two hydrogen atoms causes an increment very nearly equal to that of the calorific value of two hydrogen atoms. From this it appears that the calorific value of the carbon atoms in the di-hydro compound are the same as in the parent substance and also that the original molecule has undergone no appreciable change in configuration during this process.



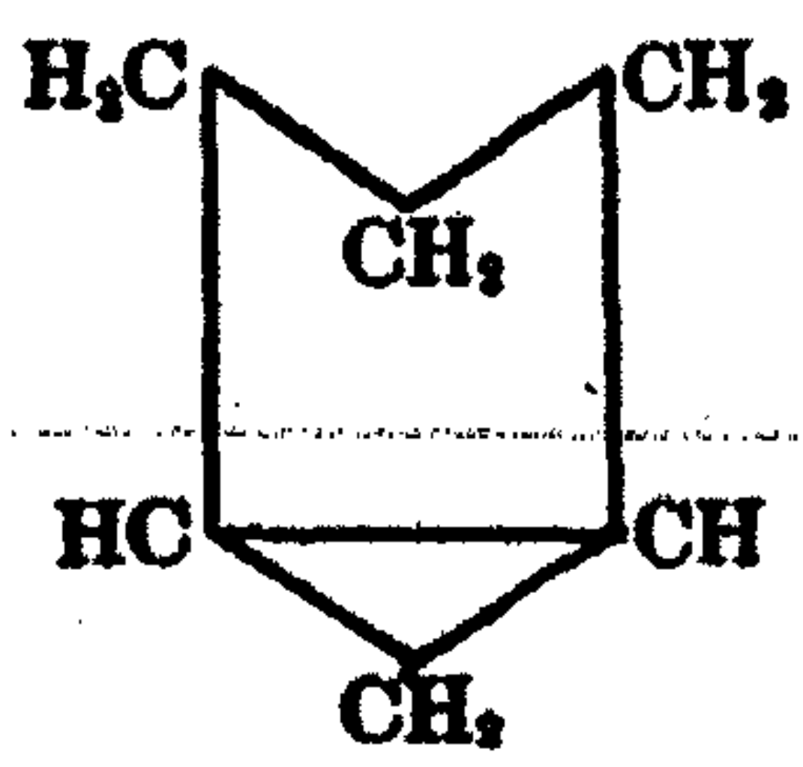
I

Di-hydrobenzene may therefore be considered as in II, in which the two three membered rings are still intact. The increase in the molecular calorific value due to di-hydrogenation, is therefore, theoretically equal to 68.9 kilogramme calories.

Further hydrogenation would give III. Here the carbon atoms 1, 2, 3, 1′, 3′ form a five membered ring. The calorific values of 1, 2, 3 will be appreciably diminished since they are now fully hydrogenised and have much greater freedom than 1′, 2′, 3′ which are still maintained in the three membered ring. The calorific value of the carbon in cyclo-pentane is 88.6 so that the calorific value of tetra-hydrobenzene should be given by $3 \times C_{96.1} + 3 \times C_{88.6} + 10 \times H_{34.46} = 898.7$. The observed values are 892.0 (Stohmann) and 893.7 (Roth and Auwers). The calculated value for the Di-hydrobenzene is 857.4 and therefore the increment for the step di-hydrobenzene to the tetra-hydrobenzene is 41.5 or 43.9 according as we use the actual value for benzenoid carbon calculated from benzene or the observed value for elementary carbon. The increment found by Stohmann is 44.0. The conversion of the tetra-hydro to the hexa-hydrobenzene results in the scission of the remaining cyclo-propane ring. From the results for the hexa compound (Stohmann 933.2; Roth and Auwers 938.5) the calorific value for one carbon atom is 86.6 and 87.4 respectively. The calculated increment for the transformation of tetra-hydrobenzene to hexa-hydrobenzene will be therefore 48.2 and 49.8. If instead of the calorific value for elementary carbon the value deduced from the molecular calorific value for cyclo-propane is used, the calculated increments are 46.5 and 48.1. The actual increments from the observed results are 41.2 (Stohmann) and 44.8 (Roth and Auwers) for the hydro-benzenes and 45.8 for the respective terephthalic acid derivatives. Thus this argument explains in a satisfactory manner the series of values obtained for the molecular heats of combustion of these compounds.

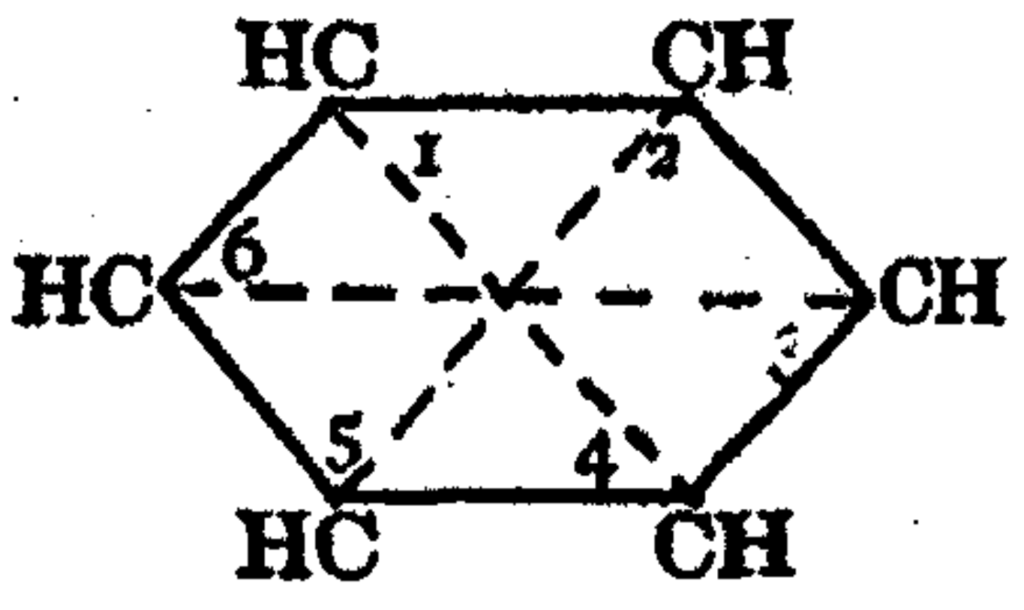


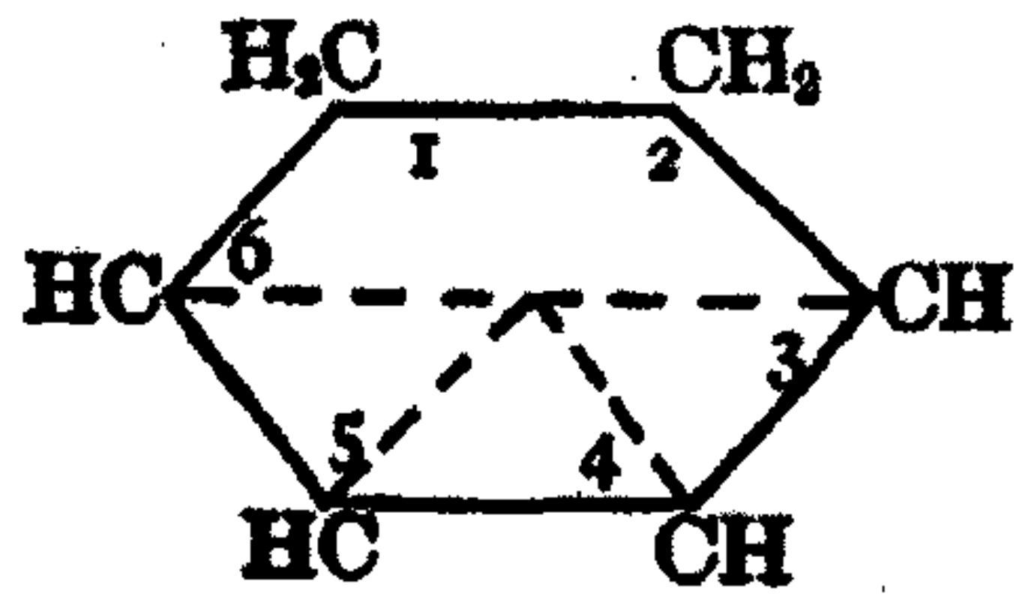
II



III

The subject, however, may be viewed from another standpoint. In dealing with the calorific value of the doubly linked carbon atom the idea was put forward that the two doubly linked carbon atoms are really members of a closed chain of force. If three pairs of such atoms are connected in ring formation we have the following system when the apices are coincident. This is what is implied in the centric formula for benzene. Di-hydrogenation would cause the destruction of three of these triangles and consequently a comparatively large decrease in the calorific value of the two carbon atoms common to both since they are now fully hydrogenated. If the system 3 4 5 6 is sufficiently stable to remain intact after this has taken place, then the hydrogenised carbon atoms 1 and 2 are comparable to those in cyclohexane. Thus the increment for the di-hydrogenation would be only 53.1. This result is not in accordance with observed facts. Similarly the increments for the remaining two stages are identical with that for the first, and are appreciably higher than the experimental figures. Taking all the evidence, the prism formula for benzene is strongly supported by the thermochemical results obtained for benzene and the hydrogenated compounds under discussion.





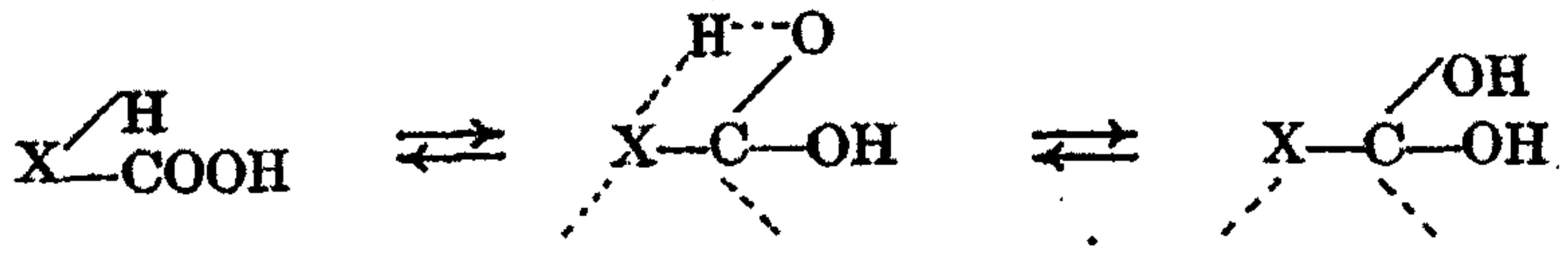
Conclusions

(1) The molecular calorific value of an organic compounds is a function of its composition.

(2) The calorific value of a carbonyl group is 60.7 kilo-gramme calories.

(3) The calorific value of the hydroxyl group is 12.9 kilo-gramme calories.

(4) The contribution of the carboxyl group is not what would be expected from the ordinary COOH representation; that is equivalent to one carbonyl group and one hydroxyl group. Thermochemical results point to the mobility of a hydrogen atom giving rise thereby to an additional, potential hydroxyl group.



(5) The value for benzenoid carbon deduced from various benzene hydrocarbons agrees closely with the values for amorphous carbon and not very different from the value for graphitic carbon.

(6) The molecular calorific value of the carbon atom in situ varies and has the lesser values when the disposition of the bonds approaches nearer to that in the symmetrical tetrahedral positions.

(7) The results obtained by various observers in connection with hydrogenated benzene compounds indicate that the benzene molecule is best represented by the prism formula.

April 21, 1925.

A REVISION OF THE ATOMIC WEIGHT OF GERMANIUM. II. THE ANALYSIS OF GERMANIUM TETRABROMIDE*

BY GREGORY PAUL BAXTER AND WILLIAM CHARLES COOPER, JR.

The value for the atomic weight of germanium, which we have recently found by analysis of germanium tetrachloride, 72.60[1], is 0.1 unit higher than the one in current use, and nearly 0.2 unit higher than the value recently found by Müller.[2] The simplest way to secure further light on the subject seemed to us to prepare and analyze the tetrabromide; for while similar constant errors might result from inadequate purification and in the analysis of such similar compounds as the chloride and the bromide, yet it seemed unlikely that these errors would be of equal magnitude in both cases. We believe that the concordance of the result of the present investigation with that of the previous one furnishes very strong if not irrefutable evidence that the atomic weight of germanium has the value 72.60.

In its general outlines the experimental procedure of this research followed very closely the methods perfected in this laboratory for the preparation and analysis of other volatile mineral halides.[3]

Purification of Materials

Reagents

Water. Ordinary distilled water was twice redistilled, once from alkaline permanganate, and once from very dilute sulphuric acid. The condensers were block tin tubes, fitted to pyrex flasks with constricted necks which served as stills. The connection was made by a water seal, no cork or rubber being used. The water was collected in pyrex flasks, generally just previous to use.

Nitric Acid. Concentrated C. P. nitric acid was distilled through a quartz condenser, the first two-thirds, as well as the last tenth being rejected. If necessary, the fractional distillation was continued until the product was free from chloride.

Silver. This substance was prepared by standard methods. These consisted in brief of the following processes: double precipitation as chloride, followed by reduction with alkaline sugar solution, fusion of the metal on charcoal, solution in nitric acid and repeated crystallization of silver nitrate, precipitation with ammonium formate, fusion on pure lime, electrolytic transport, fusion on pure lime in hydrogen, etching, drying in a vacuum at 500°. Details of these processes may be found in earlier papers from the

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*Contribution from the T. Jefferson Coolidge, Jr., Memorial Laboratory, Harvard University.

[1] Baxter and Cooper: Proc. Am. Acad., 59, 235 (1924); J. Phys. Chem., 28, 1049 (1924).

[2] Müller: J. Am. Chem. Soc., 43, 1085, (1921).

[3] Baxter, Weatherill and Scripture: Proc. Am. Acad., 58, 245, (1923); Baxter and Fertig: J. Am. Chem. Soc., 40, 1228, (1923); Baxter and Scott: Proc. Am. Acad., 59, 21, (1923); Baxter and Cooper: J. Phys. Chem., 28, 1049 (1924).

Harvard Chemical Laboratories.[1] Recent work by Baxter and Parsons[2] and Baxter[3] as well as earlier investigations have shown that these processes yield a product of adequate purity.

Two different specimens were used. The first had been prepared by Mr. M. J. Dorcas and was employed in Analyses 1-11. The second was purified especially for this investigation and served in Analyses 12 to 16.

Sodium Hydroxide. Pure material was prepared by metathesis from solutions of barium hydroxide and sodium carbonate, both of which had been recrystallized until practically free from chloride. The solution was freed from precipitate by centrifugal settling, and after evaporation in platinum dishes was allowed to crystallize. Since the product was found to contain a trace of chloride it was recrystallized several times in platinum dishes until the chloride had been completely removed.

Nitrogen. This gas was prepared free from hydrogen by a modification of the Wanklyn process. Air was charged with ammonia and passed over hot copper catalyst. The excess of ammonia was removed by wash bottles containing dilute sulphuric acid. Hydrogen resulting from catalytic decomposition of the ammonia was next burned with hot copper oxide, and the gas was then purified and dried by dilute silver nitrate solution, sodium hydroxide, concentrated sulphuric acid and resublimed phosphorus pentoxide. Finally last traces of oxygen were removed by hot copper. The apparatus, which was constructed entirely of glass, is described in detail by Baxter and Grover.[4]

Bromine. The source of bromine was a very concentrated solution of zinc bromide which has been made from pure zinc and pure bromine some years before by Dr. J. H. Hodges in an investigation on the atomic weight of zinc.[5] This bromine had been first distilled from aqueous potassium bromine in order to remove chlorine. Next one-fourth of the product was converted to potassium bromide by means of recrystallized potassium oxalate, and the remaining three-fourths of the bromine was distilled from solution in this potassium bromide. All the product was then converted to potassium bromide by means of potassium oxalate, and the potassium bromide was fused in a platinum dish with enough recrystallized permanganate to oxidize all organic matter. In order to obtain bromine the purified potassium bromide was dissolved in a solution of pure sulphuric acid. The excess of potassium permanganate contained by the salt caused a small quantity of bromine to be liberated. This bromine was removed by distillation, since it might have contained a trace of iodine. Enough pure permanganate to liberate the greater portion of the bromine was then added, and the bromine was distilled into a receiver cooled with ice. In this last step the bromine received a third distillation from a bromide. Pure

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[1] See especially Richards and Wells: Pub. Car. Inst. No. 28, p. 16 (1905).

[2] Baxter and Parsons: J. Am. Chem. Soc., 44, 577, (1922).

[3] Baxter: J. Am. Chem. Soc., 44, 591, (1922).

[4] Baxter and Grover: J. Am. Chem. Soc., 37, 1037, (1915).

Baxter and Hodges: J. Am. Chem. Soc., 42, 1242 (1921).

zinc was treated under water with this bromine to prepare the zinc bromide solution.

To recover the bromine, portions of the zinc bromide solution were treated with recrystallized potassium permanganate and dilute sulphuric acid in insufficient amounts to liberate all the halogen, and the bromine was separated by distillation. This fourth and last distillation from a bromide was considered necessary only because the solution had been standing for a long period. After separation from the aqueous layer the pure bromine was redistilled and dried for some days over resublimed phosphorus pentoxide. In all the above operations cork and rubber were rigidly excluded from the apparatus.

Recovery and Purification of Germanium

At the beginning of this investigation the greater proportion of the germanium material was in the form of germanic acid dissolved in a nitric acid solution of sodium nitrate and sometimes silver nitrate resulting from the earlier analyses of germanium tetrachloride. This material was arsenic-free so far as we knew. A smaller proportion consisted of fractions rejected during the distillation of the germanium tetrachloride because of their arsenic content. Most of these had been hydrolyzed and precipitated with hydrogen sulphide.

The germanic acid solutions were evaporated until a large portion of the germanic acid had separated. The flasks in which the evaporation took place were then connected with a condenser delivering into a receiver containing water chilled with ice. By means of a separatory funnel sufficient concentrated hydrochloric acid was admitted to the flask to dissolve the germanic acid on boiling, and the solution was distilled until sodium chloride began to separate in the still. At this point the contents of the still were tested with hydrogen sulphide and found to be free from germanium. The germanium tetrachloride and hydrochloric acid solution contained in the receiver was too strongly acid to permit hydrolysis and remained perfectly clear. From this distillate germanium hydroxide was precipitated by adding an excess of ammonia. The precipitate was washed by decantation until its colloidal tendency became so great as to prevent settling, and then was collected on a filter paper and dried at 110°.

The ammoniacal filtrate and washings were evaporated to small bulk and distilled with hydrochloric acid as described above. If the germanium tetrachloride collecting in the receiver hydrolyzed at any time, the resulting precipitate of dioxide was set aside and the combined precipitates obtained in this way were washed, collected on a filter and dried at 110°.

The residues containing arsenic were freed from the latter element by distillation from a solution in which the arsenic was in the higher state of oxidation, according to the procedure of Dennis and Papish.[1] Most of this material was in the form of sulphides. These were washed, collected and dried, and roasted at about 500° to eliminate the greater part of the arsenic. The product was treated with an excess of sodium hydroxide, and after saturation

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[1] Dennis and Papish: J. Am. Chem. Soc., 43, 2131, (1921).

with chlorine, the solution was distilled with an excess of hydrochloric acid. The germanium dioxide forming in the receiver was treated as above and the material remaining in the solution was precipitated with ammonium hydroxide.

In order to avoid loss of germanium during reduction through the presence of chloride in the various precipitates the dioxide was next ignited in a current of air saturated with moisture at room temperature. The material was contained in alundum boats placed in a quartz tube. After the tube had cooled, the air was replaced with pure dry electrolytic hydrogen and the tube was again heated to incipient redness until reduction was nearly complete. Then the temperature was raised to the melting point of germanium for a short time. At the end of this preliminary reduction the comparatively small globules of metal were fused into large globules by filling the alundum boats and heating them in a current of hydrogen until the germanium had melted. The final product weighed 48 grams. There seemed to be good reason to believe that this germanium was free from impurities, especially arsenic, because samples of the dioxide precipitated by ammonia and by direct hydrolysis of the distilled chloride gave no indication of arsenic lines when their arc spectra on graphite electrodes were photographed with a Féry quartz spectrograph.

Preparation and Distillation of Germanium Tetrabromide

Germanium tetrabromide was prepared by heating the metal in a current of nitrogen charged with bromine. Pure dry nitrogen, prepared as described on page 1365, was passed through pure dry bromine (see page 1365) in a bubbling flask, and then through a hard glass tube containing the germanium in alundum boats. The tube was inclined downward and connected at its lower end by means of a ground joint with a condensing bulb, followed by a U-tube chilled with ice. Since the boiling point of the tetrabromide[1] is 185.9° it was unnecessary to chill the condensing bulb. Fused or well-ground glass connections without any lubricant were used throughout the system.

After the nitrogen train and the germanium tube had been swept out with nitrogen for some time the bromine was introduced in the bubbling flask through a side tube, and the germanium was heated to about 250°, since as already stated by Dennis and Hance, rapid combination with the bromine does not take place below 220°. The bromine flask and connecting tubes were warmed to increase the bromine concentration until the metal glowed brightly from the heat of reaction. The tetrabromide condensed in the cool portion of the hard glass tube beyond the metal and flowed down into the condensing bulb. This transfer was assisted by occasionally warming the tube. As long as a considerable amount of unchanged metal remained in the boats very little bromine passed into the distillate. The process was continued until the metal had nearly disappeared and unchanged bromine was passing through the system. Then the condensing bulb was sealed off from the reaction tube. About sixty-five cubic centimeters of tetrabromide were obtained. Besides free bromine the product contained hydrogen bromide and

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[1] Dennis and Hance: J. Am. Chem. Soc., 44, 301, (1922).

either germanic acid or oxybromide owing to some contact with moisture. Arsenic, tin, antimony, and silicon also were to be feared. In the following table are given the boiling points of some probable impurities, together with the effect on the observed atomic weight of germanium of a proportion of 0.1 per cent of each impurity alone.

TABLE I

Boiling Points of Inorganic Bromides

	Boiling point degrees	Effect of 0.1% on atomic weight of germanium
HBr	−69.0	−0.087
Br_2	58.6	−0.094
$SiBr_4$	153.0	−0.055
$GeBr_4$	185.9	———
CBr_4	190.0	−0.076
$SnBr_4$	201.0	+0.038
$AsBr_3$	220.0	+0.020
$SbBr_3$	280.0	+0.070

The germanium tetrabromide was now purified by fractional distillation in a fashion very similar to that used in purifying other inorganic halides in this laboratory.

Dennis and Hance have found that, if excess of bromine is removed from the tetrabromide by means of mercury, mercuric bromide vaporizes to some extent with the tetrabromide when the latter is distilled, but that the bromine may easily be eliminated by fractional distillation. We therefore avoided the use of mercury. Since experience with the tetrachloride led us to expect that other impurities could be removed by fractional distillation, we depended entirely on this process henceforth.

The bulb containing the tetrabromide was sealed to two U-tubes and the second U-tube was connected through a tube containing solid sodium hydroxide to an efficient water pump. While immersed in a bath of concentrated sulphuric acid at about 120° the bulb was exhausted and the tetrabromide was allowed to boil gently for some time. In this way the air in the bulb was flushed out and at the same time a considerable proportion of the free bromine and other more volatile impurities were expelled from the tetrabromide. In the first U-tube, which was chilled with ice, a fraction of tetrabromide of about two cubic centimeters condensed. The glass tube connecting the bulb to the first U-tube was sealed off at a constriction while the tetrabromide was boiling.

In order to remove permanent gases still more completely the bulb A (Fig. 1) was attached through a special valve *a* with which it had been originally provided to three half-liter globes 1, 1, 1, followed by a second special valve *b*. The globes were exhausted to a pressure of 0.001 mm. by means of a Gaede mercury pump through a side tube *d* which was sealed while the pump was operating. Then the bulb of tetrabromide was surrounded with boiling water and connection with the exhausted globes was made by opening the special valve *a* nearest the bulb. Bromine together with a small amount of tetrabromide immediately evaporated into the globes, 1, 1, 1, again flushing out the gases in the bulb. The globes were sealed off at *c* not long after the valve was opened. Another bulb *B* attached through a vertical tube to a fractionating column *f* filled with glass pearls was next sealed to the tetrabromide bulb *A*. Beyond the fractionating column were condensing bulbs 2, 28, and a special valve *h*.

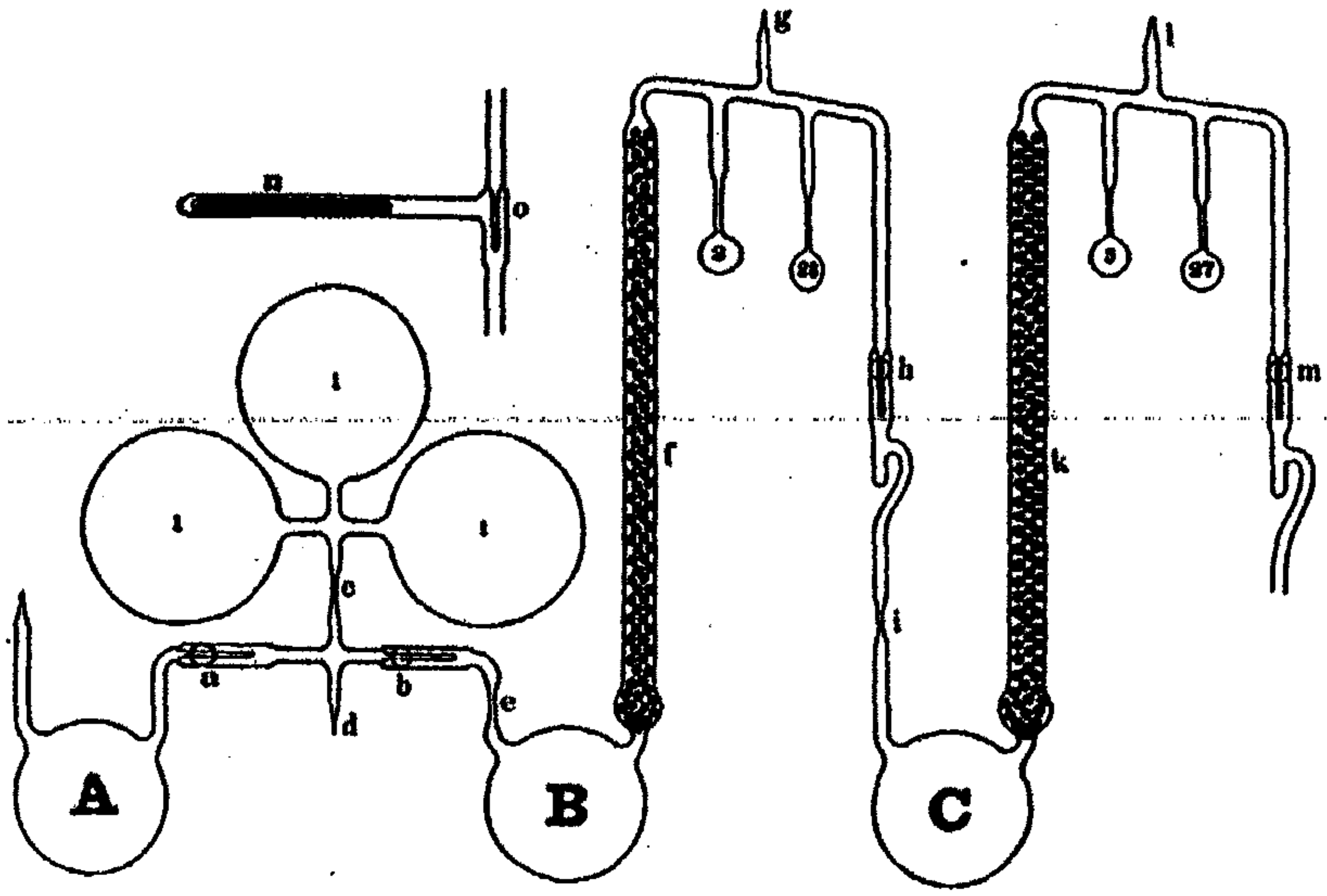

FIG. 1

The details of a special valve are shown in Figure 1. The sealed-in capillary *o* is closed at the end and is scratched with a file at several points to facilitate breaking. To open the valve the closed tube of glass weighted with mercury *n* is allowed to strike the capillary with some force.[1]

After the bulb *B* and the column *f* had been exhausted through *g*, the valve *b* was opened. Even when the tetrabromide was surrounded with boiling water, distillation did not at first take place, apparently owing to choking with bromine vapor. But when one of the small bulbs, 2, was temporarily chilled with liquid air, so that the bromine was largely removed from the system, distillation of the tetrabromide proceeded readily. After all but a few cubic centimeters of tetrabromide had been collected in *B*, the original bulb *A* was disconnected by sealing the capillary *e*.

Bulb *B* was now attached to a third bulb *C* with fractionating column and these were exhausted through *l*. Bulb *B* containing the tetrabromide was then surrounded with boiling water, while the small bulb 2 was chilled with liquid air. Refluxing in the column *f* took place vigorously while a solid

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[1] This valve was apparently devised by Bruner and Bekier [Z. Elektrochem., 18, 369, (1912)] and has been found very useful in this laboratory.

consisting chiefly of bromine condensed in the small bulb. By continually agitating the system the greater part of the bromine content of the tetrabromide was eliminated and collected in 2, which was sealed off at the capillary while still chilled. The main bulk of tetrabromide was then transferred from *B* to *C* by opening the valve *h* and warming *B*. The Hempel column operated very efficiently with negligible choking when merely aircooled. When the residue in *B* had been reduced to about two cubic centimeters the capillary *i* was sealed.

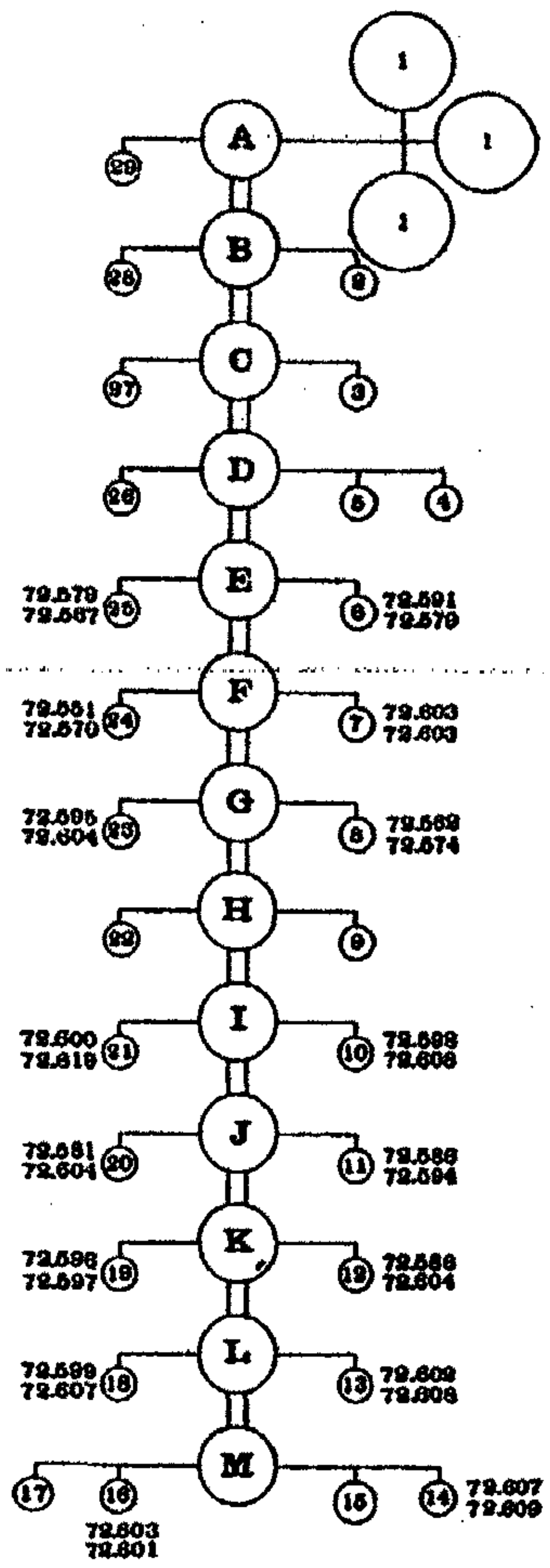

FIG. 2

Eleven more fractional distillations were now carried out with apparatus of the general type indicated in the right-hand side of Figure 1. In each distillation one or two least volatile fractions were removed from the tetrabromide by condensation in small bulbs before connecting each exhausted system with the succeeding one, and when all but about two to three cubic centimeters of bromide had been removed during a fractionation, the still was sealed off from the receiver and the residue condensed in a small bulb. The complete outline of the distillation is shown in Figure 2. In this diagram each fractionation is indicated by a lettered circle, while the fractions removed are shown by small circles numbered in the order of decreasing volatility; that is, in distillation *G* the most volatile fraction is 8 and the least volatile 23. The atomic weight of germanium found from each sample is also shown in Figure 2, the upper number in each case being that found by comparing the bromide with silver, the lower by weighing the silver bromide formed. Fractions 9, 15, 17 and 22 either were lost by the cracking of the bulbs or were preserved for future examination.

Purity of Germanium Tetrabromide

As stated above, the removal of the bromine in the less volatile fractions was very rapid. Fractions 2 and 3 consisted very largely of bromine, Fraction 4 contained a small proportion, but Fraction 5 was essentially colorless. So far as bromine and hydrogen bromide were concerned we therefore felt justified in using subsequent fractions for analysis.

Since silicon tetrabromide is more volatile than the germanium compound the more volatile fraction, 3, weighing 5.0 grams, was analyzed for silicon.

The contents of the bulb were added to pure water in a platinum crucible and the crucible was filled with freshly distilled constant-boiling hydrochloric acid. After evaporation of the solution nearly to dryness over an electric hot plate the crucible was three times more filled with hydrochloric acid and the solution evaporated. In this way the germanium was expelled while the silicon compound must have been hydrolyzed to silicic acid. The crucible was then ignited and weighed by substitution. In order to expel any silica the crucible was next filled with hydrofluoric acid which had been freshly distilled through a platinum condenser, and after evaporation of this acid and ignition, the crucible was reweighed. A loss in weight of only 0.01 mg. was observed and this result was not altered by a second evaporation with hydrofluoric acid. This seemed to be conclusive evidence that the germanium tetrabromide was never contaminated with a perceptible amount of silicon tetrabromide.

The residues from the first four fractionations, fractions 26 to 29, were hydrolyzed with ammonia and the solutions evaporated to dryness. When the arc spectra of these products were produced on graphite electrodes and photographed with a Féry quartz spectrograph, arsenic lines could not be discovered in any of the spectra, even in that of fraction 29. Fractions 26 and 27 seemed to contain no metals except germanium. Fractions 28 and 29, however, showed the merest traces of tin and antimony. The least volatile fraction of the fifth distillation was therefore believed to be pure enough for analysis.

Analysis of Germanium Tetrabromide

The analysis of germanium tetrabromide followed closely the procedure used in the analysis of the tetrachloride. After being weighed the bulb containing germanium tetrabromide was broken under an excess of sodium hydroxide and the glass was collected and weighed. The solution was diluted to considerable volume and made acid with nitric acid, and then was precipitated with a solution of a weighed, very nearly equivalent amount of pure silver. The point of exact equivalence between bromide and silver was then found with the assistance of a nephelometer. In all the experiments the silver bromide was collected and weighed.

The bulb containing the material for analysis was first scrubbed with soap solution and then was allowed to stand for some time in sulphuric acid-dichromate solution. After thorough rinsing it was soaked for at least twenty-four hours in the purest water. From this point the bulb was not touched with the fingers. Next the bulb was placed in a basket of platinum wire which had already been weighed under water with an accuracy of one milligram, and the bulb and basket together were weighed under water of known temperature. Rinsing with pure water and draining were followed by drying, first over sulphuric acid, finally over potassium hydroxide which had been fused with permanganate to destroy organic matter. The bulb was then weighed by substitution and the density of the air in the balance case at the time of weighing was found by weighing a sealed standardized glass globe.[1]

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[1] Baxter: J. Am. Chem. Soc., 43, 1317, (1921)

A 4 normal solution of pure sodium hydroxide containing a one hundred per cent excess over that necessary to form sodium bromide and sodium germanate was filtered through a platinum sponge crucible into a heavy-walled, two-liter Erlenmeyer pyrex flask provided with a carefully ground glass stopper. The weight of glass in the bulb containing the tetrabromide was estimated in computing the amount of sodium hydroxide necessary. The weighed bulb was carefully introduced, and, before the stopper was inserted, the flask was warmed gently so that ultimately the pressure should be slightly inward. After cooling the flask with tap water the inner walls of the flask were wetted with sodium hydroxide solution by inclining the flask and rotating, and then the bulb was broken by shaking the flask. A dense fog immediately appeared in the flask. Again the flask was cooled and although the fog disappeared in the course of fifteen minutes the flask was allowed to stand for about three hours longer. The resulting solution was perfectly clear except for glass fragments.

The fragments of the glass bulb were collected on a weighed, platinum sponge crucible. The solution was filtered directly into the glass-stoppered Erlenmeyer preciptating flask, and the glass was washed by decantation ten or twelve times with about one hundred cubic centimeters of boiling water and once with cold water before being transferred to the crucible. Drying at 300° for eighteen hours in an electrically heated porcelain air bath preceded the weighing of the crucible both empty and with the glass. In order to make sure that no germanium hydroxide was retained by the crucible and glass, the two were further treated with hot 4 normal nitric acid by slowly pouring from 400 to 800 cc. through the crucible. This treatment usually produced a slight loss in weight of a few hundredths of a milligram, but a second similar treatment produced no further change of appreciable magnitude.

In similar experiments with the tetrachloride[1] it was found that during the treatment of the glass with alkali, solution took place at the rate of 0.007 mg. per gram per hour of treatment with alkaline germanate solution, combined with the nitric acid treatment. A positive correction of this magnitude was therefore applied to the weight of glass obtained in each analysis. This correction did not exceed 0.03 mg. in any experiment.

From the observations with the bulb before breaking and the weight of glass corrected as above and for the buoyant effect of the air, the weight of germanium tetrabromide was found. The weight of silver necessary to precipitate the bromide was computed, and was weighed out, chiefly in the form of a very few large buttons, the final adjustment being made with small electrolytic crystals. After careful solution of the silver in halogen-free nitric acid and elimination of nitrous acid by heating the solution, in a flask provided with a spray trap in the form of a column of bulbs ground into the neck of the flask, twenty-five cubic centimeters additional of concentrated nitric acid were added, together with sufficient water to make the solution nearly tenth normal in silver. The acid solution was then added slowly with continual

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[1] Baxter and Cooper: Proc. Am. Acad., 59, 246 (1924).

agitation to the germanium solution which had been diluted to less than tenth normal concentration during the washing of the glass and also had been made acid by adding an excess of twenty-five cubic centimeters of nitric acid through a funnel tube extending to the bottom of the solution. The mixture was then allowed to stand for several days with occasional shaking, and the solution was tested for excess of bromide or silver in a nephelometer. If an excess of either was found, the deficiency of the other was made up by adding hundredth normal silver nitrate or potassium bromide until the end-point had been reached. Since at the end-point the test portions appeared almost free from precipitate, there seems good reason to believe the bromine to have been thoroughly freed from chlorine.

Occasional testing of the solution was continued for a period of at least one month in every analysis. The manipulations of precipitation and testing of the solutions were always carried out in ruby light. In using the nephelometer all the precautions noted by Richards and Wells[1] were observed, such as preparing the comparison tubes under as nearly as possible identical conditions of temperature, concentration and time.

In every analysis the silver bromide was collected on a platinum sponge crucible and weighed. First the solubility of the silver bromide was reduced by adding eight milligrams excess of silver nitrate and after being shaken vigorously the system was allowed to stand overnight. Filtration of the supernatant liquid through a large weighed platinum-sponge crucible was followed by thorough washing of the precipitate by decantation with a solution containing seven milligrams of silver nitrate and five cubic centimeters of nitric acid per liter. In Analyses 29 and 30 no nitric acid was added to the washing liquid and in Analysis 30 forty milligrams of silver nitrate were added to the original solution to lower the solubility of the silver nitrate. The precipitate was transferred to the crucible with pure water, and after being dried in an electrically heated porcelain oven for about eighteen hours at 160° it was weighed. Moisture retained by the precipitate was determined by fusing the main bulk and finding the loss in weight.

No correction is applied for silver bromide dissolved in the mother liquor and silver nitrate washings, but the solubility in the pure water used for transfer was assumed to be 0.1 mg. per liter. The precipitating flask was rinsed with ammonia and after the resulting solution had been diluted to 100 cc., its bromide content was found by comparison with standard bromide solutions in a nephelometer after adding nitric acid and silver nitrate.

In the tables the original weight of silver bromide has been corrected for bromide introduced in the comparison of germanium bromide with silver. The results of all the analyses undertaken are given.

Weighings were made on a No. 10 Troemner balance, sensitive to 0.02 mg. with a load of fifty grams. A 5 milligram rider was used to determine quantities less than this and more than 0.05 mg. Interpolation from zero points was employed only for amounts less than 0.05 mg.

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[1] Richards and Wells: Am. Chem. J., **31**, 235, (1904); **35**, 510, (1906).

Table III—Results

Atomic Weight of Germanium

Series I GeBr$_4$: 4 Ag

Ag = 107.880 Br = 79.916

Number of analysis	Fraction of GeBr$_4$	Weight of GeBr$_4$ in vacuum gram	Weight of Ag in vacuum gram	Weight of Ag added or subtracted in solution gram	Corrected weight of Ag in vacuum gram	Ratio GeBr$_4$:4 Ag	Atomic weight of germanium
1	6	6.39771	7.03767	+0.00045	7.03812	0.909008	72.591
2	25	6.79020	7.46994	+0.00020	7.47014	0.908979	72.579
3	7	10.89713	11.98727	+0.00030	11.98757	0.909036	72.603
4	24	7.72394	8.49697	+0.00100	8.49797	0.908916	72.551
5	8	9.90366	10.89499	+0.00085	10.89584	0.908940	72.562
6	23	11.17556	12.29401	+0.00010	12.29411	0.909017	72.595
7	10	9.59408	10.55436	−0.00010	10.55426	0.909024	72.598
8	21	10.69340	11.76371	−0.00015	11.76356	0.909028	72.600
9	11	10.71709	11.78974	+0.00030	11.79004	0.908995	72.586
10	20	11.79501	12.97529	+0.00075	12.97604	0.908984	72.581
11	12	10.50295	11.55424	+0.00020	11.55444	0.908997	72.586
12	19	11.94787	13.14344	+0.00025	13.14369	0.909019	72.596
13	13	10.11814	11.13101	−0.00035	11.13066	0.909033	72.602
14	18	8.38344	9.22244	0.00000	9.22244	0.909026	72.599
15	14	9.93784	10.93224	−0.00005	10.93219	0.909044	72.607
16	16	9.28357	10.21251	+0.00005	10.21256	0.909035	72.603
					Average	0.909005	72.590
				Average, omitting	Analyses 4 and 5	0.909016	72.595

TABLE IV

The Atomic Weight of Germanium
Series II GeBr$_4$: 4 AgBr

Number of analysis	Fraction of GeBr$_4$	Weight of GeBr$_4$ in vacuum gram	Weight of AgBr in vacuum gram	Loss on fusion gram	Dissolved AgBr gram	Corrected Weight of AgBr in vacuum gram	Ratio 4AgBr: GeBr$_4$	Atomic weight of germanium
17	6	6.39771	12.25240	0.00030	0.00012	12.25222	0.522167	72.579
18	25	6.79020	13.00453	0.00033	0.00011	13.00431	0.522150	72.567
19	7	10.89713	20.86771	0.00027	0.00038	20.86782	0.522198	72.603
20	24	7.72394	14.79273	0.00039	0.00010	14.79244	0.522155	72.570
21	8	9.90366	18.96701	0.00044	0.00014	18.96671	0.522160	72.574
22	23	11.17556	21.40114	0.00048	0.00026	21.40092	0.522200	72.604
23	10	9.59408	18.37240	0.00037	0.00021	18.37224	0.522205	72.608
24	21	10.69340	20.47707	0.00046	0.00020	20.47681	0.522220	72.619
25	11	10.71709	20.52364	0.00038	0.00025	20.52351	0.522186	72.594
26	20	11.79501	22.58742	0.00045	0.00020	22.58717	0.522200	72.604
27	12	10.50295	20.11287	0.00042	0.00046	20.11291	0.522199	72.604
28	19	11.94787	22.88061	0.00047	0.00017	22.88031	0.522190	72.597
29	13	10.11814	19.37595	0.00037	0.00022	19.37580	0.522205	72.608
30	18	8.38344	16.05424	0.00041	0.00017	16.05400	0.522203	72.607
31	14	9.93784	19.03070	0.00034	0.00014	19.03050	0.522206	72.609
32	16	9.28357	17.77797	0.00029	0.00029	17.77797	0.522195	72.601
						Average	0.522190	72.597
						Average, omitting Analyses 20 and 21	0.522195	72.601
						Average of Series I and II		72.598

The weights were of gold-plated brass, except the fractional weights which were of platinum, and were compared by the Richards substitution method.[3]

All weighings were by substitution. In the case of the bulb and silver, the weights were substituted for the object weighed. In the case of the glass and the silver bromide the crucibles were substituted for similar counterpoises. A small quantity of impure radium bromide was kept in the balance case to prevent electrostatic effects.

Vacuum corrections were applied as follows:

TABLE II

Vacuum Corrections

	Density	Vacuum correction per gram
Weights	8.3	——
Air	0.001293 at 0° and 760 mm.	——
Glass	2.5	+0.00033
Silver	10.49	−0.000031
Silver bromide	6.47	+0.000041

Discussion of Results

In the following table the results are arranged in the order of decreasing volatility of the fractions analyzed.

TABLE V

The Atomic Weight of Germanium

Fraction	Atomic weight $GeBr_4 : 4\,Ag$	Atomic weight $GeBr_4 : 4\,AgBr$	Average
6	72.591	72.579	72.585
7	72.603	72.603	72.603
8	72.562	72.574	72.568
10	72.598	72.608	72.603
11	72.586	72.594	72.590
12	72.586	72.604	72.595
13	72.602	72.608	72.605
14	72.607	72.609	72.608
16	72.603	72.601	72.602
18	72.599	72.607	72.603
19	72.596	72.597	72.597
20	72.581	72.604	72.593
21	72.600	72.619	72.610
23	72.595	72.604	72.600
24	72.551	72.570	72.561
25	72.579	72.567	72.573

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[3] Richards: J. Am. Chem. Soc., 22, 144, (1900).

Since the more probable low-boiling impurities, bromine, hydrogen bromide and silicon tetrabromide, if present, would lower the observed atomic weight, while the possible high-boiling impurities, the bromides, of tin, arsenic and antimony, would raise the observed atomic weight, it is natural to look for such a trend with changing volatility of material. Actually no such trend can be discovered. The variations seem to be fortuitous, except possibly in the case of the two least volatile fractions 24 and 25. But these two fractions give low values for germanium instead of high values. While these two results may have been affected by some unknown low-boiling impurity, the fact that other scattered results in the series are as low as these makes it unnecessary to assume such an explanation. Moreover, the visual evidence as to the absence of bromine and the negative test for silicon together with the spectroscopic evidence is in favor of uniform purity of all the fractions.

However, if any difference in purity exists, the middle fractions must have been the purer. Elimination of the three lightest fractions, 6, 7, 8, and the three heaviest, 23, 24, 25, raises slightly the averages of the two series to 72.596 and 72.605, with the combined average 72.601. These six fractions happen also to be the first six analyzed, and it is possible that lesser familiarity with the process may have been in part responsible for the fact that all the experiments which yielded low results are included among them.

After Analyses 11 and 27 had been completed the flask which was used at first for breaking the tetrabromide bulb was changed for a new one, since the first had been somewhat scarred in earlier work. We have no reason to believe that this change was of importance.

Furthermore a different sample of silver was used in Analyses 12-16 and 28-32 from that employed in the others; but since both specimens had been prepared by identical processes, here again there is little likelihood that the results were affected by the change. In fact the ratios of silver used to silver bromide obtained in the two parts of each analysis support this view. These ratios are given in the following table. In Analyses 6, 7, 8, 23 and 25 the silver bromide was tested for germanium by photographing the arc spectra on graphite electrodes in a Féry quartz spectrograph. No evidence of even traces of germanium could be found.

The average of the first eleven experiments differs from that of the last five by only 0.0016 per cent. Since the latter is almost identical with the value found by Baxter[1] and by Hönigschmid and Zintl,[2] 0.574453, these five experiments may be on the whole considered the most satisfactory of all. The average atomic weight of germanium found in the last five experiments in the first series is 72.601, and in the second 72.604.

The value 72.60 thus seems to represent fairly the result of our analysis of germanium tetrabromide. This is identical with the value found by analysis of the tetrachloride. As pointed out in the paper on the tetrachloride this

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[1] Baxter: Proc. Am. Acad, 42, 201, (1906).

[2] Hönigschmid and Zintl: Ann., 433, 201, (1923).

TABLE VI

Ag : AgBr

Analyses	Fraction of $GeBr_4$	Ration Ag : AgBr
1 and 17	6	0.574436
2 and 18	25	0.574436
3 and 19	7	0.574452
4 and 20	24	0.574481
5 and 21	8	0.574472
6 and 22	23	0.574466
7 and 23	10	0.574468
8 and 24	21	0.574482
9 and 25	11	0.574465
10 and 26	20	0.574487
11 and 27	12	0.574479
12 and 28	19	0.574454
13 and 29	13	0.574462
14 and 30	18	0.574464
15 and 31	14	0.574456
16 and 32	16	0.574450
	Average	0.574463
Average from Analyses 1-11		0.574466
Average from Analyses 12-16		0.574457

result is in accord with the mass spectrograph results of Aston[1] who estimates the proportions of the isotopes of germanium, 70, 72 and 74 to be 2:4:5. These figures lead to an average atomic weight of 72.55.

Summary

1. Pure germanium tetrabromide has been prepared by fractional distillation in exhausted vessels.

2. The atomic weight of germanium has been found to be 72.60 by analysis of germanium tetrabromide. This value is identical with that previously found by analysis of the tetrachloride.

We are especially indebted to the Bache Fund of the National Academy of Sciences for generous assistance in providing much of the necessary apparatus and materials, and to the New Jersey Zinc Company for the gift of germaniferous zinc oxide.

Cambridge, Massachusetts.

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[1] Aston: Phil. Mag., 47, 394, (1924).

THE DECOMPOSITION POTENTIALS AND POLARIZATION OF CERTAIN HEAVY METALLIC CHLORIDES DISSOLVED IN ANHYDROUS PYRIDINE[*]

BY RALPH B. MASON AND J. H. MATHEWS[**]

The study of decomposition potentials and polarization of non-aqueous electrolytes has mainly been limited to the lighter metals. This has been due to the fact that the lighter metals react readily with water and can be studied more satisfactorily when dissolved in a non-aqueous solvent with which they react less vigorously.

Patten and Mott[1] studied the decomposition curves of lithium chloride dissolved in pyridine and in acetone. The polarization at the anode and cathode was followed by means of the calomel electrode which was used as a reference electrode. They tried to avoid the entrance of moisture from the calomel electrode by using an intermediate solution of lithium chloride in pyridine or acetone as the case might require.

In a study of the electrical decomposition of the metallic salts dissolved in anhydrous pyridine, R. Müller[2] tested various reference electrodes, using pyridine instead of water. He found the $AgNO_3$ electrode as described by Abegg and Neustadt[3] to be the most reliable. Müller and his students worked with several salts dissolved in pyridine, using both platinum and mercury electrodes. They repeated the work of Patten and Mott and in addition ran several other salts of light metals[4]. They also worked with salts of the heavier metals[5].

The present research was carried out for the purpose of gaining some information as to what takes place when small potentials are applied to certain heavy metallic chlorides dissolved in pyridine.

Apparatus. The decomposition cell contained 2 electrodes of bright platinum foil 15 mm. by 15 mm. and about 6 mm. apart. The reference electrode was always an amalgam of the metal which was to be plated out, contact to which was made by means of a platinum wire sealed through the glass in the bottom of the cell. A side tube at the top of the cell could be opened or closed by turning the glass stopper which closed the cell to air and moisture. The cell had a resistance of 92.6 ohms when filled with N/50 KCl solution at 25°C.

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[*] A portion of a thesis submitted by Ralph B. Mason in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[**] Contribution from the Laboratory of Physical Chemistry of the University of Wisconsin.

[1] J. Phys. Chem. 12, 49 (1908).

[2] Monatsheft, 43, 2, 67)1923).

[3] Z. Elektrochem. 15, 264 (1909).

[4] Monatsheft, 43, 419 (1923).

[5] Monatsheft, 44, 219 (1924).

The Leeds and Northrup type K potentiometer and their highly sensitive ballistic galvanometer were used in this research. The rotating commutator consisted of a bakelite disc about three and one-half inches in diameter so constructed that the center brush was always in contact with the copper disc. The other two brushes were alternately brought in metallic contact with the center brush by the revolution of the disc, rotated at the rate of twelve hundred times per minute.

The thermostat was filled with a light cylinder oil the temperature of which could be controlled to .01°. The thermometer was compared with one standardized by the United States Bureau of Standards.

The pyridine was purified by the method described in the solubility of $ZnCl_2$ or by the ferrocyanide method[1] and was always very carefully dehydrated before using.

Method. The amalgam which was to serve as the reference electrode was introduced into the carefully cleaned and dried decomposition cell. The anhydrous salt was then added and the cell evacuated and filled with pure dry nitrogen. The pyridine was next distilled into the cell, special care being taken that no moisture entered during the operation. The evacuation and filling with nitrogen were repeated several times to free the solution of all dissolved oxygen. After this treatment the cell was placed in the bath, held at 30°, and allowed to stand until the solution was saturated. In this manner a reference electrode was constructed which consisted of an amalgam covered with an excess of a salt of the metal used in the amalgam.

Increasing E. M. F.'s were applied to the cell by means of a sliding wire potentiometer. The potentiometer was used to measure the E. M. F. applied to the electrodes and also the current by reading the drop in potential across a 100 ohm resistance in series with the cell. The rotating commutator was used while the polarization at either electrode or the total polarization was being read, and was so connected that the polarizing current was off while the polarization was being measured.

For the decomposition curves, current densities were plotted as ordinates and the applied E. M. F.'s as abscissa. The polarization curves were made by plotting volts of polarization as ordinates and the applied E. M. F.'s as abscissa.

Zinc Chloride in Anhydrous Pyridine

The sample of $ZnCl_2 \cdot 2C_5H_5N$ was the same as that used in the solubility determinations (see first paper in this series). The pyridine was extra pure and boiled at 115.3° at 760 mm. Hg.

The solution of $ZnCl_2$ in pyridine was a fair conductor and the polarization was quite easy to read. The decomposition potential was about 1.75 volts (Table I, Fig. 1). Around eight volts the current became somewhat unsteady due to the fact that the solution was being depleted of the dissolved salt and that chlorine was being given off at the anode, the solution turning yellowish

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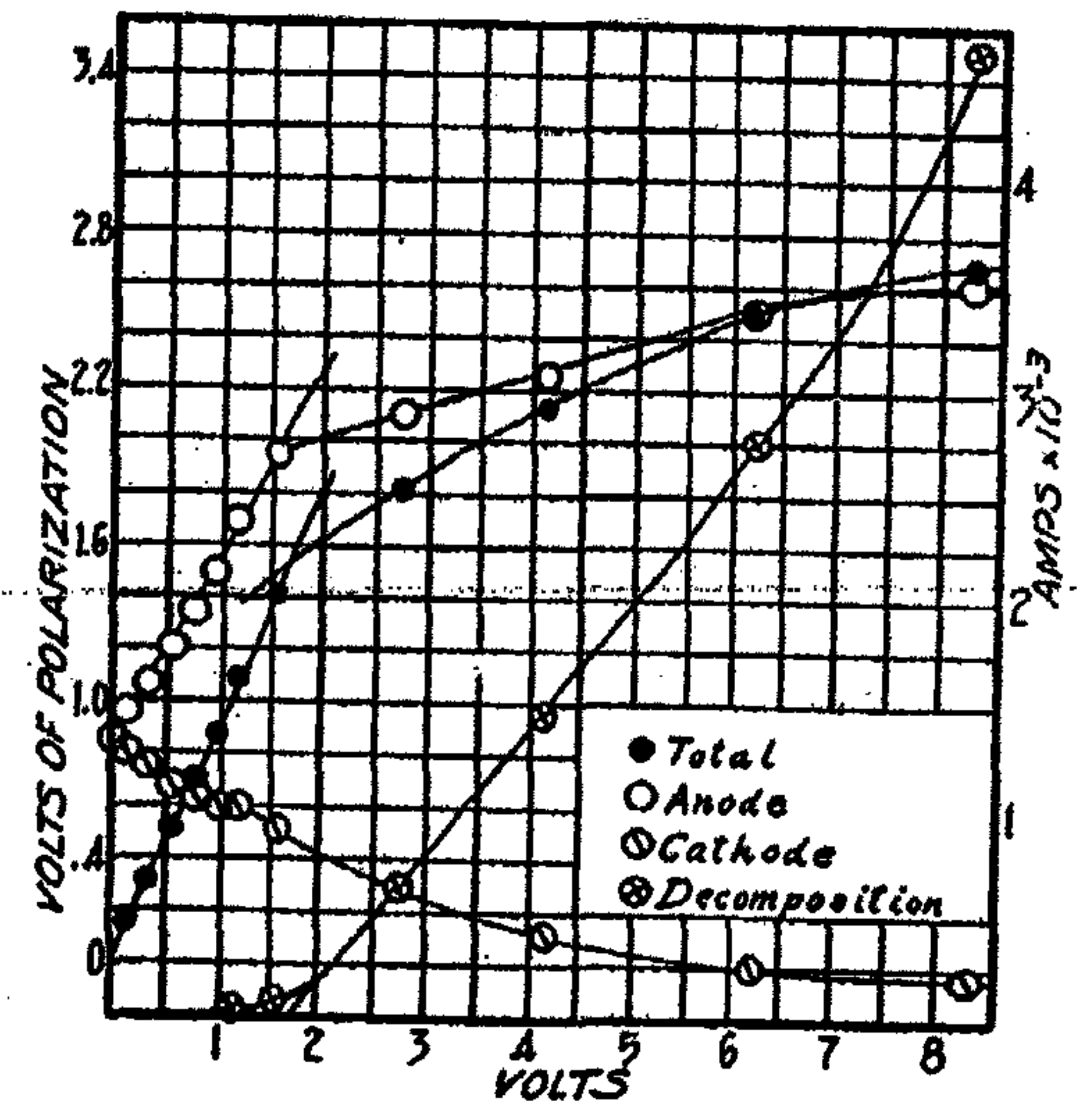
[1] Mohler: Ber. 21, 1015 (1888).

brown. The current was allowed to pass over night and in the morning the cathode was covered with a grayish spongy mass of zinc.

The break in the curve for total polarization came at practically the decomposition voltage as found by the extension of the decomposition curve to the X axis. The breaks in the polarization curves for the anode and cathode came at 1.6 volts and 1.25 volts respectively. The polarization at the cathode increased until at six volts it had reached the potential of the zinc amalgam.



. Fig. 1

Table I

Zinc Chloride in Pyridine
Saturated at 30°C.

Amps. 10^{-4}	E. M. F.	Total	Polarization Anode	Cathode
.000	.000	.000	.845	.846
.000	.158	.157	.959	.803
.000	.318	.316	1.072	.759
.010	.533	.517	1.201	.683
.015	.740	.711	1.354	.643
.020	.931	.888	1.492	.604
.25	1.148	1.092	1.694	.605
.80	1.581	1.426	1.949	.520
6.20	2.758	1.828	2.107	.273
14.44	4.140	2.132	2.252	.119
27.50	6.213	2.511	2.542	.026
46.30	8.276	2.682	2.620	*.052
65.60	10.336	2.724	2.661	*.113

*Sign changed.

It continued to increase very gradually and was several millivolts negative to the zinc amalgam at ten volts. Cohen[1] found that there was very little difference in potential between massive zinc and ten percent zinc amalgam. The polarization at the anode increased gradually after the decomposition voltage had been passed. The decomposition and polarization curves for $ZnCl_2$ in pyridine were very similar to those obtained in water using the same concentration of $ZnCl_2$. The decomposition point was somewhat lower in pyridine than in water.

Müller has run the decomposition potential and polarization curves for ZnI_2 in pyridine (saturated at 18°). His polarization curve for the cathode differed considerably from the one found here. He found that the zinc reached a minimum negative potential and then became more noble with increasing current densities. In the case of the zinc chloride solution, the potential of the zinc became gradually more negative but this was no doubt due to the use of a different reference electrode and different current densities.

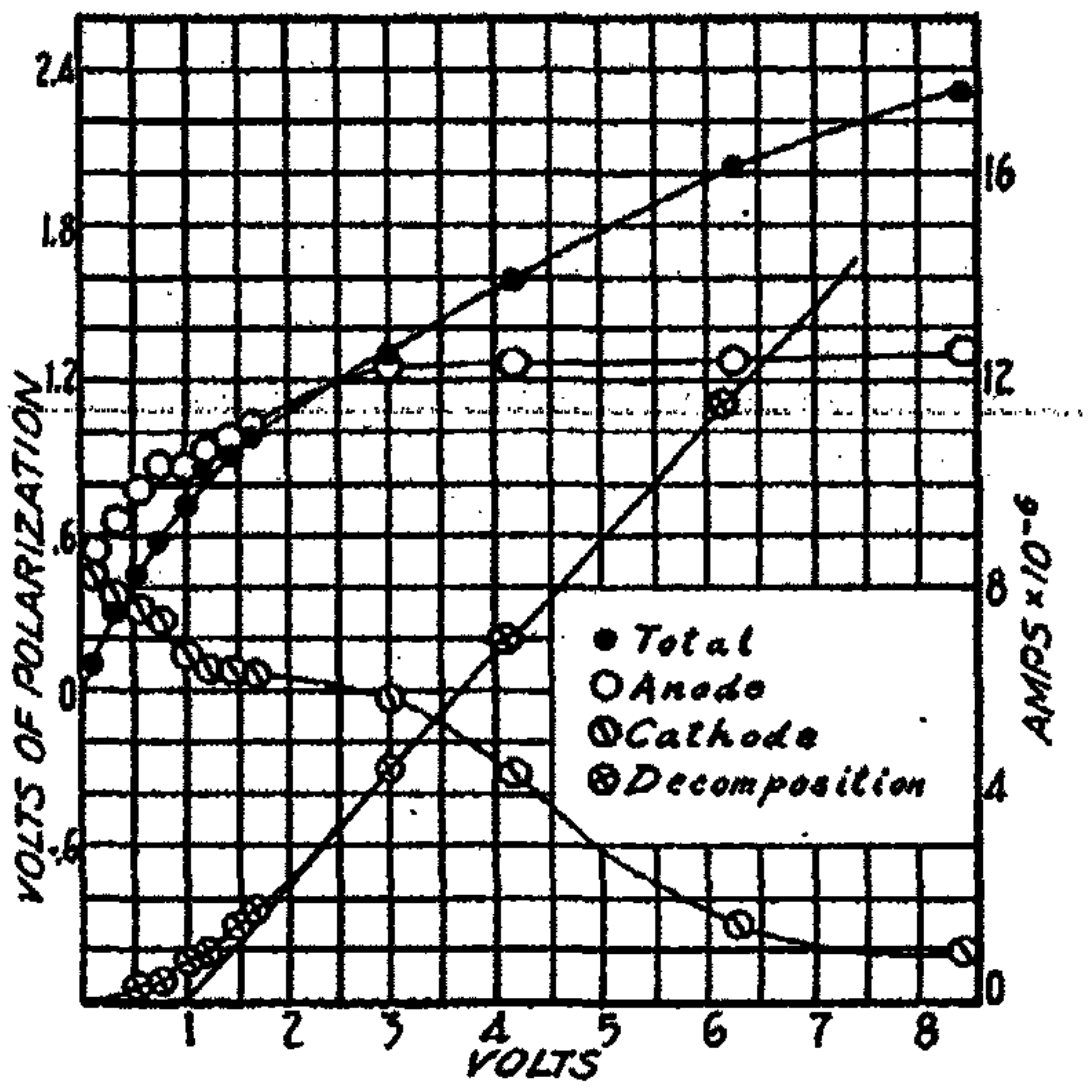


FIG. 2

Cadmium Chloride in Anhydrous Pyridine

The cadmium chloride was prepared in the same manner as for the solubility determinations. The pyridine used was extra pure and boiled at 115.3° at 760 mm. Hg. Cadmium chloride was only slightly soluble in pyridine at 30° and the solution was a very poor conductor. This made it extremely difficult to run.

The decomposition potential was about 1 volt (Table II, Fig. 2). This value is much smaller than Müller obtained for CdI_2. The potential of the cathode increased until at eight volts it was nine tenths of a volt more nega-

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[1] Kon. Akad. Wet. Amsterdam, 12, 98 (1909-10).

tive than the Cd amalgam (12.5 percent Cd). This is a large difference but was probably due to the small amount of cadmium chloride in solution. The current was allowed to flow for ten hours and the cadmium plated out on the cathode as a gray-black spongy mass. The solution turned brown as usual in chloride solutions.

TABLE II

Cadmium Chloride in Pyridine
Saturated at 30°C.

Amps. 10^{-5}	E. M. F.	Total	Polarization Anode	Cathode
.00	.000	.000	——	——
.00	.132	.110	.552	.443
.00	.334	.285	.656	.370
.03	.554	.458	.784	.330
.04	.782	.598	.873	.275
.08	1.006	.712	.861	.147
.10	1.229	.849	.928	.082
.15	1.460	.895	.978	.085
.17	1.659	.975	1.025	.072
.45	3.031	1.294	1.266	*.041
.70	4.177	1.593	1.265	*.325
1.15	6.275	2.182	1.277	*.909
1.45	8.374	2.326	1.306	*1.003
1.87	10.467	2.416	1.336	*1.067

Mercuric Chloride in Pyridine

Lang[1] and Reitzenstein[2] have studied the compound $HgCl_2 \cdot C_5H_5N$ and the formation of $HgCl_2 \cdot C_5H_5N$, $HgCl_2 \cdot 2C_5H_5N$, and $3HgCl_2 \cdot 2C_5H_5N$ have been investigated by Pesci[3]. McBride[4] determined the temperature solubility curve for $HgCl_2$ in pyridine, and Anderson[5] ran the conductance of $HgCl_2$ in pyridine at 0°, 25° and 50° and found the equivalent conductance to be very low.

The mercuric chloride was purified by resubliming. The pyridine was extra pure and boiled at 115.3° at 760 mm. Hg. The mercury used for reference electrode was specially purified (see paper on transition cells).

The decomposition potential for $HgCl_2$ in pyridine was about .65 volts (Table III, Fig. 3). There was a very peculiar hump in the curve under one volt. Attention is called to the fact that until the decomposition potential was reached, there was very little polarization at either electrode. Since the platinum and mercury are very close together in the electrochemical series

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[1] Ber. 21, 1578 (1888).
[2] Ann. Chim. Phys. 43, 839 (1891).
[3] Gazz. 25 II, 423 (1895).
[4] J. Phys. Chem. 14, 189 (1910).
[5] J. Phys. Chem. 19, 753 (1915).

the cathode polarization was very small. If chlorine was liberated before the decomposition potential was reached, it was evidently combined with something which acted as a depolarizing agent.

When mercurous chloride is added to pyridine the following reaction takes place:

$$Hg_2Cl_2 + 2C_5H_5N \rightleftarrows HgCl_2 \cdot 2C_5H_5N + Hg$$

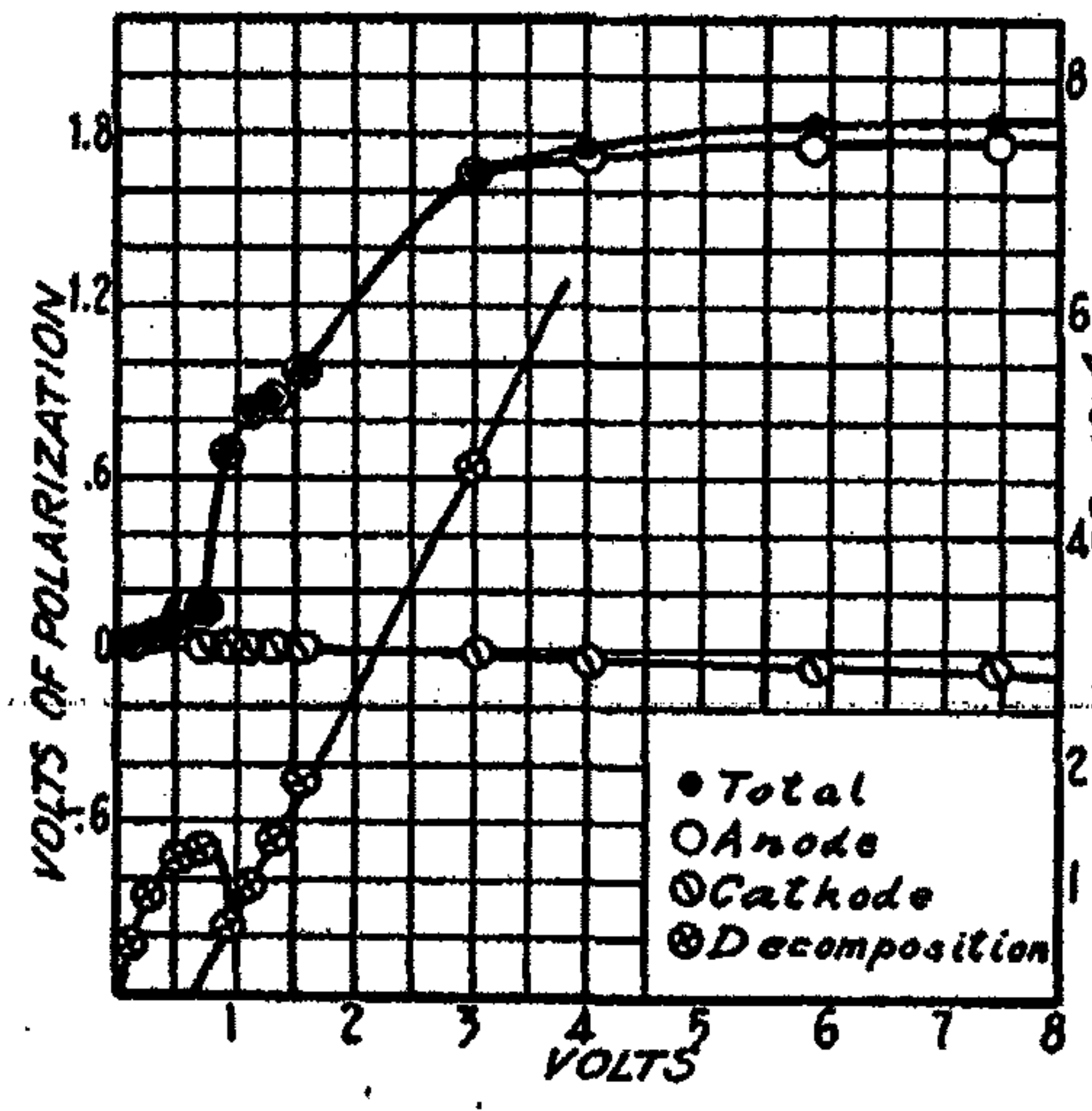

Fig. 3

Table III

Mercuric Chloride in Pyridine
Saturated at 30°C

Amps. 10^{-4}	E. M. F.	Polarization Total	Anode	Cathode
.00	.000	.000	.003	.033
.41	.126	.014	.041	.028
.85	.299	.038	.058	.022
1.19	.502	.071	.090	.017
1.23	.715	.159	.165	.011
.55	.919	.692	.713	.017
.91	1.142	.836	.853	.017
1.36	1.330	.889	.906	.016
1.86	1.545	.965	.981	.011
4.66	3.064	1.656	1.641	*.011
11.09	4.012	1.769	1.735	*.039
28.73	5.932	1.837	1.779	*.056
77.55	7.477	1.845	1.785	*.065
141.00	8.763	1.797	1.737	*.068

*Sign changed.

No doubt this reaction is somewhat reversible and a mercuric salt would be reduced to a slight extent by metallic mercury. The presence of a minute quantity of mercurous salt in the decomposition cell would explain the depolarizing action found at the anode.

Lead Chloride in Pyridine

Several compounds of lead chloride and pyridine have been described in the literature. Classen and Zahorski[1] prepared a compound to which they gave the formula $3PbCl_2 \cdot 4C_5H_5N$. Pincussohn[2] prepared another compound which he said had the formula $4PbCl_2 \cdot 3C_5H_5N$. Reitzenstein[3] prepared still another compound whose formula is $PbCl_2 \cdot C_5H_5N$. Heise,[4] from the temperature solubility curve, concluded that there was only one compound of $PbCl_2$ and pyridine between −20° and 102° and that this compound was $PbCl_2 \cdot 2C_5H_5N$. Anderson ran the conductance of $PbCl_2$ in pryidine at 0°, 25°, and 50° and found its equivalent conductance to be low.

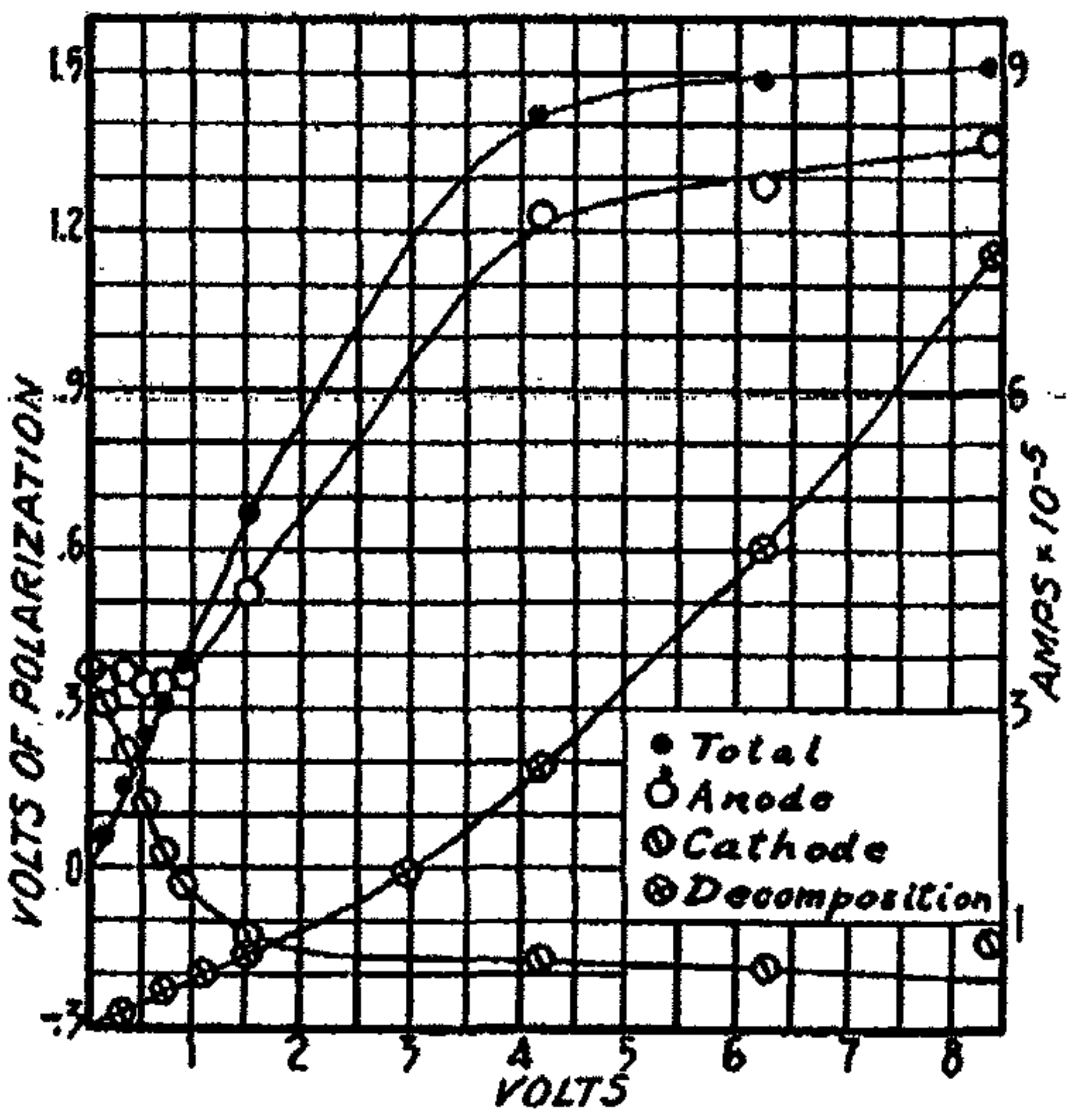

FIG. 4

The lead chloride was purified by recrystallizing twice from hot water. It was then dried at 110° for several hours. The pyridine boiled at 114.4-114.7° at 738.3 mm. Hg. (corr).

The solution of $PbCl_2$ in pyridine was a poor conductor and it was difficult to read the polarization until two volts were reached, but from this point on it was fairly easy to read. There was no definite break in the decomposition curve and the total polarization increased rather uniformly (Table IV, Fig. 4). The cathode polarization increased until the cathode was .2 volt negative to

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[1] Z. anorg. Chem. 4, 110 (1893).

[2] Z. anorg. Chem. 14, 384 (1897).

[3] Z. anorg. Chem. 18, 289 (1898).

[4] J. Phys. Chem. 16, 378 (1912).

the lead amalgam. Further increase in current density caused it to become more positive. The anode curve is interesting in that there is apparently no chlorine evolved until one volt is reached. From there on the curve is normal.

The action at the anode seems to indicate that there is present in the solution a substance which combines with small amounts of chlorine. There is the possibility that lead exhibits two valences in pyridine solution and that at the anode the lead with the lower valence is oxidized to the higher valence.

The current was allowed to flow through the cell for ten hours. A brownish flocculent precipitate formed on the cathode and remained as a yellow deposit after washing with water. The solution turned brown, as usual in chloride solutions.

TABLE IV

Lead Chloride in Pyridine
Saturated at 30°C.

Amps. 10^{-5}	E. M. F.	Polarization Total	Anode	Cathode
.00	.000	.000	.367	.367
.05	.140	.059	.366	.309
.15	.341	.152	.369	.223
.25	.536	.250	.344	.122
.32	.724	.314	.343	.035
.40	.915	.388	.366	*.028
.45	1.133			
.56	1.340			
.68	1.535	.675	.526	*.127
1.45	2.982			
2.44	4.201	1.422	1.230	*.177
4.50	6.285	1.492	1.291	*.191
7.30	8.372	1.518	1.374	*.141
15.40	10.459	1.571	1.414	*.114

*Sign changed.

Cuprous Chloride in Pyridine

Lang[1] described two compounds of cuprous chloride and pyridine, $Cu_2Cl_2 \cdot 4C_5H_5N$ and $Cu_2Cl_2 \cdot 6C_5H_5N$. Naumann[2] stated that cuprous chloride is soluble in pyridine. Müller electrolysed a solution of Cu_2I_2 in pyridine and followed the polarization at the electrodes.

The cuprous chloride was purified by dissolving some of the C. P. salt in conc. HCl. The solution was diluted with water and the precipitated Cu_2Cl_2 washed by decantation. The treatment with HCl and water was repeated and the salt finally washed onto a filter. It was washed with glacial acetic acid and finally with anhydrous ether. The white salt was dried at 110° and

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[1] Ber. 21, 1578 (1888).

[2] Ber. 37, 4109 (1904).

kept in a desiccator out of contact with air and moisture. The cuprous chloride dissolved completely in pyridine forming a beautiful green solution. The copper amalgam was made electrolytically and contained five percent copper.

The copper amalgam did not act well as a reference electrode and it was impossible to measure the polarization by the commutator method except in case of the total polarization. The polarization of the cathode and anode was therefore measured while the polarizing current was flowing. A glance at Table V and Fig. 5 will show that this method of measuring polarization gives a different type of curve than the method used in previous experiments.

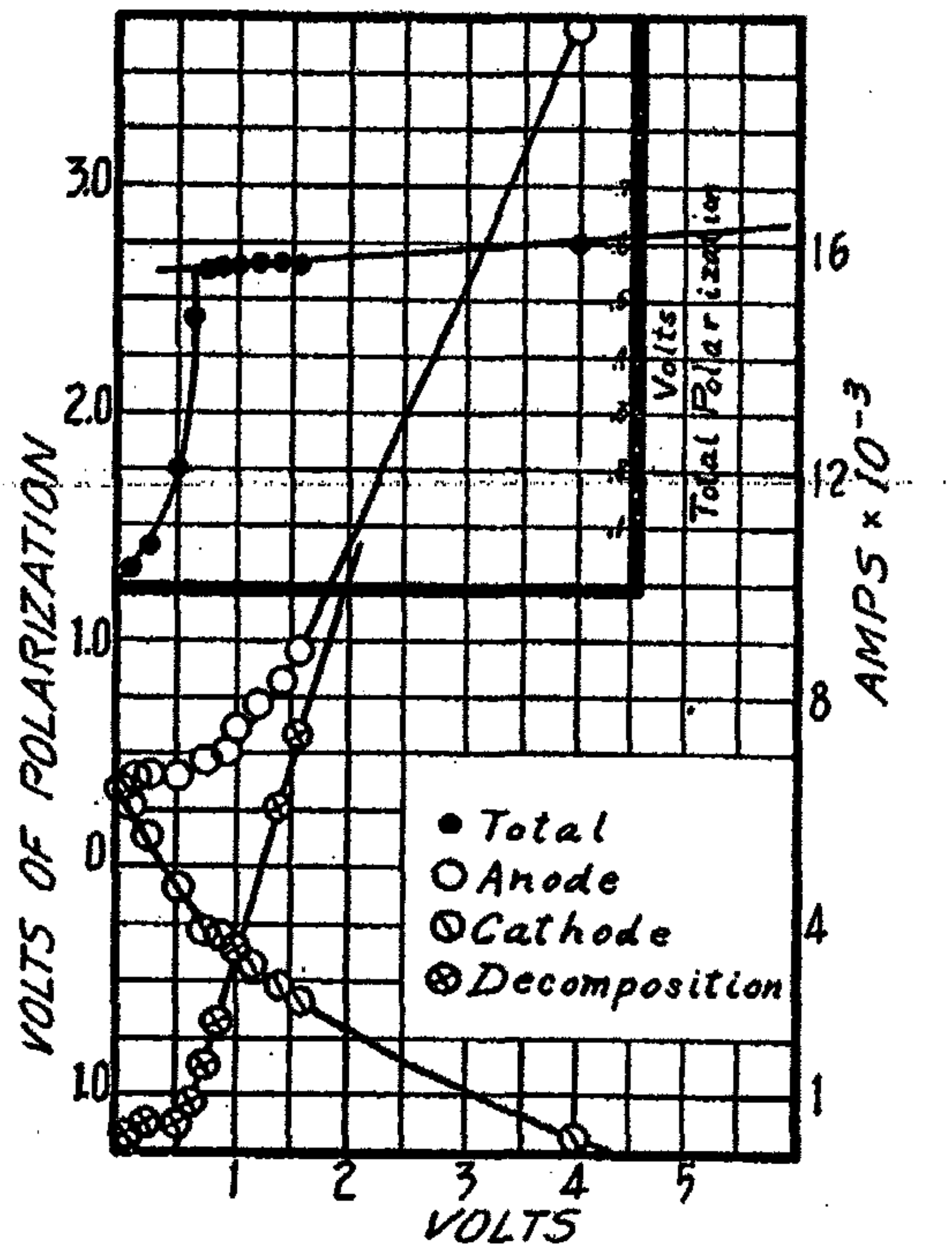

Fig. 5

The decomposition potential was .5 volt. Müller obtained this same value for the decomposition of cuprous iodide but says that it was due to traces of cupric iodide which are always present and represents the change of Cu^{++} to Cu^{+}. He obtained another decomposition point at 2.8 volts which he said was the decomposition potential of the cuprous iodide. This second break was not obtained in the case of the cuprous chloride since the cell became very erratic in its behavior after 4 volts were reached. However the solution was a good conductor and the 100 ohm fixed resistance should have been smaller. This may account for the fact that the second break was not found.

The curve for the total polarization breaks very sharply at .7 volt. Since the anode and cathode polarizations were measured while the current was flowing they are not strictly comparable with the results obtained in the pre-

TABLE V

Cuprous Chloride in Pyridine
Saturated at 30°C.

Amps. 10^{-3}	E. M. F.	Polarization (No Commutator) Total	Anode	Cathode
.00	.000	.000	.345	.345
.39	.115	.035	.390	.278
.54	.273	.077	.404	.138
.53	.512	.202	.405	*.095
.84	.668	.476	.425	*.219
1.53	.768	.551	.478	*.264
2.33	.875	.554	.540	*.304
3.34	1.015	.562	.615	*.363
4.81	1.213	.569	.718	*.446
6.15	1.414	.565	.839	*.529
7.44	1.602	.561	.949	*.596
22.98	4.007	.604	3.715	*1.208
17.96	8.637	1.486	6.935	*1.506

*Sign changed.

vious experiments. However it will be noticed that the anode polarization increased more rapidly than the cathode polarization and that there was a depolarizing action at the anode under .5 volts.

The current was allowed to pass for several hours and the electrodes were carefully examined. There was a brownish-red deposit of copper on the cathode and a thick layer of a closely adhering bluish-green compound on the anode. Müller observed the same sort of compound in the case of the cuprous iodide and said that it was a cuprous compound. In the case of the cuprous chloride solution, the compound formed has the same appearance as $CuCl_2.2py$ and since it is only very slightly soluble in pyridine, it seems more likely to be the cupric salt.

The cuprous salt could ionize in the following way:

$$Cu_2Cl_2 \rightleftarrows CuCl_2 + Cu^+$$

We would then have the cupric salt deposited at the anode. Or if chlorine is liberated at the anode, it could react with some cuprous chloride in solution and form the less soluble cupric salt which would separate out on the electrode.

The formation of this salt at the electrode explains why it was practically impossible to measure the polarization of the anode against the reference electrode.

Cupric Chloride in Pyridine

The compound $CuCl_2 \cdot 2C_5H_5N$ was isolated by Lang. Lachowicz[1] prepared another compound whose formula is $2CuCl_2.3C_5H_5N$. Kohlschuetter,[2]

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[1] Monatsheft, 10, 890 (1889).
[2] Ber. 37, 153 (1904).

Naumann[1], and Mathews and Spero[2] all obtained blue solutions when the cupric chloride was dissolved in pyridine. Anderson claimed that cupric chloride gives a green solution in pyridine and that the blue solution is due to traces of moisture.

Pure cupric chloride was recrystallized from a saturated solution by precipitating with gaseous HCl. This was repeated twice and after filtering, the salt was dehydrated. The dehydrated salt was treated in two ways. One portion was heated for ten to twelve hours at 105°-110° and the pyridine distilled directly into the flask. This gave a blue solution. The other portion was heated to 160° in a stream of HCl gas and cooled in an atmosphere of N_2. It was then heated on the air bath to 160° as specified by Anderson. This gave a green solution in pyridine. Traces of moisture added to this solution did not cause it to turn blue.

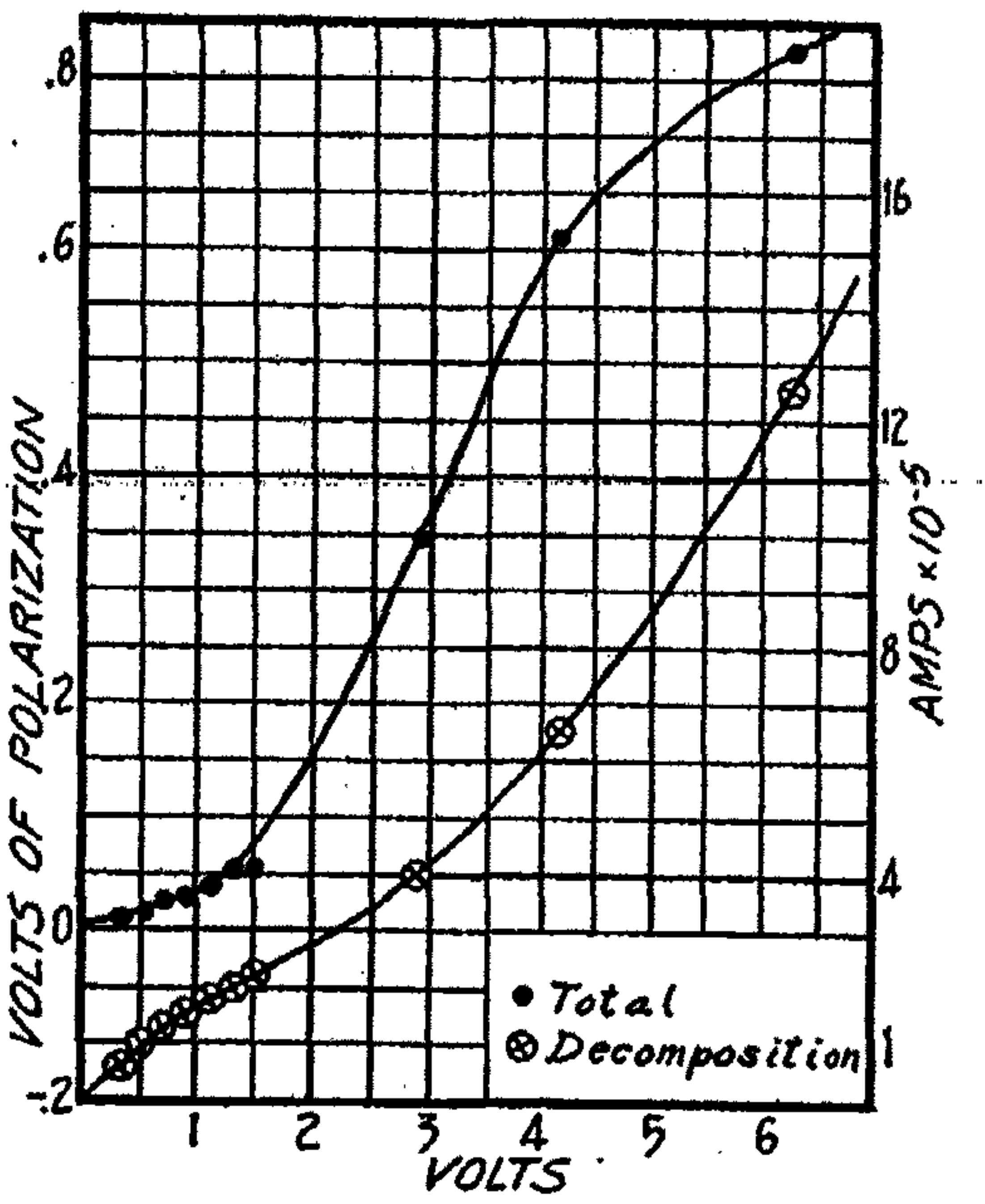

FIG. 6 (a)

Copper amalgam can not be used as a reference electrode in the electrolysis of cupric chloride. If metallic copper is added to a solution of $CuCl_2$ containing an excess of salt, after long standing, the excess salt disappears and the solution turns green. The following reaction takes place

$$CuCl_2 + Cu \rightleftarrows Cu_2Cl_2$$

and since the Cu_2Cl_2 is much more soluble in pyridine than $CuCl_2$, the excess salt disappears.

Since there was no reference electrode, only the decomposition potential curves and total polarization curves are shown for the cupric chloride solu-

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[1] Ber. 37, 4609)1904).

[2] J. Phys. Chem. 21, 402 (1917).

tions. The results of the salt that was heated only to 110° are given in Table VI a, Fig. 6 (a) while Table VI b, Fig. 6(b) gives the results of the salt prepared by heating to 160°.

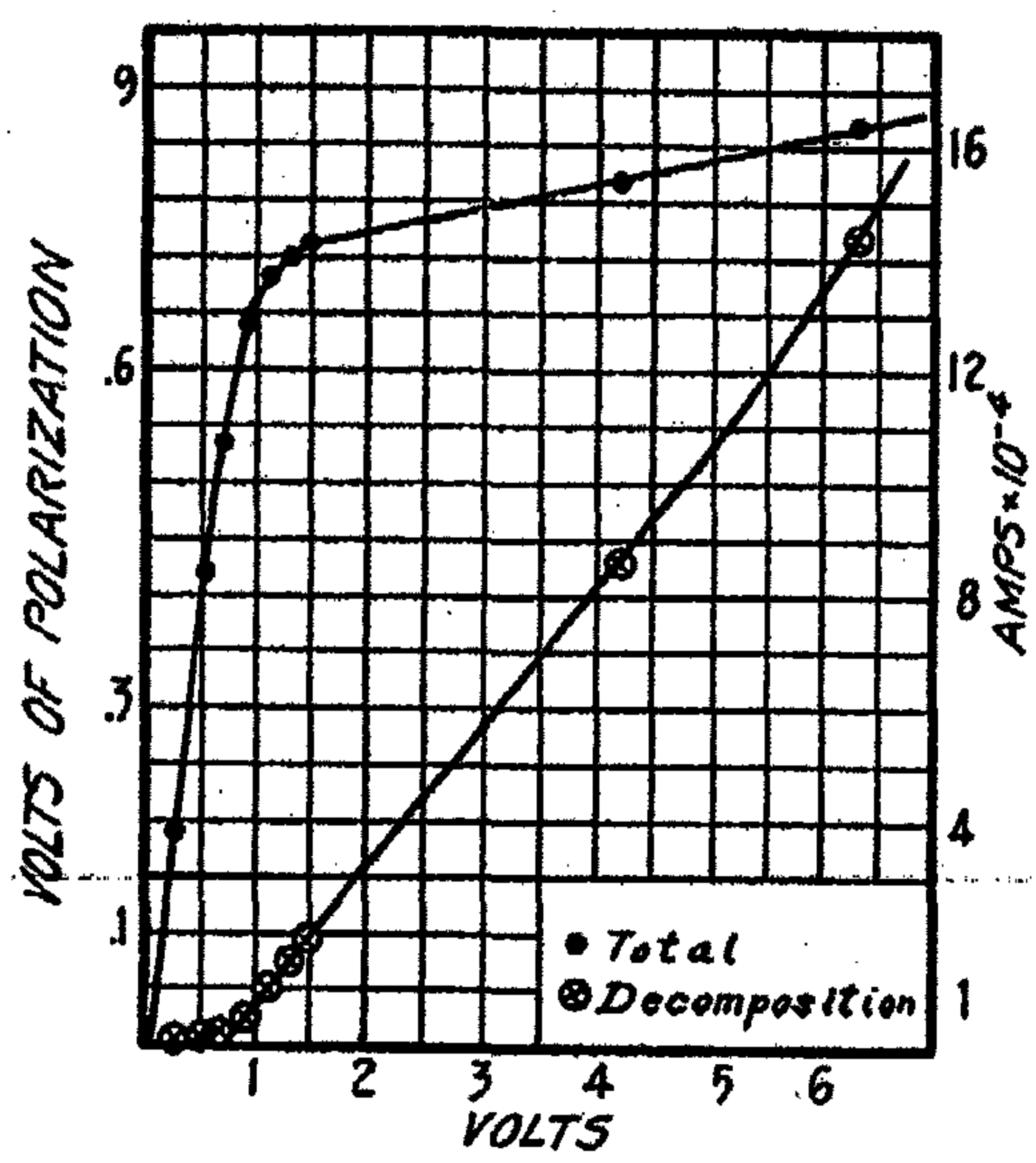

Fig. 6 (b)

TABLE VI

Cupric Chloride in Pyridine
Saturated at 30°C.

(a)

Amps. 10^{-6}	E. M. F.	Total Polarization
.00	.000	.000
.30	.164	.004
.60	.346	.010
1.00	.559	.015
1.25	.740	.027
1.57	.930	.030
1.82	1.133	.037
2.00	1.346	.055
2.20	1.537	.057
4.05	2.920	.345
6.54	4.187	.610
12.50	6.290	.775
20.65	8.382	.837
33.70	10.460	.890

(b)

Amps. 10^{-6}	E. M. F.	Total Polarization
.00	.000	.000
.75	.078	.005
1.00	.290	.194
1.30	.508	.423
2.35	.719	.534
5.70	.914	.649
10.30	1.126	.682
14.90	1.321	.707
19.20	1.497	.714
86.0	4.2	.771
144.9	6.3	.821
216.2	8.4	.867
297.7	10.5	.875

Both solutions were very poor conductors. In the case of the blue solution there was no definite decomposition point and there was very little polarization under 1.5 volts. The green solution showed a decomposition potential at about .7 volts and the polarization increased rapidly until 1.5 volts was reached. The current was allowed to pass over night and copper plated out on the cathode in both cases. The blue solution very quickly turned green due to the passage of the current. A very little cuprous chloride obscured the blue of the cupric. When the cupric chloride was heated to 160°, it is probable that a small amount was changed to the cuprous and this accounted for the color and the fact that the green solution was a better conductor.

Mercuric Sulfate in Pyridine

Mercurous salts are decomposed by pyridine into mercury and the mercuric compound. This has been observed by Lang (loc. cit.) and others. The decomposition is not surprising when we recall the action of ammonia on mercuric salts and remember the basic nature of pyridine.

Table VII

Mercuric Sulfate in Pyridine
Saturated at 30°C.

Amps. 10^{-5}	E. M. F.	Total	Polarization Anode	Cathode
.00	.000	.000	.004	.004
.05	.132	.048	.001	*.046
.10	.335	.113	.000	*.106
.15	.564	.159	.001	*.132
.20	.768	.214	.001	*.149
.25	.970	.291	.030	*.185
.30	1.169	.354	.076	*.155
.35	1.363	.456	.182	*.225
.40	1.567	.581	.208	*.387
1.25	4.1			
2.30	6.2			
3.20	8.3			
5.50	10.4			

*Sign changed.

In searching for a reference electrode which could be used in pyridine solution as the calomel is in aqueous, a mercuric sulfate electrode was suggested. Therefore the decomposition of a saturated mercuric sulfate solution was studied. The results obtained are given in Table VII. The solution was an extremely poor conductor and the measurement of the polarization very difficult. There was apparently no decomposition point, due to the extremely low solubility and low current density obtained. It was therefore concluded that the mercuric sulfate was insoluble enough not to interfere with the decomposition of another electrolyte in the decomposition cell. Some mercury was covered with a layer of anhydrous mercuric sulfate and an excess of cupric chloride added to the cell. In the course of a day the excess of cupric chloride disappeared and a dark blue compound appeared on the surface of the mercuric sulfate. The following reaction had taken place

$$CuCl_2 + HgSO_4 \longrightarrow CuSO_4 + HgCl_2$$

The mercurous sulfate was more soluble than the cupric sulfate and mercuric chloride, which is quite soluble, had gone into solution. However not all of the blue color had disappeared. The cupric sulfate is insoluble in pyridine but reacts with it to form an insoluble complex.

Discussion of Results

A study of the behavior of certain metallic chlorides in pyridine when an electric current is flowing has been made, not so much for the purpose of finding the decomposition potential, the nature of the deposit, etc., but rather, to test the behavior of the reference electrode. These observations were incidental to the other, nevertheless interesting. In each case, the reference electrodes employed were the electrodes used in the transition cells described in the following paper.

The reference electrode consisted of an amalgam covered with a paste of the salt of the metal in the amalgam. The inert platinum electrodes were used as collectors of small amounts of chlorine and the metal in question. In this way a study could be made of what happens to the electrolyte when a small potential is applied and at the same time the action of the reference electrode could be determined.

A study of the polarization curves for lead chloride shows that the cathode behaves in a regular manner. With increasing applied E. M. F. the amount of lead plated out on the cathode increases and this is shown by the gradual decrease in the potential between that electrode and the reference electrode. After the electrode becomes a massive lead electrode the polarization becomes constant and we have the potential of massive lead against lead amalgam.

On the other hand the polarization at the anode does not start until nearly one volt is reached. This means that either chlorine is not plated out on the electrode or the reference electrode does not function in the case of small amounts of chlorine. For larger amounts of chlorine the electrode is apparently functioning and the polarization reaches a constant value. From the most peculiar behavior of the lead electrolyte found later it is probable that there is no chlorine separated out until a potential of one volt is reached. Evidently there is present in the solution a good depolarizing agent for small amounts of chlorine. For larger current densities, the chlorine is liberated more rapidly than the depolarizing agent can react with it and chlorine is separated out at the electrode.

Nothing can be said in regard to the copper-cuprous chloride electrode, since a study could not be made of the polarization at each electrode while the current was off. No doubt this study could be made in drier weather, but during the summer, when this work was done, there was too much leakage on the electrical apparatus.

The mercury electrode was similar to the lead electrode with respect to the anode polarization. There is a small amount of chlorine given off but at about one volt there is a break in the curve and from there on the amount increases rapidly.

The cadmium and zinc electrodes are normal in their behavior and are apparently reversible with respect to either small amounts of chlorine or of the metal. The cadmium shows a large difference in potential between the massive metal and the amalgam. This is due no doubt to the low solubility of the cadmium chloride and the small number of cadmium ions in solution. In the experimental cells the cadmium and zinc electrodes behave much better than any of the others tried.

Summary

1. The study of decomposition potentials and polarization curves has been used in the search for reference electrodes in anhydrous pyridine solutions. The Hg-Cd. $CdCl_2$ and Hg-Zn. $ZnCl_2$ reference electrodes were found to be the most satisfactory of all the electrodes investigated.

2. The decomposition potentials and polarization of saturated solutions of $ZnCl_2$, $CdCl_2$, Cu_2Cl_2, $CuCl_2$, $HgCl_2$, $PbCl_2$, and $HgSO_4$ in anhydrous pyridine have been determined. Where practical both the total polarization and the polarization at either electrode were investigated.

3. The solutions of $CdCl_2$ and $ZnCl_2$ in pyridine gave results very similar to those obtained when water was used as the solvent. The pyridine solutions of $PbCl_2$, $HgCl_2$ and Cu_2Cl_2 acted as if there was present a depolarizer for small amounts of chlorine.

4. Due to low solubility and conductance, the $CuCl_2$ solutions were very difficult to work with and the results obtained depended upon the method used to prepare the anhydrous salt. The cuprous chloride solution was a very good conductor but due to the formation of a compound on the anode, it was difficult to follow the polarization.

Madison, Wisconsin
May 1925.

INFLUENCE OF ADSORPTION ON THE COLOUR OF SOLS AND OF PRECIPITATES

BY N. R. DHAR

There is still considerable uncertainty concerning the colour of sols. The theoretical work on the optics of sols deals almost entirely with the light which is scattered from a given sample of a sol. In order to test the conclusions arrived at, spectrophotometric observations on the absorption of light by the same sample of the sol, have usually been undertaken. Steubing[1] has however, shown that a simple relation between the scattered and absorbed light need not necessarily exist.

Colloid chemists have naturally laid special emphasis on the relation of colour to the size of the particles of a sol.

Wo. Ostwald[2] comes to the following conclusions:—"With increasing degree of dispersion (i.e. decreasing size of particles) the absorption band of any colloidal solution moves to the shorter wave lengths" He also states that the absorption of a highly dispersed sol approximates to the absorption of the corresponding molecular solution. Regarding the first conclusion the following observations of Bancroft[3] will be of interest. "Colloidal gold solutions can be prepared which are red, violet, or blue by transmitted light. In general the blue gold solution contain coarser particles than the red ones, but this is not always true."

More or less similar conclusion is arrived at by Svedberg[4] and he observes that, as regards light absorption, there is no real difference between colloidal solutions made up of observable discrete particles and the corresponding molecular solutions.

In this paper I shall report certain results which will show that the colour of sols and of freshly coagulated substances depends a great deal on the nature of the material adsorbed by the sols or the coagulated mass. We shall first take the case of manganese dioxide sol.[5]

When a sol of MnO_2 is prepared by the interaction of $KMnO_4$ and H_2O_2 it is negatively charged and has a deep brown, almost black, colour. When such a negatively charged sol is treated with a few drops of $FeCl_3$, charge-reversal takes place and the sol becomes positively charged. This positive sol can be dialysed for about a week and no trace of ion is available in the wash water. Now the colour of the positively charged sol is distinctly reddish in comparison with with the colour of the negatively charged sol. When the positive sol is coagulated by some electrolyte the supernatant clear li-

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[1] Ann. Physik, (4) 26, 329 (1008).

[2] Kolloidchem. Beihefte, 2, 409 (1910-11); "Licht and Farbe der Kolloide" (1924).

[3] "Applied Colloid Chemistry", p. 203 (1921).

[4] Svedberg: "Die Existenz der Molecule" (1912).

[5] Ganguly and Dhar: J. Phys. Chem: 26, 701, 836 (1922); Sarkar and Dhar: Z. anorg. Chem. 121, 135 (1922); Chatterji and Dhar: Kolloid-Z. 33, 18 (1923).

quid is free from ferric iron whilst the coagulated mass when dissolved in HCl gives a slight indication of ferric ion. It appears probable, therefore, that the positively charged sol of MnO_2 is really a mixture of a large quantity of hydrated MnO_2 and a very small quantity of $Fe(OH)_3$ and that is why the colour is distinctly more red than the negatively charged sol.

When hydrated MnO_2 is precipitated by the interaction of $KMnO_4$ and $MnSO_4$ in presence of various electrolytes, we have observed different colours of the precipitated MnO_2. We have proved that MnO_2 in the course of its formation adsorbs appreciable quantities of positive ions. When MnO_2 is precipitated in presence either of $AgNO_3$, $Bi(NO_3)_3$, $HgCl_2$, $Ni(NO_3)_2$, or $Pb(NO_3)_2$ the precipitate has a deep black colour; when precipitated in presence of $Ba(NO_3)_2$, $Mg(NO_3)_2$, etc., it is black, whilst when it is precipitated in presence of $FeCl_3$, $Fe_2(SO_4)_3$, etc., the colour of the hydroxide is distinctly reddish. When precipitated in presence of $AuCl_3$, $CaCl_2$, $SrCl_2$, $Al(NO_3)_3$, ammonium metavanadate, uranium nitrate, or platinic chloride the colour is reddish brown. In presence of cadmium sulphate the colour is brownish yellow, in presence of the thallous salts it is brownish grey, whilst in presence of stannous chloride it is distinctly grey, and with copper sulphate it is brownish black. When no electrolyte is added the colour of the precipitate is reddish brown. Hence it is quite clear that the colour of the manganese dioxide obtained as a precipitate depends a great deal on the nature of the ions adsorbed by it when in the course of its coagulation.

Negatively charged stannic hydroxide sol can be prepared very readily and the sol is optically clear, whilst it is difficult to prepare a positively charged stannic hydroxide sol. When a few drops of ferric chloride are added to stannic chloride and the mixture is allowed to dialyse for a week, an unstable positively charged sol of stannic hydroxide is obtained. This positively charged sol has a distinctly yellowish colour possibly due to the adsorption of ferric ions. The sol cannot be freed from its yellow colour by further dialysis.

We[1] have prepared negatively charged $Fe(OH)_3$ sol either by shaking freshly precipitated $Fe(OH)_3$ with arsenious acid or by the interaction of $FeCl_3$ and KOH in presence of free arsenious acid. The latter method is more satisfactory. In either of these two methods the sol can never be freed from the arsenious acid and the question at once arises whether the sol of $Fe(OH)_3$ also contains ferric arsenate. The colour of the negatively charged dilute sol is yellowish brown, whilst in a concentrated condition it is dark brown. Consequently there is not much difference in the colour of the positively charged and negatively charged $Fe(OH)_3$ sols. The negatively charged sol can be prepared by the interaction of $FeCl_3$ and KOH in presence of such substances as glycerine, sugars etc. By the gradual addition of KOH to a misture of $FeCl_3$ and glycerine or sugars there are three definite stages through which the colloid passes—first it becomes positively charged and

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[1] Sen and Dhar: Kolloid-Z. 33, 193 (1923); J. Phys. Chem. 27, 376 (1923); Sen, Ganguly and Dhar: J. Phys. Chem. 28, 313 (1924).

then coagulation occurs and on charge-neutralisation it finally passes into a negatively charged colloid.

We[1] have prepared negatively charged chromium hydroxide sol by the interaction of chromium nitrate and caustic alkali in presence of arsenious acid; but there is not much difference in the colour of the positive or negative chromium hydroxide sol and it was not expected.

In presence of protective substances like glycerol, cane sugar, grape sugar, etc., the hydroxides of copper, cobalt, and nickel can be obtained either as positively charged or as negatively charged colloid.

When a dilute solution of $Ni(NO_3)_2$ is added to glycerol and carefully mixed and a few drops of dilute NaOH is added a green positively charged $Ni(OH)_2$ sol is obtained. No change of colour takes place on the addition of an excess of alkali. It appears, therefore, that the colour of the positively and negatively charged colloid of $Ni(OH)_2$ is the same and is practically identical with the colour of $Ni(NO_3)_2$. We have shown that in ammoniacal nickel salt solution part of the nickel exists as a negatively charged $Ni(OH)_2$ sol. On the other hand marked colour changes are observed with cobalt nitrate. When a little cobalt nitrate is mixed with an excess of glycerol and a few drops of KOH is added, the colour remains practically the same as that of cobalt nitrate but when large excess of alkali is added a deep blue sol is obtained. In presence of cane sugar and a large excess of alkali a violet coloured negatively charged cobalt hydroxide sol is obtained.

Grimaux[2] long ago suggested that in ammonical copper salt solution a part of the copper is complex and a part is suspended as copper hydroxide.

When a copper salt is mixed with an excess of glycerol and alkali is added drop by drop, at first we observe practically no change of colour but when an excess of alkali is added a deep blue colour is obtained. This observation can also be repeated with several sugars. It appears, therefore, that the colour of the positively charged cupric hydroxide which is first formed when there is an excess of cupric ions is different from that of the negatively charged colloid of copper hydroxide, which comes into existence when the alkali is in excess.

Masson and Steele[3] have shown that when caustic alkali is added to water containing cupric tartrate in suspension and the whole thing is vigorously shaken a complex tartrate is formed according to the following chemical change:—

$$5NaOH + 4CuC_4H_4O_6 = Na_2C_4H_4O_6 + Na_3C_{12}H_7Cu_4O_{18} + 5H_2O.$$

They have observed that the solution is neutral.

Kahlenberg[4] however maintained that the blue salt is produced by the interaction in the proportion $CuC_4H_4O_6 : KOH$ and represented by the formula $K_2Cu_2C_8O_{13}H_8$.

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[1] Sen and Dhar: Kolloid-Z. **34**, 262 (1924).

[2] Compt. rend. **89**, 1434 (1884).

[3] J. Chem. Soc., **75**, 725 (1899).

[4] Z. physik. Chem. **17**, 590 (1895).

It appears, therefore, that there is considerable difference of opinion among different workers with regard to the constitution of Fehling's solution. We can assume that Fehling's solution consists mainly of negatively charged $Cu(OH)_2$ stabilised by the adsorption of tartrate and hydroxyl ions. In this connection the following lines of Masson and Steele's paper would be interesting. "Sulphuretted hydrogen solution decomposes all the cuprotartrates precipitating cupric sulphide or a mixture of this with the sulphide of the other metal. The ease with which this occurs is a little surprising as truly negative metallic radicals do not generally break up in this way."

It is well known that when caustic alkalis are added to the copper salt solution a deep blue negatively charged sol of $Cu(OH)_2$ is obtained which can be readily retained when filtered through an ordinary filter paper. With regard to these substances we made the following statement in a previous paper[1]:—"It is very difficult to explain the production of the same colour in all these cases on the view of complex formation as the same colour is developed by so many different reagents. We have to assume that the positive ion $Cu(NH_3)_4^{\cdot\cdot}$ in ammonical copper solutions, the negative ion $Cu(OH)_4''$ in alkaline copper hydroxide solutions, the negative ion $C_{12}H_7Cu_4O_{13}'''$ in tartrate solutions. The complex copper salt solutions containing alkali and glycerol or sugars, having such different compositions, all have the same blue colour. The real explanation of the existence of the same blue colour in all these different substances seems to lie in the fact that we are probably considering the same substance in all cases, namely negatively charged colloidal $Cu(OH)_2$ due to the adsorption of hydroxyl ions, which are present in all cases and this negatively charged colloidal $Cu(OH)_2$ has the blue colour." Consequently the conclusion of Wo. Ostwald and Svedberg, which states that as regards light absorption there is no real difference between colloidal solutions and the corresponding molecular solutions, is not applicable to these cases.

In this connection the following remarks of Bancroft[2] would be of interest. "If we measure a copper electrode in a solution of alkaline copper tartrate we find that the concentration of copper ion is extremely low. That is all the measurement tells us. If the copper is in true solution, it must be present as a complex salt, as is unquestionably the case with potassium silver cyanide. If we have peptised copper oxide or hydroxide present, there is no need to assume the existence of a complex copper salt at all. It seems practically certain that the effect of sugars in preventing the precipitation of the heavy metal hydroxides by the alkalies is due to the formation of colloidal solutions."

When $Fe(OH)_3$ is precipitated in presence of $K_2Cr_2O_7$, $KMnO_4$, $Na_2S_2O_3$, etc., the colour of the hydroxide is different from the colour of the freshly precipitated $Fe(OH)_3$ obtained in absence of the above electrolytes.

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[1] Sen and Dhar: J. Phys. Chem. 27, 376 (1923).

[2] "Applied Colloid Chemistry" 212 (1921).

Schenck[1] has shown that in presence of $Al(OH)_3$, $Cu(OH)_2$ does not turn black readily. We have observed[2] that all those salts, which produced hydroxides soluble in caustic alkali namely salts of Zn, Al, Sn, Pb, etc., retard markedly the change of both blue copper hydroxide to the black form as well as that of the blue variety of cobaltous hydroxide to the pink form. It seems probable that the presence of $Al(OH)_3$, $Sn(OH)_4$, $Pb(OH)_2$ etc., in the colloidal state tends to peptise the cobalt hydroxide or cupric hydroxide and hence dehydration of these hydroxides become difficult and that is why retardation in colour change takes place.

When iodine is adsorbed by starch, saponarin, basic lanthanun acetate, cholalic acid, etc., blue substances are obtained. Barger and Miss Field[3] who have done some good work on these compounds have classified these blue products in the following way according to their degree of dispersion.

"I. The first group contains highly colloidal substances, such as starch, basic lanthanum acetate, the product of the action of 70% sulphuric acid on cellulose, thallonic acid, isolichinin, and various other ill-defined plant substances. In this group the blue compound is never obtained other than amorphous.

II. The members of this group are crystalline semi-colloids with molecular weight of something like 500; the blue compound is generally obtainable both in amorphous and crystalline conditions. Examples are: cholalic acid and the glucoside saponarin.

III. In the third group the blue iodine compounds are only known in the crystalline state, as in the case of the alkaloid narceine. Another example of this class is the product of the action of iodine or ergoxantheine. Possibly the second and the third of these groups are not sharply differentiated."

Just as the colour of a gold sol depends upon the size of the particles of the sol, Harrison[4] has directed attention to the similarity of the colour of the adsorption complexes of iodine with starch and dextrines, where similar variations of colour are produced by varying the size of the particles of carbohydrate.

Berczeller[5] shows that similar variations in the colour of the adsorption compounds of lanthanum hydroxide can be produced by varying the size of the particles of the hydroxide. The above author has also drawn attention to the colour variation in certain copper compound, in certain reactions of bile pigments and some furfural aldehyde reactions.

In a previous paper[6] I have shown that on the addition of an alcoholic solution of iodine to starch the conductivity of the mixture is much greater than the sum of the conductivity of the individual substances. The substance obtained by the adsorption of iodine by starch is appreciably conducting and

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[1] J. Phys. Chem. 23, 284 (1919).

[2] Chatterji and Dhar: Trans. Faraday. Soc. Discussion Oct. 25 (1920).

[3] J. Chem. Soc. 101, 1394 (1912).

[4] Kolloid-Z. 10, 45 (1912).

[5] Biochem. Z. 84, 160 (1917).

[6] Dhar: J. Phys. Chem. 28, 125 (1924).

behaves like an unstable iodide. It seems probable that micellar ions are given out.

It will be noted that the same blue colour is obtained when iodine is adsorbed by such different substances as starch, dextrine, cholalic acid, basic lanthanum acetate, etc. It seems likely, therefore, that this blue colour is due to the existence of iodine as the dispersed phase in all these adsorption compounds, where starch, dextrine, etc., serve as the dispersing media. It would be interesting to determine what colour iodine would have in the colloidal state.

When small quantities of $AgNO_3$ are added to dilute K_2CrO_4 containing gelatin the colour of the silver chromate obtained is yellow, just like that of K_2CrO_4. When an excess of $AgNO_3$ is added, the yellow sol of Ag_2CrO_4 becomes red possibly by the adsorption silver ions. The following results were obtained in a previous paper.[1]

No.	Concentration of the Gelatin = 5%		
1	N/1250	Yellow	N/63
2	N/625	"	N/108.2
3	N/416	"	N/195.6
4	N/312.6	"	N/291.6
5	N/250	"	N/500
6	N/208	Just red	—
7	N/200	Red	—

We have also observed that yellow Ag_2CrO_4 sol carries a negative charge whilst the red sol is positively charged. Consequently Ag_2CrO_4 peptised by gelatin exists as a yellow coloured negatively-charged sol by the adsorption of chromate ions and as a positively charged red sol by the adsorption of silver ions. Hence the behaviour of Ag_2CrO_4 peptised by gelatin is similar to those of the halide of silver, though no appreciable difference in colour is noticeable with negatively and positively charged sol of the same silver halide.

Summary and Conclusion

1. In this paper several cases have been reported, where the colour of the positively charged sol is different from that of the negatively charged sol of the same substance or from that of the electrolyte from which the sol is prepared.

2. The colour of freshly precipitated MnO_2, $Fe(OH)_3$ etc., depends a great deal on the nature of the substance adsorbed by the precipitates in the course of their formation.

3. It seems probable that the blue colour of adsorption compounds of iodine with starch, dextrine, cholalic acid, basic lanthanum acetate, etc., is due to the existence of iodine in the colloidal condition in such compounds.

Chemical Laboratory,
University of Allahabad,
Allahabad,
April 30, 1925.

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[1] Sen and Dhar: Kolloid-Z. 34, 270 (1924).

THE BEHAVIOR OF SILICA GEL TOWARDS CERTAIN ALKALIES AND SALTS IN AQUEOUS SOLUTION*

BY W. A. PATRICK AND E. H. BARCLAY

From numerous studies on adsorption by silica gel in this laboratory, it has been known that sodium or potassium hydroxide is adsorbed from aqueous solution according to the Freundlich adsorption equation. It was further known, that by immersing gel, which had adsorbed sodium hydroxide, in solutions of salts of heavy metals, the sodium was more or less replaced by the heavy metal in question. In this manner, gels impregnated with heavy metal oxides can be prepared, whereas the pure gel usually does not adsorb or remove compounds of heavy metals directly from solution.

Although the adsorption of ions and related subjects are treated more or less fully by Freundlich,[1] it is clear that the adsorption of, say, sodium hydroxide,—if it is true adsorption,—cannot be explained either by the capillary adsorption theory[2] or by the Gibbs' adsorption formula. In the latter case, for instance, the alkali in raising the surface tension, would bring about a diminution in the concentration of the surface layer.

The following experiments were taken up, therefore, with a view to explaining the mechanism involved in the removal of alkalies from solution, and the subsequent replacement of the alkali metals by other heavy metals from solutions of salts of the latter.

Experimental Part

The experiments consisted briefly in treating certain samples of silica gel with sodium hydroxide solutions, and, after the attainment of equilibrium, determining the amount of alkali adsorbed by difference in concentration of the solutions. After this, the gel containing the adsorbed alkali was quickly rinsed and then immersed in solution of either copper nitrate, silver nitrate or ferric sulfate, and the replacement of sodium determined by changes in concentration of the latter solutions.

A certain weight of silica gel, 20 mesh, of known water content, was placed in each of five 150 cc. glass stoppered bottles. The gel was prepared in the usual manner as described by Patrick and McGavack. The weight of gel averaged five grams and the water content varied from 8 to 11%. Each of these figures was known accurately for each experiment. Into these bottles were placed solutions of sodium hydroxide of known volume and known, but varying, concentrations. These bottles were then shaken at 20° for three hours—more than sufficient time to come to equilibrium. Ten cc. were then pipetted from each bottle and titrated by standard hydrochloric acid.

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*Contribution from the Chemical Laboratory of Johns Hopkins University.

[1] "Kapillarchemie," (2nd Ed.) pp. 279-288.

[2] Patrick and McGavack: J. Am. Chem. Soc. 42, 946 (1920).

For the next treatment, the caustic solutions were poured from the gel, and two quick rinsings of 25 cc. each with distilled water were made. Then 25 cc. of the various salt solutions were poured into each of the bottles, which were again shaken for 5 hours. The salt solutions used were $AgNO_3$ (0.1M), $Cu(NO_3)_2$ (0.1036M) and $Fe_2(SO_4)_3$ (0.178M). Finally, two 10 cc. samples were extracted from the equilibrium mixtures, the one sample analyzed for the heavy metal ion, and the other analyzed for sodium after precipitating the silver as AgCl, the copper as CuS or the iron as $Fe(OH)_3$. It was found necessary in the latter case to add one gram of sodium chloride to coagulate the colloidal ferric hydroxide. The silver determinations were made according to Treadwell and Hall,[1] the copper according to Haen and Low[2], and the iron was titrated by permanganate according to Fresenius. The sodium was weighed as chloride in the silver experiments, and as sulfate in the other two.

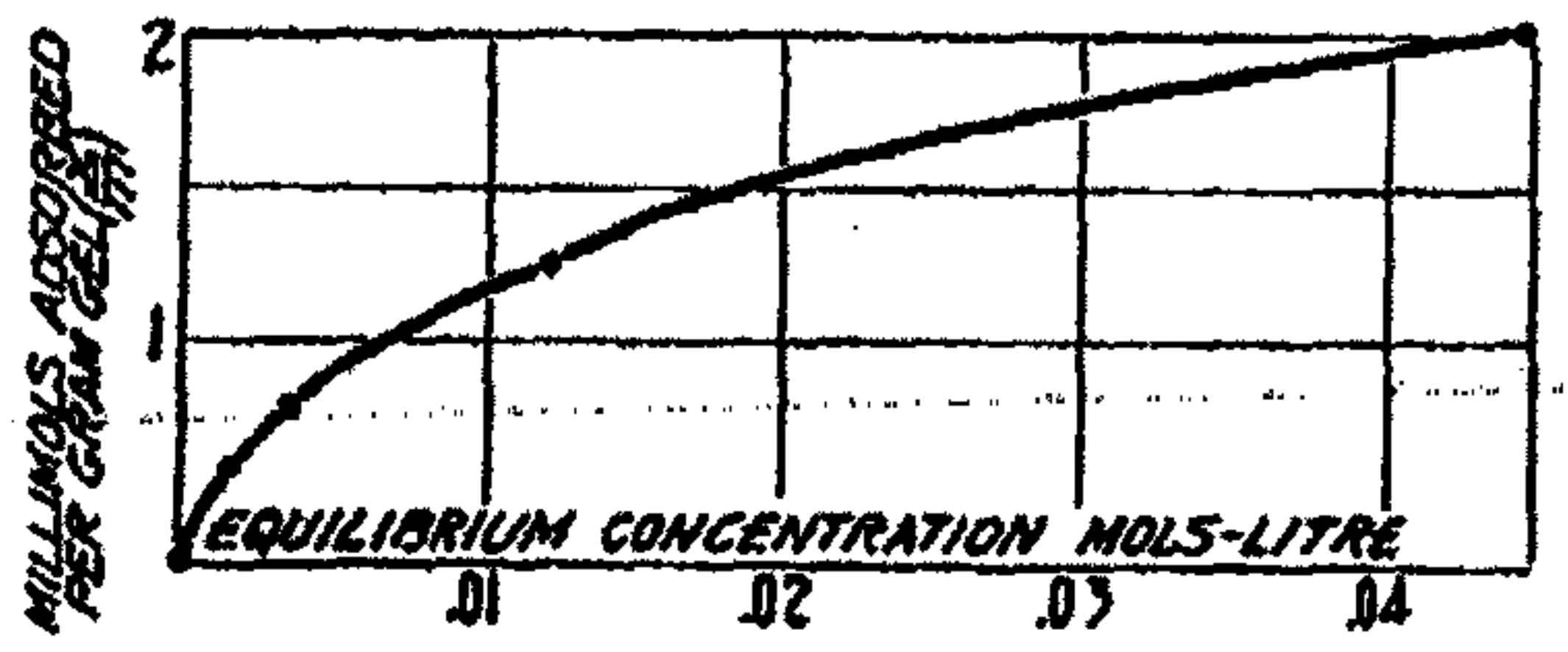

FIG. 1

Adsorption of NaOH

Table I gives data on the removal of sodium hydroxide from its solution for various concentrations. These results are plotted in Fig. 1 and represent the average values of twenty experiments. Applying the Freundlich adsorption equation $X/M = KC^{1/n}$, K and n are found to be 0.0071 and 2.56 respectively.

TABLE I

Adsorption of NaOH by silica gel.

Original Conc. NaOH Mols/Litre	Equilibrium Conc. Mols/Litre	Millimols adsorbed per gram gel = X/M
0.0127	0.0	0.29
0.0264	0.0016	0.58
0.0371	0.0036	0.77
0.0667	0.0118	1.26
0.1325	0.0447	2.02

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[1] "Analytical Chemistry" 5th Ed., Vol. II p. 705-6.

[2] Ann. Chem. Pharm. 91, 237 (1854).

TABLE II

Replacement of Silver

Millimols sodium adsorbed originally	Millimols heavy metal lost from solution	Millimols alkali salt in final equilibrium soluti
1.30	1.20	1.22
2.46	1.79	1.93
2.98	1.98	2.16
5.36	2.38	2.59
8.41	2.46	2.78
Replacement by Copper		
1.20	0.93	1.45
2.40	1.49	2.74
3.36	1.83	3.60
5.22	2.19	4.38
7.86	2.27	4.70
Replacement by Iron		
1.25	0.63	1.05
2.65	0.84	2.18
3.70	1.30	3.80
5.88	1.57	4.46
10.06	2.47	7.30

Table II gives the data for the replacement of the sodium ions by other ions. In each case this data is an average of five experiments. Column 1 gives the mols NaOH adsorbed in the gel before treatment with the other solutions. Column 2 gives the loss of mols of Ag, Cu, or Fe from the solutions, and Column 3 expresses the mols of sodium salt that had returned to the solution due to the replacement by other ions. Theoretically, of course, the figures of columns 2 and 3 in the case of silver should be equal, and in the case of copper and iron the last columns should be respectively double and triple the second column. That is to say, it appears from the measurements, that, as far as the replacement goes, the laws of stoichiometry hold. The discrepancies are, however, due to the fact that the two rinsings did not remove quite all the sodium hydroxide solution wetting the gel. This is supported by the fact that the discrepancies are greater where the greater concentrations of sodium hydroxide were originally used.

In the case of silver or copper solutions, no adsorption takes place by pure silica gel. In the case of iron solutions, however, a slight adsorption does take place, amounting to 0.00036 mols per 4.5 gm. gel from a solution of ferric sulfate of 0.089 mols/litre. This value, therefore, had to be deducted from the loss of ferric ions due to replacement, in order to give column 3.

Curves of Figs. 2-4 show graphically the measurements given in Table II.

Discussion of Results

From a study of the above curves, it is clear, first, that sodium hydroxide is removed from solution by silica gel to a greater extent the greater the concentration of alkali in the surrounding solution; and, second, that the sodium ions are replaced by other ions in accordance with stoichiometric laws, i.e., one silver ion replaces one sodium ion and one ferric ion replaces three sodium ions.

It is evident that we are dealing with phenomena that partake of the nature of chemical combination and adsorption. The removal of sodium hydroxide is in accordance, as above mentioned, with the Freundlich adsorption equation $X/M = KC^{1/n}$, whereas, if chemical combination were the explanation, the phenomenon would be in accordance with the equation $X/M = KC^{\circ}$, that is, the same amount of alkali would combine with the gel regardless of the concentration of the solution.

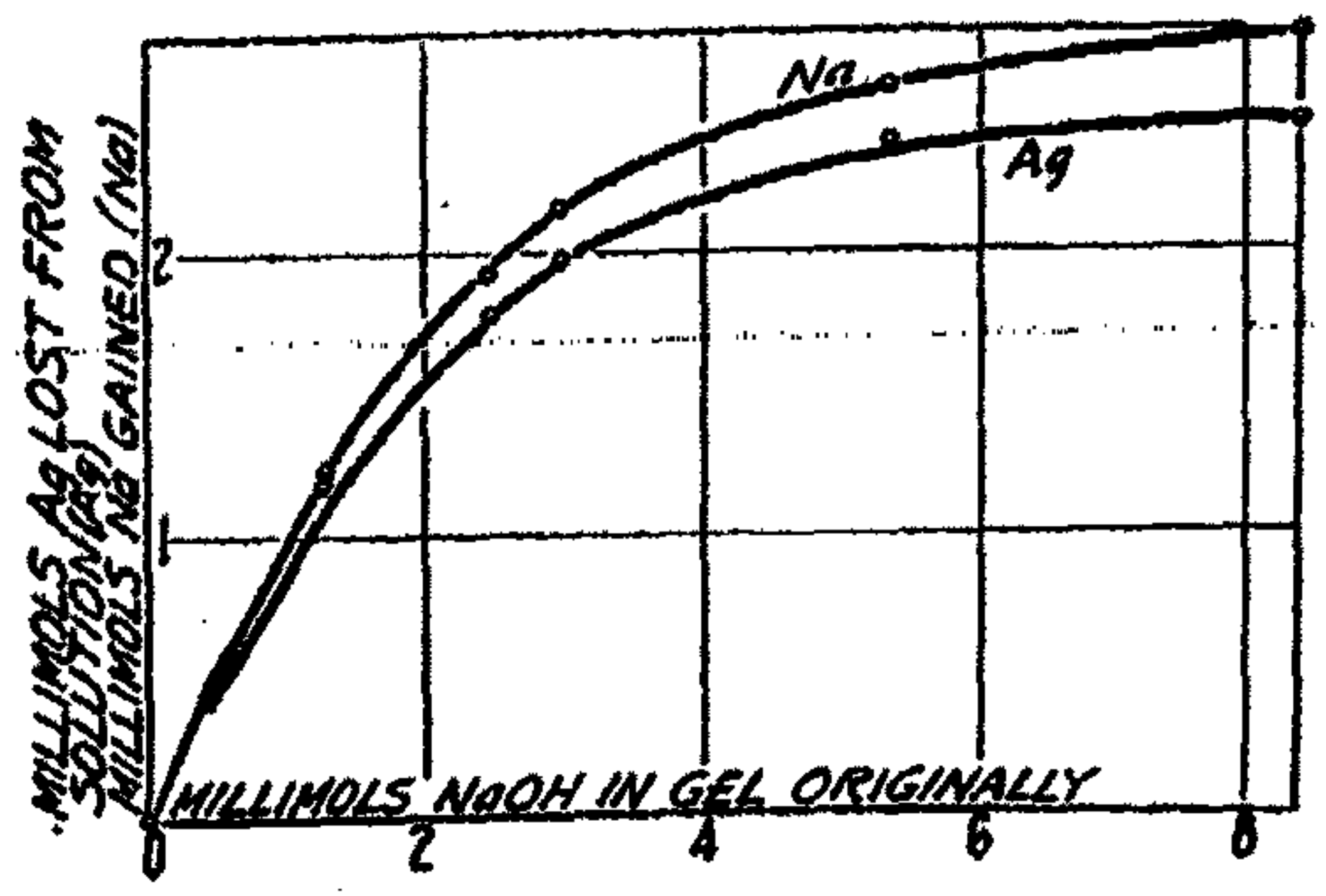

FIG. 2
Replacement of Na by Ag

At first sight it may be thought possible to explain the fact that the composition of the "silicate" was not constant by assuming that hydrolysis took place. But if this were so, the hydrolysis would be greater in the more dilute solutions and consequently the apparent "adsorption" less in more concentrated alkali solutions—just the opposite phenomenon that we have observed.

The objections to an adsorption explanation are largely based on the fact that such an explanation can only be justified on the assumption of strong attractive forces between the silica and alkali. These forces must be stronger than the forces holding the components of many molecules together, and, therefore, they are nothing but chemical forces. From this standpoint it seems unreasonable to classify such phenomena under a separate heading.

There is no doubt that there are many different kinds of adsorption if we define the latter as phenomena which give rise to a relationship that may be expressed by the formula $X/M = KC^{1/n}$. It would be most clarifying if adsorption phenomena were subdivided into three kinds:

1. Chemical adsorption
2. Molecular layer adsorption
3. Capillary adsorption.

Chemical adsorption would include all cases where attractive forces between the adsorbent and adsorbed substance were so strong as to be equal to real chemical attractive forces; the failure of the product to exhibit constant proportions being due to the fact that the adsorbent is composed of large particles,—conditions being such as to prevent the adsorbent from becoming molecularly dispersed. In the case of silica gel and sodium hydroxide, the latter molecules may be regarded as combining with the colloidal particles of silica. If the silica were of true molecular dimensions, we should expect the alkali to unite in proportions to give some definite silicate. On the other hand, the ratio of alkali to silicate would increase with decreasing size of silica particle. The case of the α and β stannic acids is exactly analogous. It has been shown by Mecklenburg[1] that the α stannic acid consists of smaller particles than the β form, and that the former is more reactive towards all reagents.

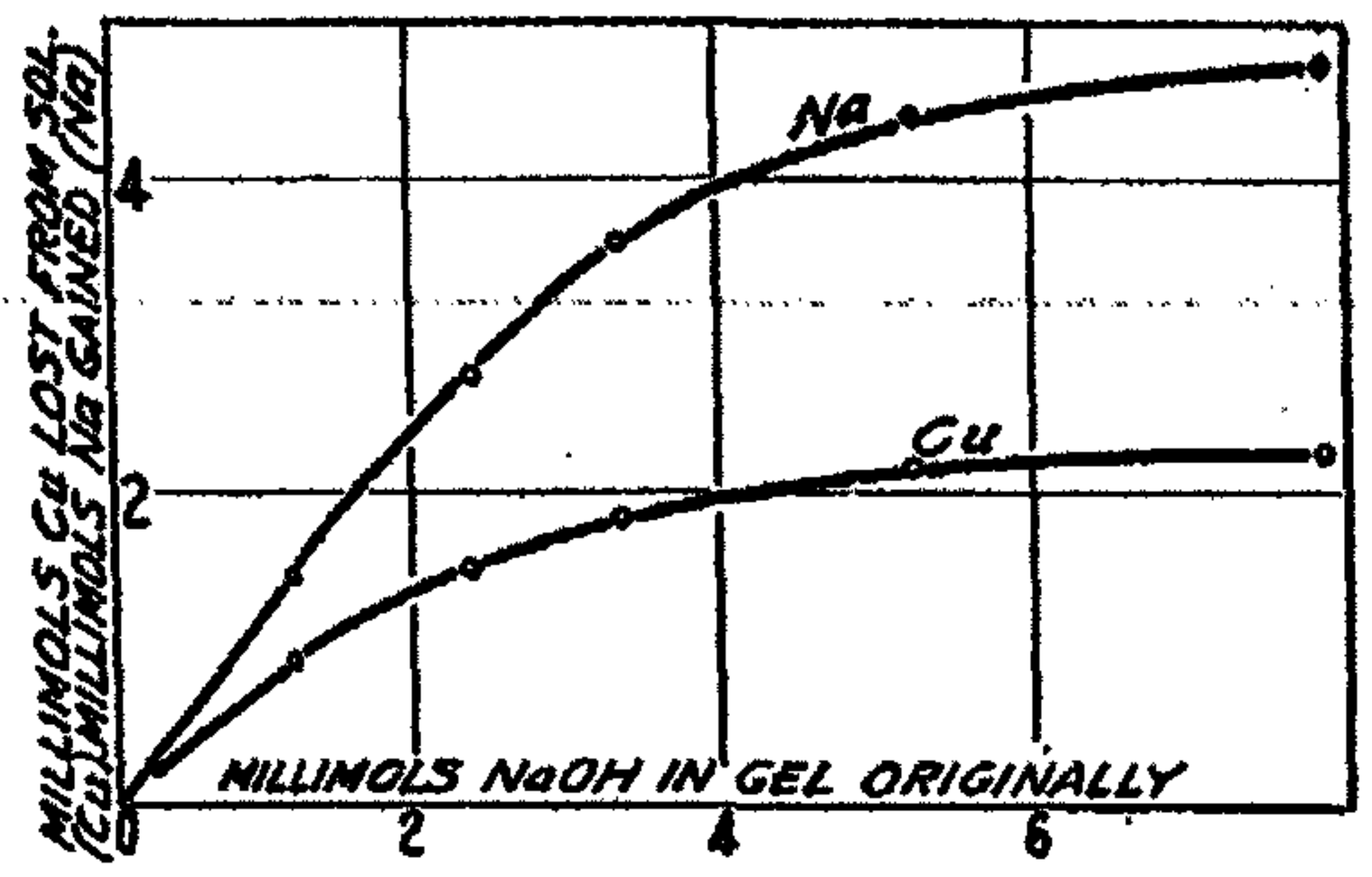

FIG. 3
Replacement of Na by Cu

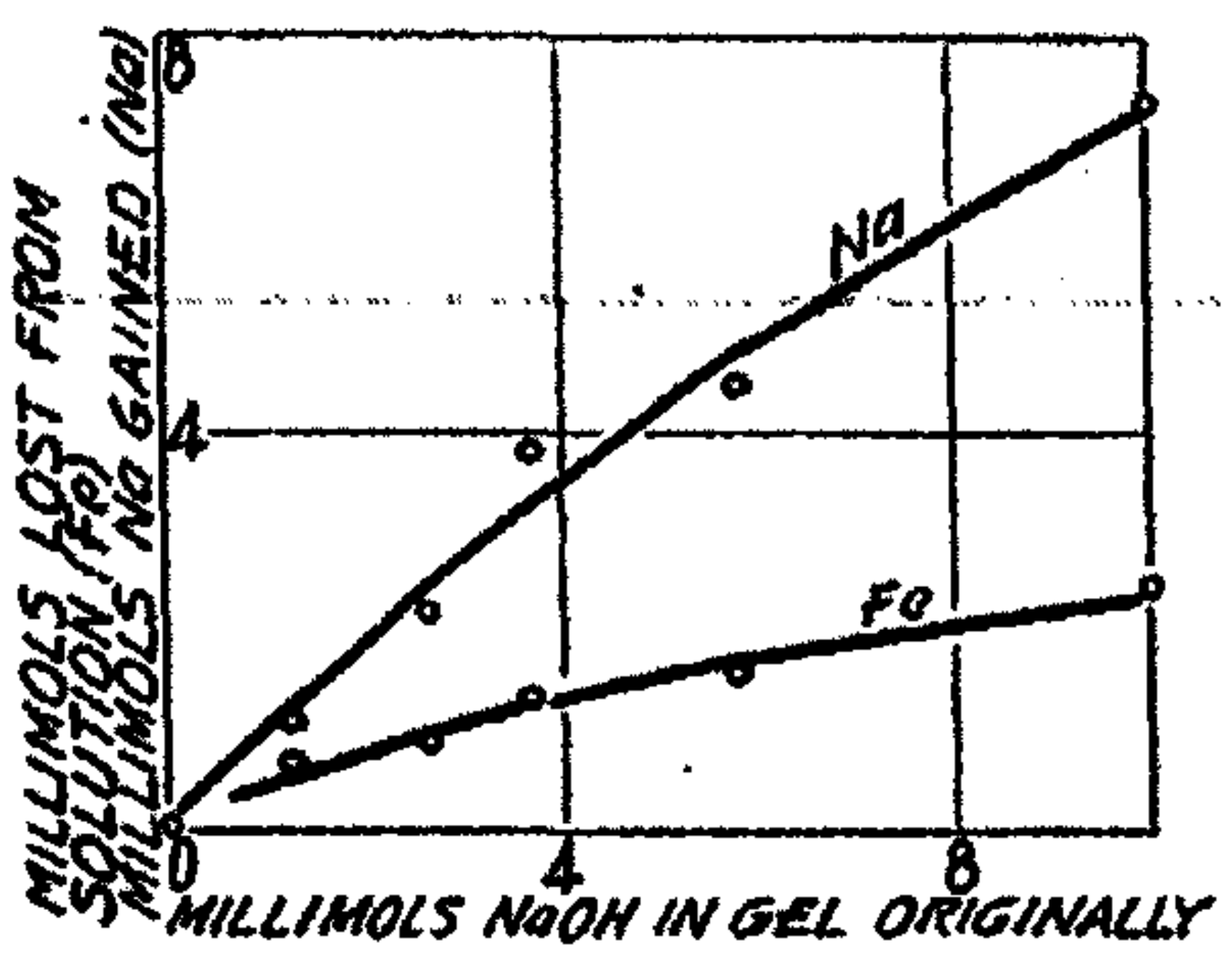

FIG. 4
Replacement of Na by Fe

There still remains to be explained the fact that the ratio of alkali to silica increases as the concentration of the alkali solution increases. This may be explained by assuming that the alkali peptizes the silica gel, i.e.—makes the silica particles smaller,—or that the thickness of the alkali "layer" increases as the amount of alkali in solution increases.

The retention of alkali by silica gel is therefore due to the action of chemical forces; and the reason for the relatively small percentage of alkali taken up is that a large particle of silica is reacting. The exchange of the sodium cation with the other metallic ions is, of course, readily accounted for on the basis of the great insolubility of the heavy metal oxides.

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[1] Z. anorg. Chem. 64, 368 (1909).

Summary

1. The removal of sodium hydroxide from aqueous solution by silica gel, and the subsequent replacement of the "adsorbed" sodium ions by silver, copper and ferric ions, has been studied.

2. It was found that the removal of sodium hydroxide could be accounted for by the Freundlich adsorption equation.

3. A classification of the various kinds of adsorption phenomena is proposed.

4. Explanations of the mechanism involved in the removal of alkalis from solution by silica gel, based on the colloidal nature of the adsorbent, have been given.

THE BEHAVIOR OF SILVER IODIDE IN THE PHOTO-VOLTAIC CELL. A NOTE.

BY ALLEN GARRISON

A paper on this subject[1] has been criticized by Price[2]. The basis of the criticism is Table II page 336, from which Price claims to have made calculations proving that the electrode was behaving as a massive silver electrode rather than a "dilute" silver electrode. Price has merely reversed the calculations made by the author and obtained as his conclusion the same constant used by the author in preparing Table II.

The experiments recorded in Table II were performed as rapidly as possible in order that the character of the electrode should not change while changes in the silver ion concentration (C_{Ag^+}) were made. Therefore the addition of silver nitrate and potassium iodide were made rapidly and the relative changes in C_{Ag^+} calculated from the electrode potentials. Thus in the first paragraph on page 337 there is the following statement concerning Table II:

"After each observation a little $AgNO_3$ or KI was added to the solution as is indicated thus changing the ratio of the concentrations of the silver and iodine ions. This change can be calculated from the electrode potentials. The silver ion concentration in moles per liter corresponding to each electrode potential is recorded in column 2 and the corresponding iodine ion concentration in column 3."

Price evidently overlooked this paragraph and supposed that the values C_{Ag^+} were estimated from the ionic activities. The values were calculated from the electrode potentials the assumption being made that the electrode was a massive silver one. By reference to Table I page 335, it may be seen that the actual variation of the silver from the massive state while distinct was small compared with the changes in C_{Ag^+}. Therefore the electrodes in Table II were not behaving as pure silver electrodes but as "diluted" silver and the values of C_{Ag^+} are intended to express only the order of magnitude of the concentration change.

It may be mentioned that all the calculations were not made at the average temperature 27° due to the intermittent heating of the light.

It is not surprising that, upon reversing the calculations made by the author, Price should discover that RT/F is approximately a constant. Since the entire basis of the criticism rests on this calculation, it is obviously without foundation.

The information which Price desired may be obtained by applying a similar calculation to Table I setting the concentration of silver = 1 for electrode No. 1.

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[1] J. Phys. Chem. 28, 333 (1924).

[2] J. Phys. Chem. 29, 557 (1925).

In considering electrodes of this type and those containing no silver[1] it may be pointed out that there are two distinctly different ways in which the electrode can act as an iodine electrode.

(a) The salt and electrolyte retain some iodine in solution which may ionize thus,

$$I_2 \rightleftarrows 2\,I^- + 2(+)$$

(b) The iodine ions may be liberated directly from the crystalline lattice the charge being conducted directly through the cyrstal thus,

$$AgI \rightleftarrows Ag + I^- + (+)$$

In the case of fused silver iodide on gold it is not necessary that the electrode be regarded as an iodine electrode of type (a). It is possible that the very large photo-potentials obtained with the gold-silver iodide electrodes are due to the reaction type (b). The usual electrode equations would not be expected to hold for this type of reaction since the light is regarded as causing an increase in the solution pressure of the halide. This is in accord with the general theory that the light causes a separation of the ions in the lattice and an increase in solubility product.

The Rice Institute,
Houston, Texas.

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[1] Garrison: J. Phys. Chem. 29, 58 (1925).

A PRECISE AUTOMATIC PRESSURE REGULATOR

BY LOUIS E. DAWSON

In a previous publication[1] the author described an automatic pressure regulator especially designed for pressures below that of the atmosphere. Certain necessary modifications were suggested to adapt such a regulator to the regulation of pressures above that of the atmosphere. The regulator here described differs slightly in form but involves the same principle as that previously described. In its present form it may be used for regulating pressures above as well as below atmospheric pressure. Also, improvements have been made in the adjustment of the regulator, which permit it to regulate pressures above as well as below atmospheric pressure to a very high degree of accuracy. No adjustment of the apparatus is necessary to compensate for differences in atmospheric pressure when the pressure is measured with a manometer which has one end open to the atmosphere and the other connected with the system to be maintained under constant pressure. This holds true only when the effective pressure desired is the difference between the atmospheric pressure and a second pressure mechanically produced, for example, when using the pressure for filtration or for viscosity or plasticity measurements with variable pressure viscosimeters of plastometers. Under other conditions, as for example, when heating or distilling under constant pressure, the atmospheric pressure changes must be compensated for by changes in the setting of the regulator from time to time.

With the regulators made by the author, pressures above that of the atmosphere, from about 100 cm. to 250 cm. of water and up to about 50 cm. of mercury, were maintained without any fluctuation in the manometer levels. Pressures above and below these limits may be obtained by using longer or shorter regulators or for pressures below atmospheric by reversing the connections. These are being used in the Carbohydrate Laboratory with the Bingham and Green variable pressure viscosimeters and they may be used for other purposes which require little consumption of air where a variation of not more than 0.1 mm.[2] of water pressure is desired. A regulator described by J. Rutten[3] for use in vacuum distillation is similar in one respect to the author's regulators. All have two tubes dipping into a reservoir of mercury, one for passage of air with mercury and the other for the return of the mercury to the reservoir.

Description of the Regulator

Figure 1 shows the general form of the regulator. It is made of average weight soft glass or Pyrex glass, the latter being preferable. It consists es-

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[1] Louis E. Dawson: Ind. Eng. Chem., 16 160 (1924)

[2] E. C. Bingham ("Fluidity and Plasticity", p. 306 (1922)) states that manometers may be read to 0.1 mm., that mercury manometers can be used to as low as 10 cm. of mercury, and that water manometers can be used to as low as 50 cm. of water with sufficient accuracy for viscosity measurements.

[3] Chem., Weekblad, 1, 635-8 (1903-4); Proc. Akad. Wet. Amsterdam, 6, 665-8 (1904).

sentially of some form of trap or baffle (*a j*) connected by means of two vertical tubes of different diameters and lengths (*b* and *c*) with a reservoir of mercury (*d*). The regulator is connected to a tank, in which the pressure is to be maintained constant through tube (*f* or *g*), depending on whether the pressure is above or below atmospheric pressure. Its action depends upon the passage of a controlled quantity of air through the tube of smaller diameter (*b*). When enough mercury in the reservoir to uncover the lower end of the smaller tube has been forced through both tubes into the trap, air begins to pass through with the mercury. The passage of this air alters the pressure in the tank. The quantity of air passing is then checked by a rise of the mercury in the reservoir (*d*) due to its return through the larger tube (*c*) under the changed pressure, thus more or less closing the end of the tube and controlling the quantity of air passing through the tube of smaller diameter.

The trap (*a j*) should be so constructed that the mercury which is forced up with the air is rapidly returned to the reservoir. Tube (*a*) is made from glass tubing about 2-1/2 cm. in diameter, and is about 8 cm. long. The tube (*j*) is connected into the side of (*a*) in such a way that the mercury strikes the top of (*a*) and has little chance of getting into the tube (*j*); in case it does it is allowed to rapidly return to the bottom of (*a*). It is about 1-1/2 cm. in diameter and about 8 cm. long. The reservoir (*d*) is about 2-1/2 cm. in diameter and about 6 cm. long. The small tube (*b*) connecting the reservoir and trap extends about 3 cm. into the reservoir. Its lower end is flared open to about 1-1/2 to 2 times its diameter. The diameter of this tube depends upon the source of pressure supplying the tank. With a very small capacity pump the tube probably needs to be less than 2 mm. internal diameter, but for most sources of pressure an internal diameter of about 2 or 3 mm. will be very satisfactory. The tube (*c*), through which the mercury returns, is about 8 or 10 mm. in diameter. It may be advantageous, although seldom necessary, to have the tube (*g*) extend into (*j*) through a double seal, with holes at (*h*) to take care of any sudden spurts of air and mercury when changes in adjustments of pressures are carelessly made. The apparatus is mounted on a board (Figure 2) pivoted at the top. For the purpose of regulating the pressure at different values, the regulator can be supported at various angles from the vertical by means of a metal strip (*r*) (Figure 2), with one end fastened to a pivot at the bottom of the board, and the other end passing through a bracket (*s*) (Figure 2) with a set screw. For pressures above that of the atmosphere, the tube (*f*) (Figure 1) is connected with the tank in which the pressure is to be maintained constant. For pressures below that of the atmos-

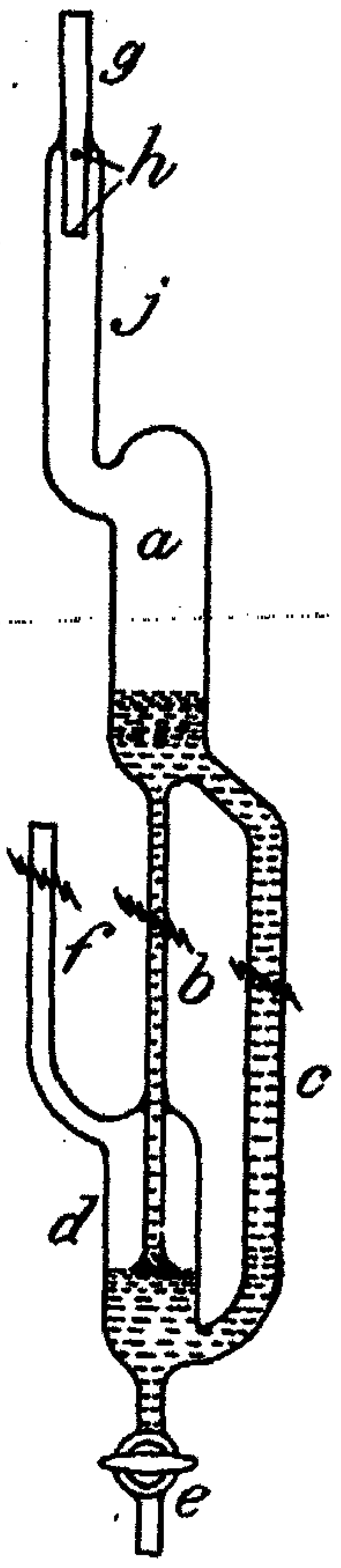

FIG. 1

phere, the regulator is connected through (*g*) to the tank. Except with pressure regulators for pressures between that of the atmosphere and 250 cm. of water above, the upper end of the trap at (*g*) (Figure 1) is left open to the atmosphere.

With pressures above that of the atmosphere between 50 cm. and 250 cm. of water, there is likely to be a fluctuation of about 1 mm. of levels in the water manometer. In order that the regulator shall maintain a pressure between these limits with no fluctuation of the levels in the water manometer, the regulator is connected through the tube (*g*) (Figures 1 and 2) to a tube about 8 or 10 mm. in diameter with a right angle bend at the bottom. The tube is allowed to dip into a jar of water to a depth of about 35 cm. (*u*) (Figure 2). The air coming from the regulator bubbles through the water, which stabilizes the slight fluctuations produced by the regulator. Over a period of 24 hours or more there may be a slight drop in pressure in the system to be maintained under constant pressure, owing to evaporation of water from the jar through which the air bubbles. The amount or rate of decrease in pressure will depend upon the total area of the water, or the diameter of

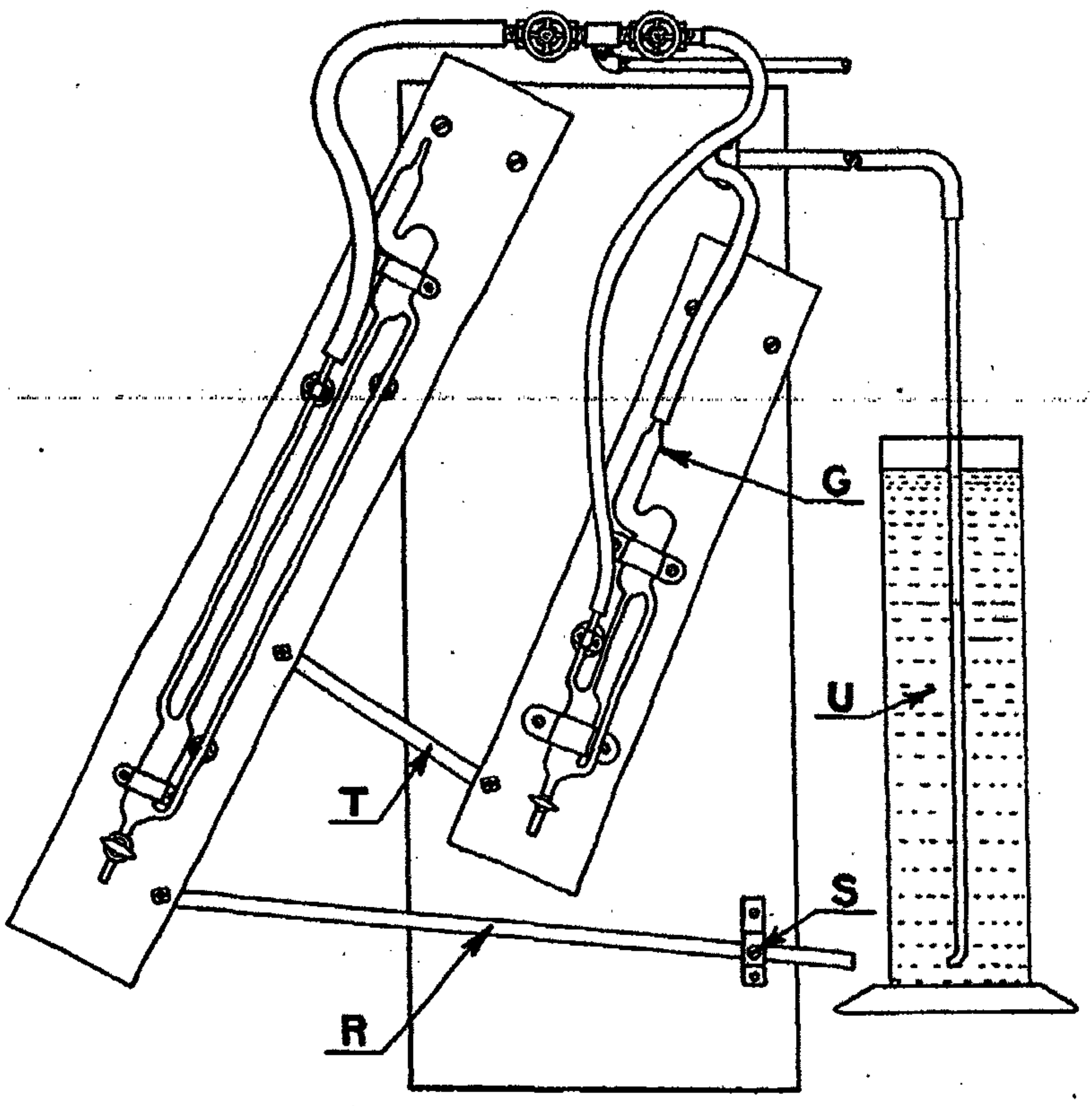

FIG. 2

the vessel at the surface of the water, to be lowered by the evaporation. With a vessel of large diameter the rate of decrease in pressure will be much less than with a vessel of small diameter.

Operation and Adjustment

The apparatus is about half filled with mercury and when being adjusted for the first time it is placed in the vertical position for the maximum pressure regulation. Pressure is carefully applied and the mercury withdrawn through the stop-cock (*e*) (Figure 1) until the mercury is about 3 cm. above the end of the tube (*b*) in the trap (*a*) when the air is passing through. When the regulator first starts operating the air may go through in pulses, but it should begin to pass steadily through in less than 1 minute. For most efficient work, the effect of the surface tension of the mercury at the flared end of the tube (*b*) must be minimized by allowing an uninterrupted but not excessive stream of air to pass through the small tube (*b*) of the regulator. When thus operating there is no variation in the manometer readings. This also applies in the case of the regulator for vacuum previously described.[1]

Entire System under Pressure with a Source of Variable Pressure

Above Atmospheric Pressure. The source of pressure used by the author varies from 20 to 110 pounds per square inch above that of the atmosphere. With the following arrangement these variations are kept from causing fluctuations of pressure in the tank that is to be kept under constant pressure.

The system is connected to the source of compressed air through the valve (*a*) (Figure 3). The air passes through a trap (*c*) made of a larger piece of pipe and fittings, which is filled with glass wool to hold back dust, oil, and water that might clog the capillary tube (*d*). The volume of air passing through the system is reduced by the capillary tube (*d*). This tube is 9 cm. long and has a bore 0.4 mm. in diameter. It may be by-passed by a valve (*x*) to allow quick filling of the system.

The glass capillary tubes are supported in 1/4 inch pipe-nipples, provided at both ends with brass unions, by which they are connected into the pipe line. The capillary may be fastened in the pipe with rubber stoppers, cut short and forced into the openings of the unions, and then the capillary pushed through the perforations in the rubber stoppers. They may also be fastened in the pipe by means of sealing wax, litharge and glycerine, or other cements.

When the source of pressure fluctuates over a wide range, a pre-regulator and 5-gallon tank are needed to supply the tank to be maintained under constant pressure with a nearly steady current of air. The pre-regulator used by the author has the tube (*b*) (Figure 1), about 45 cm. long by 3 mm. inside diameter, and operates with a total difference in level of mercury of about 49 cm. This pre-regulator may be mounted in the vertical position for all pressures up to about 45 cm. mercury in the main tank (*h*).

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[1] Loc. cit.

The air enters the 5-gallon tank (*e*), and is maintained at approximately constant pressure by means of the pre-regulator (*f*). From the tank (*e*) the air passes through a capillary tube (*g*), which reduces the volume of air passing into the tank (*h*). This capillary is 18 cm. long and has a bore 0.75 mm. in diameter. It is by-passed by the valve (*y*) to allow rapid filling of the tank (*h*). The tank (*h*) is a 30-gallon household galvanized-iron range boiler. The pressure in this tank is kept constant by means of the regulator (*j*) mounted on a board. The regulator used by the author has the tube (*b*) (Figure 1) 42 cm. long and 3 mm. inside diameter. The board is pivoted at the top and may be supported at various angles from the vertical as already described (Figure 2). A pipe line is run from the tank (*h*) (Figure 3) to the point (*k*) where the pressure is to be used. A mercury manometer (*m*) for measuring the pressure is connected to the same line.

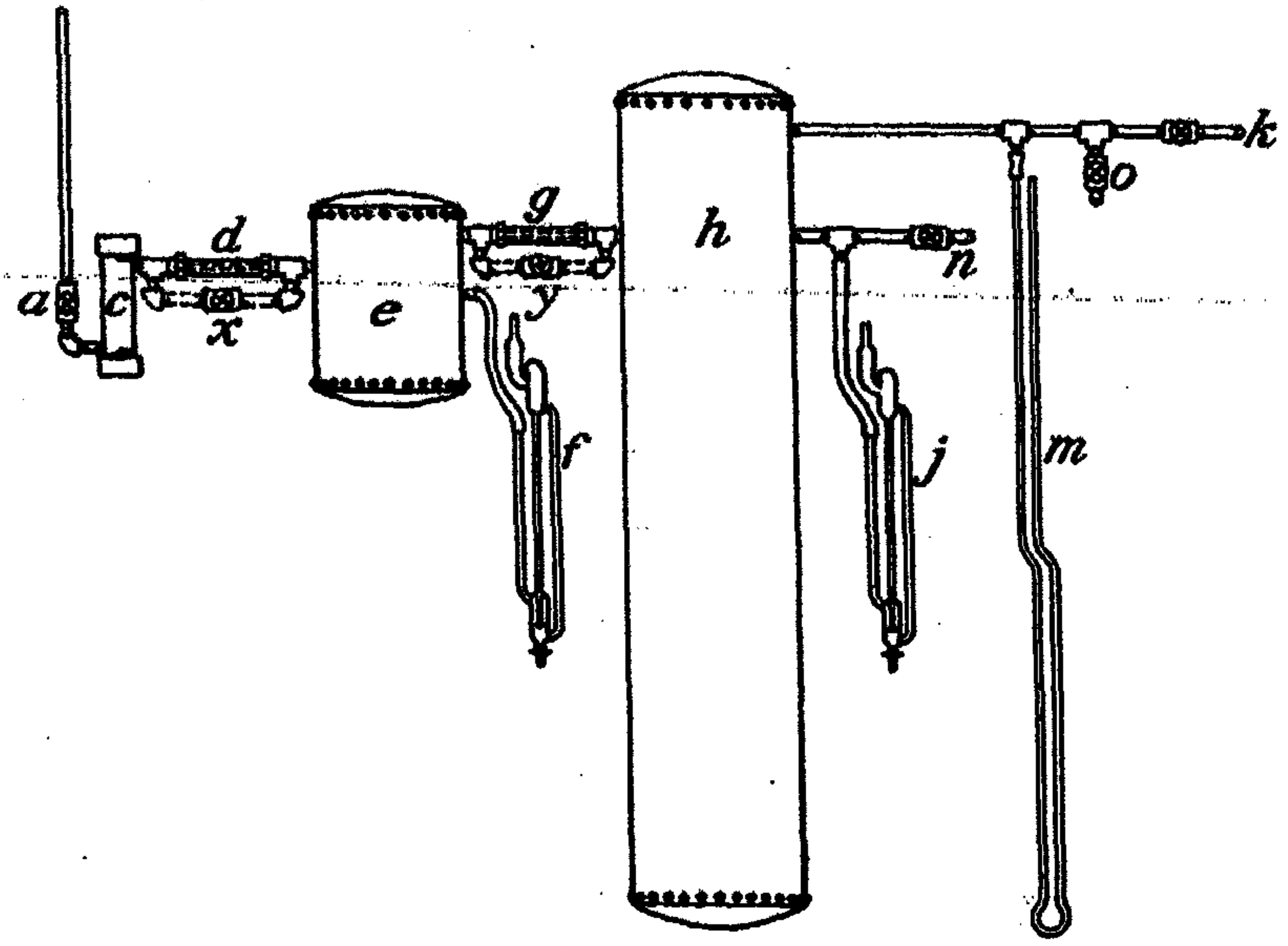

FIG. 3

Diagrammatical arrangement of system for regulation of pressure when the source of pressure fluctuates.

For pressures above that of the atmosphere, from 50 cm. of water up to about 15 cm. of mercury, a short regulator is used. It has a tube (*b*) (Figure 1) about 15 cm. long and is connected to the system through the valve (*n*) (Figure 3).

For the pressures which are to be measured on the water manometer, which is connected to the system through the valve (*o*) (Figure 3), a tube dipping into a jar of water is connected to the short regulator at (*g*) (Figures 1 and 2). The air then passes from the short regulator through the tube dipping into the water and bubbles out into the atmosphere through the water. Figure 2 shows how the short and long regulators are mounted and arranged so that they may be set for regulation at any pressure within the limits of these regulators.

The only adjustments necessary in changing the pressure in the system from one value to another is to change the degree of inclination of the regulators by shifting the point where (*r*) (Figure 2) is clamped at (*s*), both regulators being connected with a short strip (*t*). For pressures beyond the range of the water manometer, the valve (*o*) (Figure 3) is closed. For pressures beyond the range of the small regulator, the valve (*n*) is closed. No valve is needed on the mercury manometer (m) or the large regulator (*j*).

A reducing valve, such as is used for reducing the pressure of compressed gases in cylinders, may be used instead of the first capillary (*d*), the pre-regulator (*f*) and the 5-gallon tank (*e*). This is probably a more expensive arrangement, however. With this reducing valve it is necessary also to change the adjustment of the valve control when changing from one pressure to another in the tank (*h*).

Below Atmospheric Pressures. For pressures below that of the atmosphere the system described in the preceding section may be used after making the following modification: The valve (*a*) (Figure 3) opens to the source of vacuum. The pre-regulator and the regulators connected to tank (*h*) are connected to the system through the tube (*g*) (Figure 1) instead of tube (*f*).

Modification of System with Source of Air Pressure Constant

When the source of air pressure is practically constant, the control of the volume of air entering the system to be maintained under constant pressure is effected by including capillary tubing of a suitable size and length in the piping between the valve (*a*) (Figure 3) communicating with the source of pressure and the tank (*h*), instead of the capillaries, pre-regulator, and 5-gallon tank.

Device providing for the Accurate Setting of Regulation at a Definite Value

When it is necessary to maintain a pressure above atmospheric to within 1 mm. of a desired definite value, adjustment by varying the angle of inclination of the mercury regulator alone is too coarse. The following simple arrangement provides for a fine setting after an approximate adjustment of the mercury regulator has been made. A vertical tube, about 1 cm. in diameter, of convenient length, and bent at right angles within 3 cm. of the bottom, is connected at the top of the tube (*g*) (Figure 1) of the mercury regulator and inserted in a cylinder 5 cm. or more in diameter containing a column of water. The air from the mercury regulator passes through this vertical tube and bubbles up through the column of water into the atmosphere. The fine changes in setting at the pressure desired are made by varying the height of the column of water. The height can be conveniently controlled by providing the cylinder at the bottom with a T-tube, one branch of which is connected to a water supply and the other to a drain.

It may be advisable to eliminate any danger of slow mercury poisoning by conducting the air coming out of any mercury regulator into a hood or the outdoor atmosphere.

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THE FIXATION OF ATMOSPHERIC NITROGEN BY YEAST AS A FUNCTION OF THE HYDROGEN ION CONCENTRATION*

BY ELLIS I. FULMER AND LEO M. CHRISTENSEN

It has been previously stated[1] that yeast will grow continuously and in an apparently good state of nutrition on a synthetic medium with atmospheric nitrogen as the sole source of that element. In omitting the ammonium salt not only was the yeast deprived of its usual source of nitrogen but the physico-chemical environment of the medium was seriously disturbed[2]. While continued growth is maintained by yeast on the synthetic medium devoid of all but atmospheric nitrogen the quantitative estimation of the nitrogen fixed in that medium was not feasible because of the relatively small crop of yeast obtained.

In order to obtain quantitative results on the nitrogen fixation by the yeast it seemed advisable to add some of the growth stimulant, bios, with the minimum addition of nitrogen. It had been shown previously[2] that bios does not play the same rôle as ammonium salts in yeast nutrition. In the work here described molasses was used in the medium as the source of bios. Data are here presented showing that the fixation of atmospheric nitrogen by yeast in this medium is markedly affected by the hydrogen ion concentration.

In dealing with Azotobacter Lipman[3] recognized the fact that the reaction of the medium is important. Fred[4], in studying two different cultures of nitrogen-fixing bacteria, noted that while no growth occurred at pH6.4-6.6 that growth did occur at pH6.6-6.8. However in the above work the pH changed from 7.2 to 5.1 during the growth of the organism. Gainey[5] came to the conclusion that the presence of Azotobacter in the soil is correlated with the absolute reaction of the soil solution and that the maximum hydrogen ion concentration tolerated by the organisms is at about pH 5.9 to 6.0. Later Gainey[6] made a thorough study of the growth and nitrogen fixation by Azotobacter in a synthetic medium as a function of pH. He concluded that the data presented "point very definitely to a limiting hydrogen ion concentration of pH 5.9 to 6.0 for the various cultures of Azotobacter employed when grown under the conditions of the experiments. Vigorous growth and nitrogen fixation took place at pH 6.1 to 6.5, the optimum for nitrogen fixation apparently being somewhat higher than the optimum for growth."

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*From the laboratory of biophysical chemistry. Chemistry department, Iowa State College.

[1] Fulmer: Science, (2) 57, 645 (1923).

[2] Fulmer, Sherwood and Nelson: Ind. Eng. Chem. 16, 921 (1924); Fulmer: Colloid Symposium Monograph, 2, 204 (1925).

[3] 25th Ann. Report New Jersey Agr. Exp. Sta., 237 (1904).

[4] J. Agr. Res. 14, 317 (1918).

[5] J. Agr. Res. 14, 265 (1918); Abs. Bact., 6, 14 (1922).

[6] J. Agr. Res. 24, 759 (1923).

In our general studies of yeast nutrition we have maintained two types of yeast designated in this laboratory as Nos. 11 and 12 both of which came originally from a Fleischmann yeast cake. When plated on synthetic agar media[1] No. 11 forms small circular colonies with regular edge while the colonies of No. 12 are larger with radiate edge. In beer wort No. 11 grows on the bottom of the medium while No. 12 grows on the surface. In medium E[2] containing ammonium salt No. 11 grows more readily than No. 12, the former growing entirely on the bottom of the medium while No. 12 at certain stages of its growth shows a tendency to "creep" up the sides of the flask. These two types resemble those described by Eddy, Kerr and Williams[3]. It was soon apparent that No. 12 grew much more readily than No. 11 in an ammonia free medium and it was used in the studies here described.

The medium contained per one hundred cubic centimeters 6 grams of cane molasses and 0.50 grams of dipotassium phosphate, the latter acting as buffer. The pH of the media was adjusted after sterilization in order to obviate any changes in hydrogen ion concentration that might take place during the sterilization process. For this adjustment of reaction under sterile conditions a special apparatus and method was devised which have been previously described[4]. After inoculation several of the flasks were heated to kill the yeast and these flasks were used as blanks. The flasks were then sealed with paraffin leaving a capillary vent for pressure equalization. Incubation took place at 30°C. While growth is much more rapid under aeration the danger of contamination in a large series is considerable in spite of all precautions so the method outlined above was adopted.

At specified intervals the flasks were removed for examination and analysis. The cultures were examined for mold growth and a gram stain was made. The yeast count was also determined. The nitrogen in the medium was determined by the Gunning modification of the Kjeldahl method. After the digestion had become clear crystalline potassium permanganate was added and the digestion continued for four hours. After the usual distillation the ammonia was determined colorimetrically by Nessler's reagent.

Discussion of Results

In Table I will be found data from typical series of experiments. The amount of fixation at various time intervals at a given pH was not determined from a single flask but each experiment represents a separate culture. It is at once apparent that the medium according to the method of analysis used lost nitrogen in the beginning and that the actual gain did not show until after six to eight weeks at which time the cells had begun to break up. It is

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[1] Fulmer and Grimes: J. Bact. 8, 585 (1923).

[2] Fulmer, Nelson and Sherwood: J. Am. Chem. Soc., 43, 191 (1923).

[3] J. Am. Chem. Soc., 46, 2846 (1924).

[4] Christensen and Fulmer: Ind. Eng. Chem. 17, 935 (1925).

also notable that the maximum gain takes place at the same pH in which there is maximum loss. This phenomenon has been observed many times in our work and after considering all phases of the matter our hypothesis is as follows. Yeast is known to be rich in ring nitrogen compounds and in the early stages of growth the nitrogen may be thrown into a compound not to be analyzed by usual methods. Later in the growth these compounds may be transformed into materials amenable to the analysis as used. A detailed analytical study is being made in an attempt to account for all of the nitrogen of the yeast.

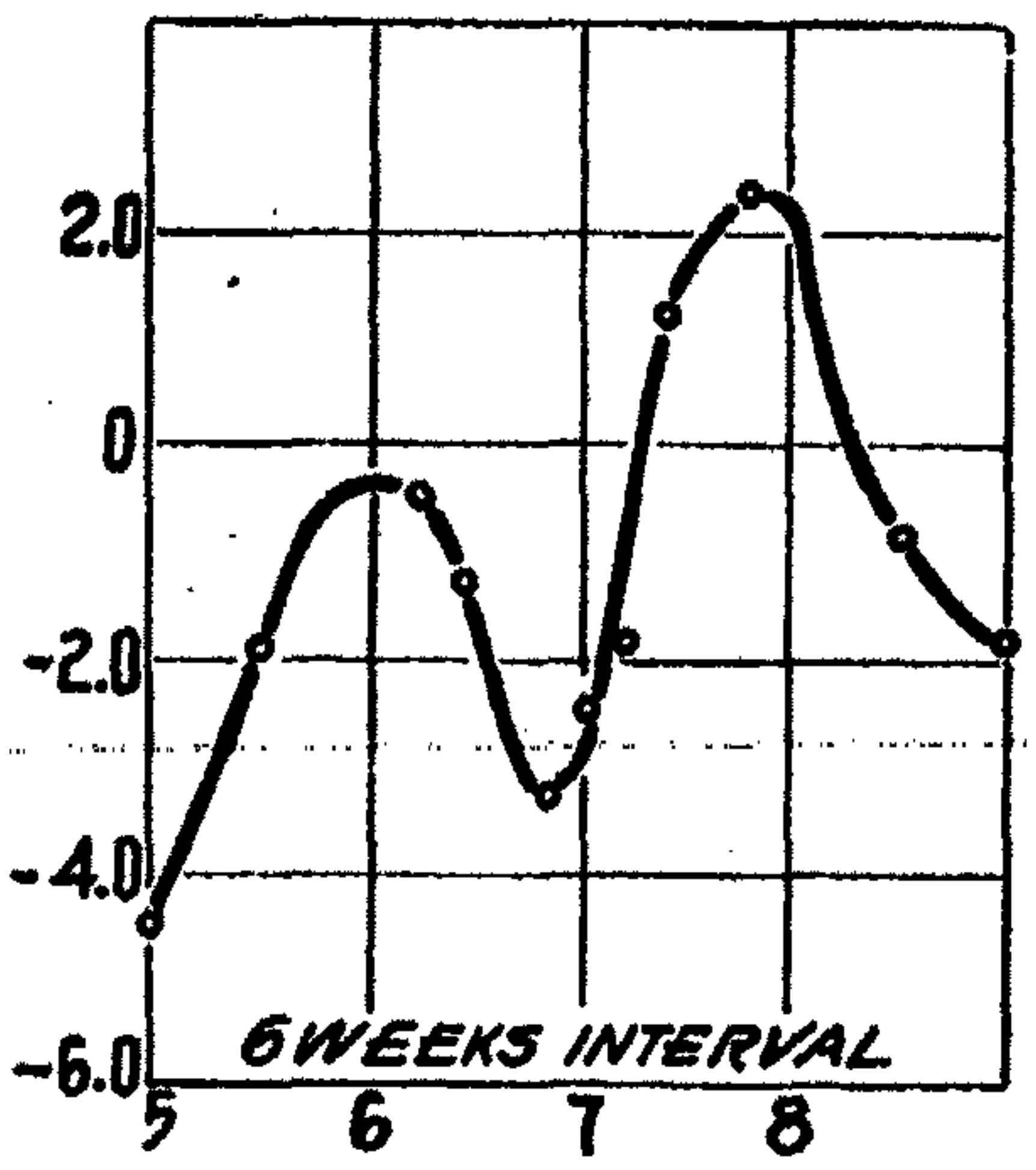

FIG. 1

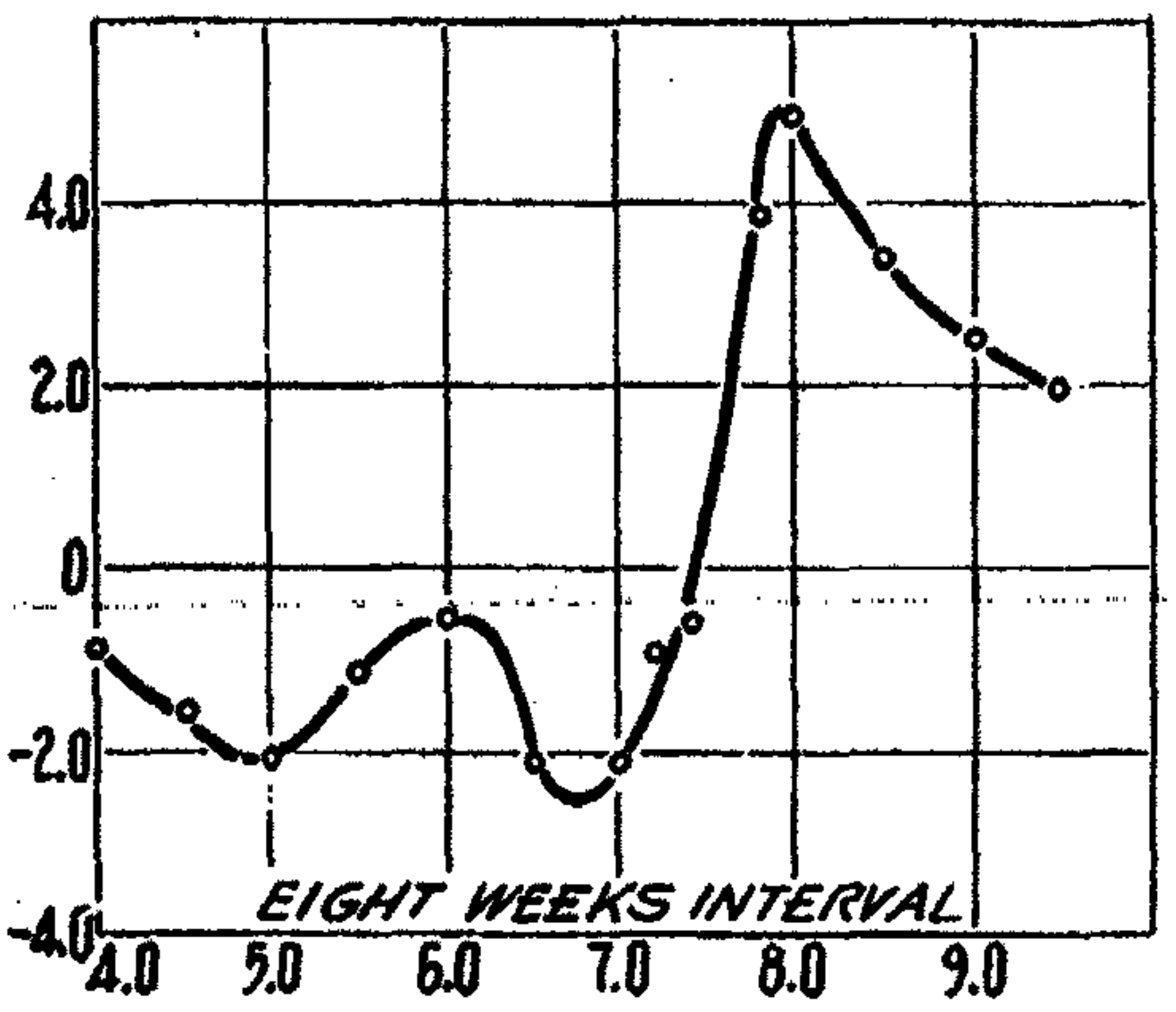

FIG. 2

TABLE I

pH	Gain in nitrogen in mgms/100 cc of culture Time in weeks					
	1	2	3	4	6	8
4.0	——	——	——	——	——	−0.92
4.5	——	——	——	——	——	−1.52
5.0	——	——	——	——	−4.46	−2.10
5.5	——	——	——	——	−1.91	−1.19
6.0	——	——	——	——	——	−0.51
6.2	——	——	——	——	−0.50	——
6.4	——	——	——	——	−1.25	——
6.5	——	——	——	——	——	−2.10
6.8	——	——	——	——	−3.22	——
7.0	——	——	——	——	−2.48	−2.10
7.2	−3.60	−3.40	−4.72	−4.19	−1.85	−0.92
7.4	−2.60	−3.50	−2.56	−2.46	+1.19	−0.65
7.6	−3.20	−4.50	−3.63	−3.36	(+2.01)	(+1.35)
7.8	−1.00	−1.20	−5.35	−3.63	+2.31	+3.82
8.0	−0.90	−3.20	−7.00	−3.71	(+1.64)	+4.90
8.5	——	——	——	——	−0.84	+3.32
9.0	——	——	——	——	−1.80	+2.41
9.5	——	——	——	——	——	+1.99

At any rate it seems probable that the failure of several investigators to observe fixation with microorganisms may have been due to this time element. Lipman[1] in his experiments on the fixation of atmospheric nitrogen by yeasts and molds allowed his cultures to stand for a month. The data show conclusively that the yeast used does fix atmospheric nitrogen in the medium employed and that the fixation is a function of the hydrogen ion concentration. There are two optimal concentrations at pH of 6.0 and 7.9 respectively. The optimum on the alkaline side is much more potent that the acid optimum concentration. The results of the sixth and the eighth week analysis are plotted in Fig. 1 and 2. The effects of the composition of the medium and of temperature are being studied as they influence the fixation as a function of pH.

Conclusion

The amount of nitrogen fixed by yeast in molasses at 30°C is a function of hydrogen ion concentration there being two optimal concentrations one at pH = 6.0 and the other at pH = 7.9 with the latter concentration the more potent.

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[1] J. Biol. Chem. **10**, 169 (1911).

THE EFFECT OF TEMPERATURE OF FORMATION ON THE PHYSICAL CHARACTER OF HYDROUS ALUMINUM OXIDE*

BY JOHN H. YOE

In general, it may be stated[1] that "precipitates are less gelatinous and more crystalline the higher the temperature of formation." Hence, we would expect variation in adsorptive capacity, density, particle size, etc., of hydrous oxides formed at different temperatures, other conditions being kept constant.

It has recently been shown[2] that the adsorptive power of hydrous alumina for arsenite ions decreases, the higher the temperature at which it is precipitated. Under the conditions of these experiments, adsorption at 25° by the hydrous aluminum oxide formed at 0° was about 2.5 times greater than that formed at 100°, and about 5.5 times greater than that formed at 100° and boiled under a reflux condenser for 24 hours. The effect was greater over the range from 0° to 50° than from 50° to 100°. Boiling under a reflux condenser for 24 hours cut down the adsorptive power more than 50 percent of that formed at 100° but not boiled. This effect of temperature of formation on the adsorptive power may be due to the hydrous alumina precipitating in a less flocculent and more compact condition with increasing temperature and, hence, having a smaller surface when formed at higher temperatures. Boiling the hydrous oxide should give a still more compact precipitate. Moreover, since the solubility of the smaller particles is greater than that of the larger ones, the latter would grow at the expense of the former and the total surface of the adsorbent would be correspondingly decreased. It is also possible that the porosity of the hydrous alumina decreases the higher the temperature at which it is formed.

It seemed probable that a careful determination of the rates of settling of hydrous aluminum oxides formed at different temperatures would give a convenient and rapid method of tracing the relative effect of temperature of formation on hydrous oxides, i. e., denser and larger particles would settle more rapidly than smaller and more flocculent ones. Such a series of measurements is described in this paper. No measurable difference in the velocity of settling was observed except in the case of the hydrous alumina precipitated at 100° and boiled under a reflux condenser for 48 hours. A microscopic examination of hydrous aluminum oxides formed at temperatures ranging from 0° to 100° C. has also been made.

Experimental

Hydrous Aluminum Oxide.—Fifteen cc. of a standard solution (50 g. $Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$ per liter) were put in a tall Pyrex beaker and diluted with 175 cc. of water. The beaker was placed in a water-bath and the

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* Contribution from the Cobb Chemical Laboratory of the University of Virginia.

[1] Bancroft: Ind. Eng. Chem., 13, 158 (1921).

[2] Yoe: J. Am. Chem. Soc., 46, 2390 (1924).

alum solution allowed to come to the desired temperature. In case of temperatures above 50°C., a few drops of water were added from time to time to compensate loss due to evaporation, the solution being kept thus at a constant volume. A glass stirrer was adjusted to a definite position in the precipitation beaker. The stirrer was driven by an adjustable speed motor and was maintained at 500 revolutions per minute in all precipitations. The temperature and stirrer being adjusted, ammonium hydroxide solution (approx. 0.1N) was added from a burette at a uniform rate until the equivalent amount (previously determined) had just been introduced. Forty-seven cc. of the ammonium hydroxide solution were required. The solution was added uniformly over a period of 15 minutes. Precipitations were made at 0°, 20°, 22°, 50°, 94°, and 100°C.; and at 100° and boiled 48 hours under a reflux condenser. One precipitation was made at 66° and the mixture boiled 62 hours under a reflux condenser. Each suspension was brought to 20°, transferred to the settling tube, thoroughly mixed, the tube quickly placed in the water-jacket, and the settling time noted. Readings were made at 10 cm. intervals.

Settling Tube.—This consisted of a Pyrex glass tube of uniform bore, 2.5 cm. in diameter and 100 cm. long, carefully adjusted to a vertical position. The tube was surrounded by a larger tube (6 cm. diameter) through which was passed water maintained at 20°C. by a previous passage through a thermostat. Both ends of the water-jacket tube and the settling tube were closed with rubber stoppers. The bottom stopper of the water-jacket carried a small glass tube through which the water entered, and through the top stopper were inserted the settling tube, a thermometer, and a small glass out-let tube. A meter stick was placed vertically on the back side of the apparatus: The water in the tubes served as a magnifying lense, and readings could easily be made to 0.5 mm.

Velocity of Settling.—All readings were plotted on co-ordinate paper and the time in minutes to each succeeding 5 cm. distance was read off. The results are recorded in Table I. The readings above 40 cm. and below 65 cm.

TABLE I

Distance Settled. Cm.	Temperature of Formation—°C												
	0	0	0	20	22	50	50	66*	94	100	100	100	100†
	Minutes Settling												
40	49	44	40	50	39	57	45	42	30	45	—	—	—
45	55	50	44	57	43	65	52	47	35	51	—	—	—
50	67	61	52	68	52	77	61	54	44	61	48	48	26
55	83	76	63	82	64	98	76	66	58	77	55	60	31
60	110	101	83	122	84	135	99	87	78	103	67	80	37
65	193	175	142	213	150	248	168	162	136	168	97	127	49

*Boiled 62 hours under a reflux condenser.

†Boiled 48 hours under a reflux condenser.

have not been included in the table. In the case of those above 40 cm. the "edge" of the settling precipitate was frequently not sharply defined and, hence, only approximate readings could be made. This was invariably true in the case of precipitates formed at 100°C. Readings were not recorded below 65 cm. because of the slowing down of the settling rate due to the massing of the precipitate.

In Table II are recorded the velocities of settling, in cm. per sec., for the first 50 cm. The temperature at which the precipitate was formed is given at the top of each column.

TABLE II

Temperature °C.	0	0	0	20	22	50	50
Velocity cm/sec.	0.012	0.014	0.016	0.012	0.016	0.011	0.014
Temperature °C.	66*	94	100	100	100	100†	
Velocity cm/sec.	0.015	0.019	0.014	0.017	0.017	0.032	

*Boiled 62 hours under a reflux condenser.
†Boiled 48 hours under a reflux condenser.

Discussion of Results

The velocities of settling recorded in Table II refer mainly to the smaller and lighter particles of hydrous aluminium oxide, since the larger and heavier ones settled more rapidly and, therefore, were not present in the upper portion of the precipitate after the first few minutes of the settling period. As seen in Table II, the velocities thus determined show very little variation, regardless of the temperature at which the hydrous oxide was formed, with the exception of that formed at 100°C. and boiled under a reflux condenser for 48 hours. The velocity of settling of the hydrous oxides formed at temperatures ranging from 0° to 100° was approximately constant at 0.014 cm. per second. The rate of settling of the hydrous alumina precipitated at 100° and boiled under a reflux condenser 48 hours was 0.032 cm. per second, i. e., the boiling more than doubled the settling rate.

Microscopic Examination

Each of the precipitated aluminas was carefully examined with a hand lens and also under the microscope. It was observed that the hydrous alumina formed at 0° was extremely gelatinous, whereas that formed at higher temperatures was less so, although still quite voluminous. It was thought that a better study of the character of the white, translucent precipitates could be made if they were stained with some highly colored substance. Accordingly, a 0.01 per cent solution of alizarin (0.6N in acetic acid and 3N in sodium acetate) was tried but was not successful. A suitable stain for hydrous alumina might prove very helpful in making microscopic examinations of the latter.

An attempt was made to measure the diameters of the particles by means of an eye-piece micrometer but this did not prove satisfactory due to the very irregular shapes of the particles and to the great variation in particle size, *even within the same specimen of hydrous oxide.*

The statement[1] that aluminum hydroxide precipitated by ammonia at 66°, and the mixture then heated to boiling, gives a granular product was not confirmed, although a number of attempts were made. The hydrous alumina thus formed was quite voluminous in each case. Some of the precipitates were made with aluminum nitrate solutions and were stirred gently by hand instead of at 500 r. p. m. by a motor driven stirrer.

Summary

1. Hydrous aluminum oxide has been formed at various temperatures, ranging from 0° to 100°C., all other conditions as to concentration, rate, and order of mixing solutions, and rate and type of stirring, being kept constant. Two of the precipitated mixtures were boiled under reflux condensers for 48 hours and 62 hours, respectively. The velocity of settling under uniform conditions has been determined for the hydrous oxide formed at each temperature. The average velocity of settling the first 50 cm. was 0.014 cm. per second and was approximately the same for all precipitates, except the one boiled 48 hours. The rate of the latter was about double that of the others.

2. The hydrous aluminum oxide formed at 0° was extremely gelatinous, whereas that formed at higher temperatures was less so, although still quite voluminous. Alumina precipitated at 66° by ammonia, and the mixture heated to boiling, gave a voluminous product and not a granular one as reported by W. E. Taylor.

University, Virginia
July 22, 1925

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[1] Taylor: Chem. News, 103, 169 (1911).

CALCIUM PHOSGENO-ALUMINATE: A PHYSICO-CHEMICAL STUDY[1]

BY A. F. O. GERMANN AND C. R. TIMPANY

As a result of a study of the chemical properties[2] of solutions of aluminium chloride in liquid phosgene, one of us has postulated the existence in this solution of a compound, $COAl_2Cl_8$[3], which behaves like a weak acid, to which may be applied the designation phosgeno-aluminic acid. In this acid phosgene performs the functions performed by water in the well known aquo-acids, hydrogen being replaced by carbonyl, and oxygen by chlorine.

The solution has been shown to be a weak conductor of electricity[4], phosgene being a poorly ionizing solvent, with a dielectric constant of 4.34[5]. As most of the familiar acids are weak acids, while their salts are more highly ionized, it may be predicted that in any group of unknown acids, the majority of them will also be weak, while their salts will be more highly ionized. There is thus a greater probability that a particular individual, chosen at random, will be a weak acid than that it will be a strong acid, and its salts will probably be more highly ionized than the acid. It is the object of the present investigation to test this theory, using calcium phosgeno-aluminate, $CaAl_2Cl_8$, as the salt of the phosgeno-acid, $COAl_2Cl_8$.

Since the various dilutions were made up gravimetrically rather than volumetrically, the densities had also to be determined, and the calculation of the data for the latter presupposed a knowledge of the vapor pressure curve. Hence, the present paper contains data for the vapor tensions, densities and conductivities of solutions of calcium phosgeno-aluminate at 25° and at 0°, from the most dilute solutions, up to supersaturation, about 35%.

A large sample of the pure salt was prepared by the method recently described by us[6]. The salt was in the form of minute, partially effloresced crystals, containing 25.75% of phosgene of crystallization. The sample was kept in a tightly stoppered bottle, inside of a desiccator with an air-tight lid. That some phosgene was lost each time the desiccator was opened to remove a sample was evident from the odor, but that these losses were serious, and would have to be carefully taken into consideration was not appreciated until analyses made after the completion of the work here described showed that the phosgene content had fallen to 15%. In a mathematical analysis of the extent to which these losses affect the individual samples removed from the bottle, account was taken of the fact that approximately the same weight of phosgene was lost each time the cover was removed, and that on a percentage

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[1] From a thesis submitted to Stanford University by C. R. Timpany in partial fulfilment of the requirements for the degree Master of Arts.

[2] Germann: J. Phys. Chem., 28, 879; Germann and Gagos: 965 (1924).

[3] Germann: Science, 61, 71 (1925).

[4] Germann: J. Phys. Chem., 29, 1148 (1925).

[5] Schlundt and Germann: J. Phys. Chem., 29, 353 (1925).

[6] J. Am. Chem. Soc., 47, 2275 (1925).

basis the losses became progressively greater, as the total amount of salt remaining in the bottle became smaller[1]. Two checks on the validity of the assumptions made in this analysis are furnished by the following facts: (A) the last series of conductivity measurements (series F) was carried out with a sample of definitely known phosgene content; the values obtained for this series are in perfect harmony with those obtained in other series; (B) a measurement of the density of a 20% solution of the salt was made with dilatometer L, using a sample of completely dephosgenated salt; the values obtained both at 25° and at 0° (see end of Table II) fall precisely on the average curve previously drawn.

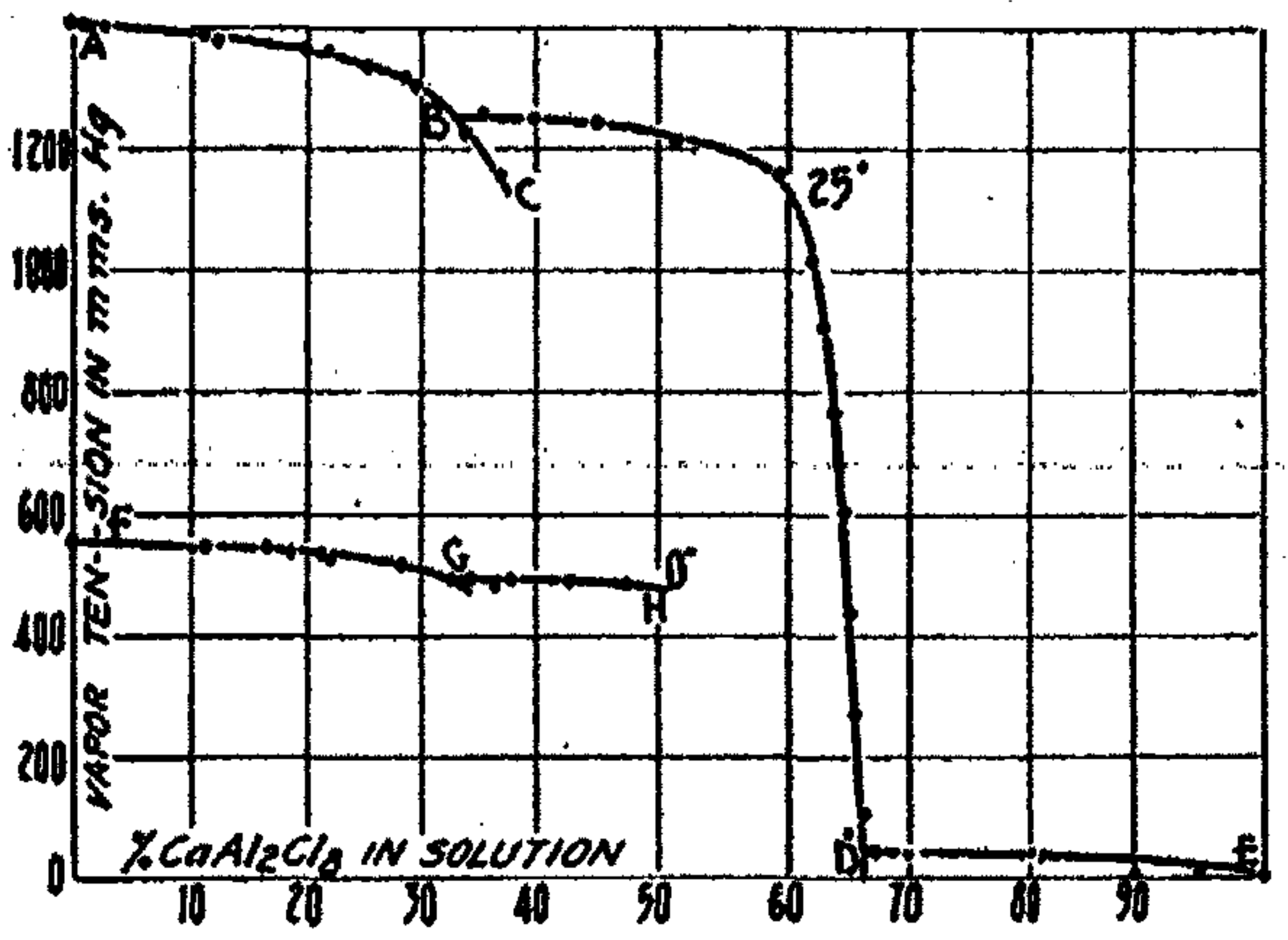

FIG. 1

Vapor Tension Curve of $CaAl_2Cl_8$ in $COCl_2$ at 25°C and at 0°C.

Pure phosgene was obtained by fractionating technical phosgene essentially as described by Germann and Gagos,[2] except that bubble distillation instead of surface distillation was employed. The vapor tension of the phosgene used was 555 mm. at 0°, and 1405 mm. at 25°. The vapor tension measurements were carried out in the manner already described by Germann and McIntyre for similar measurements with solutions of phosgeno-aluminic acid[3]. The density measurements were made by the method described by Germann[4], using the same pycnometers used by him. The conductivity measurements were made with the same type of cell as that used by Germann[5]; the 1000 cycle microphone hummer with tuning fork attachment, the bridge and resistance boxes were the same as used by him. The only changes in the set-up were: (A) a thermionic amplifier, as described by Hall and Adams[6], was used to increase the current through the telephone, to increase its sensitivity in finding

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[1] For the details of this analysis, see C. R. Timpany: Stanford University Thesis, (1925).

[2] J. Phys. Chem., 28, 965 (1924).

[3] J. Phys. Chem., 29, 102 (1925).

[4] J. Phys. Chem., 29, 138 (1925).

[5] J. Phys. Chem., 29, 1148 (1925).

[6] J. Am. Chem. Soc., 41, 1515 (1919).

the balance position on the bridge; (B) the electrodes of the cell were held apart by means of small glass pins, sealed into holes drilled in the electrodes; the cell constant was 0.0296 at 25° and 0.0290 at 0°.

In all calculations the weight of solvent in the experimental tube was corrected for the weight of vapor above the liquid, and for the weight of phosgene of crystallization accompanying the sample of salt used. Table I contains the experimental data obtained in the vapor tension measurements; series A was by the gravimetric, series B and C by the volumetric method. Table II contains the data obtained in the density measurements; the two pycnometers used are designated L and S. Table III contains the conductivity data for 25°, Table IV, the data for 0°; in the conductivity tables, each measurement is designated by a letter with subscript, a letter being assigned to each series of measurements made with a particular sample of salt, and the subscripts to the various dilutions obtained by changing the weight of solvent; the molecular conductivities have not been corrected for the conductivity of the solvent.

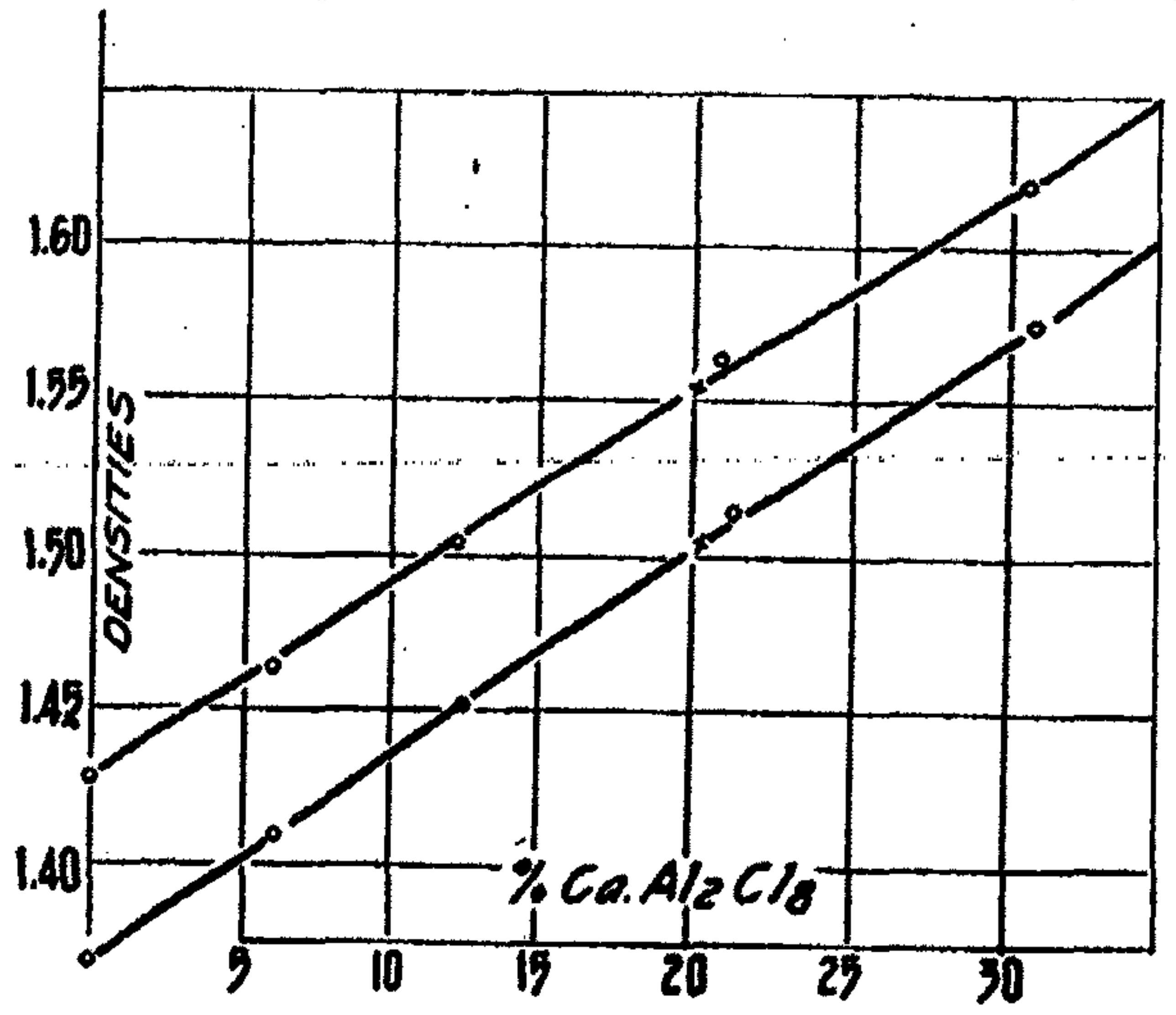

Fig. 2

Densities of Solutions $CaAl_2Cl_8$ in $COCl_2$.

Discussion

Figure 1 shows the form of the vapor tension curves, the 25° curve being a complete diagram for the system $CaAl_2Cl_8.COCl_2$ at this temperature, the 0° curve merely to the separation of crystals. In the 25° curve, AC represents the equilibrium between solution and vapor; AB for the unsaturated solutions, and BC for the supersaturated solutions; at B crystals begin to separate, indicating a solubility of 33.5%; the corresponding point on the 0° curve, at G, indicates a slightly lower solubility at 0°, or about 32.5%. The nearly horizontal portion of the curve BD represents the constant vapor tension of the saturated solution in equilibrium with vapor and solid, while the nearly vertical portion of BD represents the adsorption isotherm of the crystals deposited by the solution. The final horizontal section DE represents the constant vapor tension of the crystals, whose composition is given by the intersection at D, namely 66% $CaAl_2Cl_8$ and 34% $COCl_2$: the diphosgenate of calcium phosgeno-aluminate, $CaAl_2Cl_8.2COCl_2$, contains 65.6% of $CaAl_2Cl_8$, and 34.4% $COCl_2$, a very satisfactory agreement. Another deduction that can be made from the vapor tension curve is the molecular weight of the solute. Using the formula $m = \frac{gMp'}{p - p'}$, where m is the molecular weight of the solute, M that of the solvent, p the vapor tension of the solvent, p' that of the solution, and g the weight of solute in 1 gram of solvent, and using the value 1395.5 mm. for the vapor pressure of the solution at 25° when the concentration is 5% (from the curve), the molecular weight of the solute is 766. The molecular weight of $Ca_2Al_4Cl_{16}$ is 756.

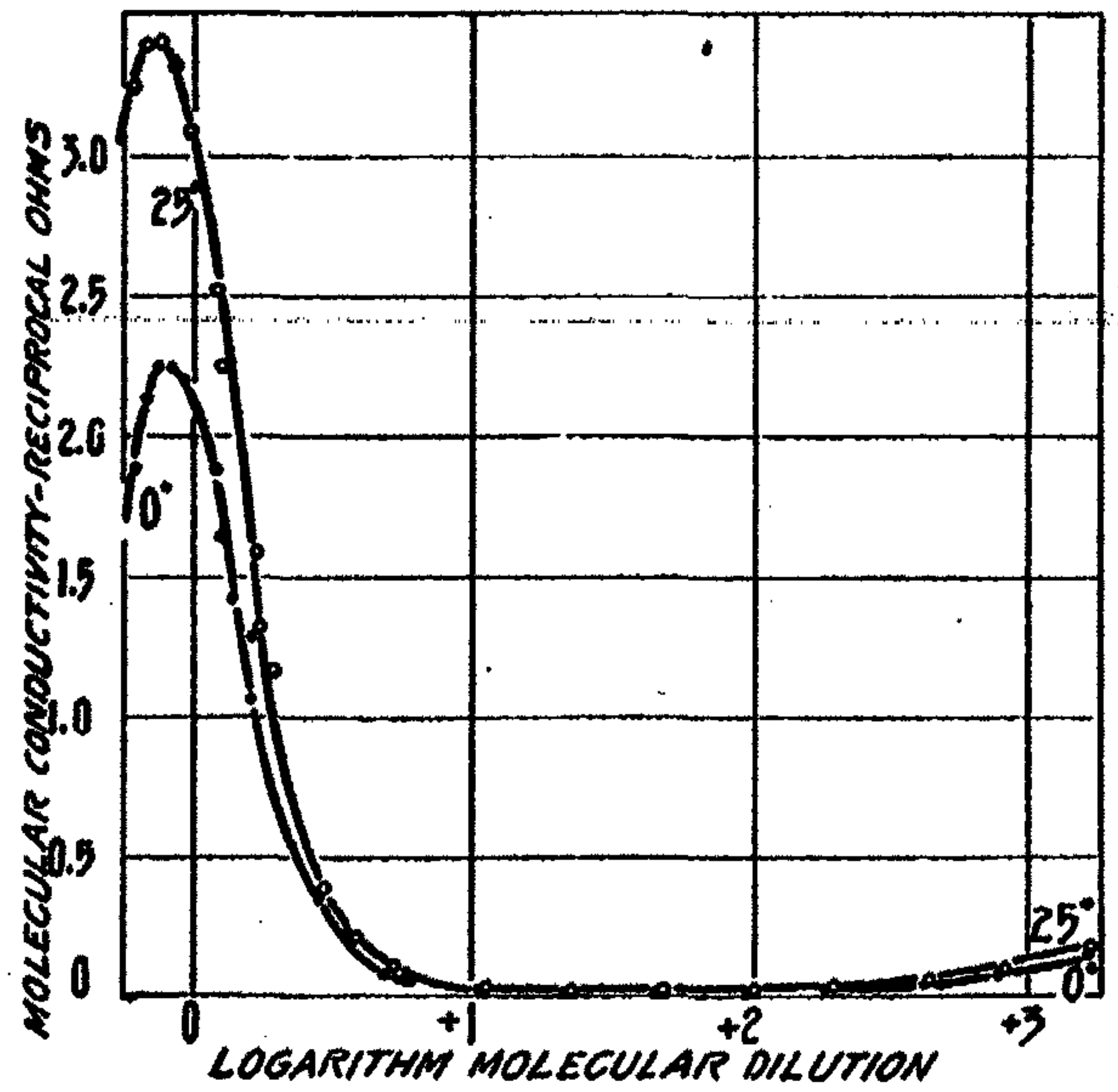

FIG. 3
Molecular Conductivities $CaAl_2Cl_8$ in $COCl_2$.

Figure 2 gives the density curves at the two temperatures.

Figure 3 shows the form of the conductivity curves at the two temperatures, the logarithms of the molecular dilutions plotted as abscissas, and molecular conductivities as ordinates. The general form of the conductivity curves is the same as that found for the conductivity of aluminium chloride in phosgene[1]. For an interpretation of the phenomenon, which is commonly known as the Gibbs effect, reference may be made to the aluminium chloride paper, or to the paper by Franklin on the conductivity of sulfur dioxide solutions[2].

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[1] Germann: J. Phys. Chem., 29, 1148 (1925).

[2] J. Phys. Chem., 15, 675 (1911).

TABLE I.

Vapor Tensions $CaAl_2Cl_8 \cdot COCl_2$

Series A at 25°		Series A at 0°	
% $CaAl_2Cl_8$.	Vap. Tens. mm. Hg.	% $CaAl_2Cl_8$.	Vap. Tens. mm. Hg.
3.06%	1400 mm.	2.99%	554 mm.
11.24	1385	10.28	547
22.04	1358	18.65	541
28.01	1320	22.95	530
49.65	1195	36.71	483

Series B at 25°		Series B at 0°	
11.43%	1380 mm.	10.60%	549 mm.
12.70	1376	11.50	546
15.48	1374	13.73	544
18.90	1365	16.39	542
22.30	1354	19.17	540
26.00	1339	21.54	537
30.18	1304	24.62	531
36.00 (cryst.)	1255	28.56	517
34.35	1228	29.77	514
37.90 (cryst.)	1250	31.20	507
37.48	1155	32.15	495
40.20 (cryst.)	1247	32.66 (cryst.)	498
43.00 "	1246	34.24 "	493
45.80 "	1242	38.10 "	490
52.10 "	1215	42.95 "	493
59.40 "	1153	47.40 "	484
62.40 "	1017	Series C at 25°	
63.60 "	908	64.6% (cryst.)	73 mm.
64.10 "	767	66.4 "	43
64.80	602	69.8 "	39
65.40 "	439	80.2 "	36
65.75 "	272	90.3 "	8
66.45 "	103	94.8 "	4
67.25 "	51	100. "	0

TABLE II

Densities of $CaAl_2Cl_8$ Solutions in $COCl_2$

Pycnometer	% $CaAl_2Cl_8$	Temperature	Density
S	0%	25°	1.3693
S	0	0	1.4270
L	0	25	1.3646
L	0	0	1.4265
L	0	25	1.3700
S	6.03%	0	1.4638
S	6.23	25	1.4091
L	12.10	0	1.5010
L	12.19	25	1.4470
L	12.44	0	1.5037
L	12.55	25	1.4528
S	20.70	0	1.5620
S	21.32	25	1.5150
L	30.52	0	1.6199
L	30.73	25	1.5748
L	20.10	0	1.5550
L	20.26	25	1.5055

TABLE III

Conductivities of Solutions of $CaAl_2Cl_8$ in $COCl_2$ at 25°

Solution	% $CaAl_2Cl_8$	Dilution in liters	Specific Cond. × 10^6	Molecular Cond.
A_1	0.017%	1643.	0.106	0.1742
A_2	0.034	825.	0.1057	0.0873
A_3	0.064	433.5	0.1288	0.0558
B_1	0.142	195.2	0.1853	0.0362
C_1	0.276	99.9	0.1880	0.0188
C_2	0.568	48.5	0.2560	0.0124
D_1	1.183	23.17	0.6217	0.0144
D_2	2.37	11.52	2.350	0.0271
D_3	5.06	5.34	19.86	0.106
E_1	6.70	3.993	58.15	0.232
E_2	8.73	3.035	125.1	0.380
E_3	13.08	2.039	569.5	1.161
E_4	14.78	1.745	755.0	1.318
E_5	19.72	1.277	1762.	2.250
F_1	14.86	1.733	915.0	1.586
F_2	20.37	1.232	2047.	2.520
F_3	25.00	0.983	3142.	3.090
F_4	27.70	0.877	3785.	3.315
F_5	30.64	0.782	4355.	3.405
F_6	33.49	0.709	4788.	3.395
F_7	36.80	0.635	5105.	3.240

TABLE IV

Conductivities of Solutions of $CaAl_2Cl_8$ in $COCl_2$ at 0°

Solution	$\%CaAl_2Cl_8$	Dilution in liters	Specific Cond. × 10^6	Molecular Cond.
A_1	0.017%	1586.0	0.1000	0.1586
A_2	0.033	800.0	0.0967	0.0774
A_3	0.062	425.8	0.1208	0.0514
B_1	0.141	187.4	0.1428	0.02675
C_1	0.276	96.0	0.1710	0.01632
C_2	0.564	46.93	0.2258	0.01059
D_1	1.81	22.34	0.5270	0.01177
D_2	2.36	11.12	2.230	0.02500
D_3	4.96	5.230	18.13	0.09480
E_1	6.70	3.843	63.78	0.2450
E_2	8.70	2.934	120.3	0.3530
E_3	14.68	1.695	631.8	1.070
E_4	17.60	1.397	1025.	1.432
E_5	19.51	1.250	1318.	1.647
F_1	14.81	1.679	778.	1.306
F_2	20.23	1.203	1568.	1.887
F_3	24.77	0.963	2280.	2.194
F_4	27.43	0.860	2611.	2.244
F_5	30.30	0.770	2912.	2.242
F_6	33.07	0.697	3067.	2.137
F_7	36.30	0.628	3000.	1.883

The fact we wish to emphasize here is that the molecular conductivity of calcium phosgeno-aluminate in phosgene is at all concentrations a greater than the molecular conductivity of aluminium chloride in phosgene (phosgeno-aluminic acid). For example, at the minimum point on the curve, at a dilution of twenty five liters, the former conducts three times as well as the latter (at 25°), at 1000 liters ten times as well, and on the other end of the curve the maximum conductivity of the solution of calcium phosgeno-aluminate is thirty-four times the maximum conductivity of the aluminium chloride solution. The fact that the molecular volumes and hence the molecular conductivities are calculated on the basis of the formula $CaAl_2Cl_8$, instead of double this, does not change these conclusions, since the vapor tension measurements of Germann and McIntyre[3] lead to the formula Al_2Cl_6 for aluminium chloride in phosgene; hence both would be affected in the same way by taking account of the true molecular weights of the two solutes.

The prediction that solutions of calcium phosgeno-aluminate in phosgene would be more highly ionized than similar solutions of aluminium chloride has thus been found to be in accord with the facts. The conception of the solution of aluminium chloride in phosgene as a weak phosgeno-acid, based

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[3] J. Phys. Chem., 29, 102 (1925).

on chemical grounds, is therefore supported by the fact that its calcium salt is much more highly ionized, as was made highly probable by the theory. Much additional information is of course necessary to test the theory further, but the information already available seems to indicate that the field is a very fertile one.

The phosgene for this research was supplied by Edgewood Arsenal.

TABLE V

Interpolated Values of Densities and Vapor Tensions

% $CaAl_2Cl_8$	Mol. conc. 0° $CaAl_2Cl_8$	Density at 0°	Pressure at 0°	Mol. conc. at 25°	Density at 25°	Pressure at 25°
0%	0.0000	1.4275	555.0mm.	0.0000	1.3685	1405.0mm
5%	0.1930	1.4577	551.0	0.1857	1.4025	1395.5
10%	0.3942	1.4888	547.0	0.3800	1.4350	1386.5
15%	0.6040	1.5207	542.5	0.5832	1.4685	1377.0
20%	0.8229	1.5540	537.5	0.7961	1.5033	1364.0
25%	1.0502	1.5865	529.5	1.0181	1.5380	1342.0
30%	1.2860	1.6190	510.0	1.2491	1.5725	1301.0
35%	1.5291	1.6510	469.0	1.4888	1.6065	1212.0

TABLE VI

Interpolated Values of Molecular Conductivities

Mol. Vol. $CaAl_2Cl_8$	Mol. Cond. in Mhos.		Mol. Vol. $CaAl_2Cl_8$	Mol. Cond. in Mhos.	
	at 0°	at 25°		at 0°	at 25°
0.60 liter	1.875	3.155	3.00 liter	0.360	0.395
0.65	2.025	3.285	5.00	0.150	0.165
0.70	2.150	3.390	7.50	0.065	0.075
0.75	2.225	3.410	10.	0.030	0.040
0.85	2.250	3.355	15.	0.012	0.020
0.95	2.225	3.160	25.	0.005	0.010
1.00	2.150	3.035	50.	0.005	0.010
1.10	2.025	2.810	100.	0.015	0.020
1.25	1.750	2.520	250.	0.030	0.035
1.50	1.375	2.050	500.	0.055	0.060
1.75	1.060	1.585	1000.	0.105	0.120
2.00	0.825	1.130	10000.	0.425	0.440
2.50	0.520	0.630			

Summary

This investigation was undertaken to gain further evidence as to the validity of the theory of phosgeno-acids and salts. The vapor tensions, densities, and conductivities of solutions of calcium phosgeno-aluminate in phosgene have been determined at 0° and at 25°. A résumé of the results obtained has been collected in Tables V and VI. The solubility and molecular weight of calcium phosgeno-aluminate in phosgene have been found. The solution has been shown to be a better conductor than the solution of aluminium chloride in phosgene, and additional evidence thus provided, indicating that the latter solution is to be regarded as the solvo-acid which, by neutralization, yields the salt, calcium phosgeno-aluminate.

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VAPOR-PRESSURE LOWERING AS A FUNCTION OF THE DEGREE OF SATURATION. I

BY ISAAC BENCOWITZ[1]

Introduction

Numerous functions expressing the relation of the vapor pressure of binary solutions, one of the components of which is non-volatile, are found in the literature. It was known for many years that water which contained some non-volatile substance dissolved in it boiled at a higher temperature than pure water. This indicated that the presence of the solute had lowered the vapor pressure of the solvent. The first generalization made in this connection was that of von Babo, who, in 1848, pointed out that the relative lowering of vapor pressure is independent of the temperature, providing the solution is dilute.

Wüllner[2] came to the conclusion that the lowering of the vapor pressure of water by non-volatile solutes was proportional to the concentration of the solute. Later, Tammann showed that this was not quite accurate. A great deal of apparent contradiction was removed by the experimental and theoretical work of Raoult,[3] who confirmed in certain cases both the laws of von Babo and Wüllner. The most important advance made by Raoult, however, lay in the introduction of the concept of molecular lowering of vapor pressure.

In 1858, Kirchhoff[4] obtained the formula,

$$Q = RT^2 \frac{d}{dt} \ln \frac{P_o}{P}$$

which expresses the vapor pressure as a function of the differential heat of solution. Notwithstanding the fact that this expression is theoretically sound, its validity was questioned until the experimental work of Roozeboom[5] and Sholtz[6] established it without doubt[7].

However, it must not be forgotten that this equation, as well as all relations which pure thermodynamics yields, is only an indirect relation, i.e. it does not give us a picture of the intermolecular forces which exist in the solution and determine its properties. Kirchhoff's law expresses the dependence of the vapor pressure on the differential heat of solution but does not disclose the nature of the function relating the differential heat to the

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[1] National Research Fellow in Chemistry.

[2] Pogg. Ann. 103, 529 (1858).

[3] Compt. rend. 103, 1125 (1886); 104, 1430 (1887); Z. physik. Chem. 2, 353 (1888).

[4] Pogg. Ann. 103, 177 (1858).

[5] Z. physik. Chem. 4, 31 (1889).

[6] Wied. Ann. 45, 193 (1892).

[7] Woitaschewsky: Z. physik. Chem. 78, 110 (1912). For the theoretical significance of this formula, see Porter: Trans. Faraday Soc. 11, 19 (1915).

temperature[1]. Van Laar,[2] on the basis of molecular attraction, obtained an equation for the vapor pressure of liquid-systems which can be used very satisfactorily as an empirical equation to fit any type of vapor pressure curve.[3]

For binary solutions, one of the components of which is nonvolatile, the equation takes the form:

$$P = P_0(1 - N)C^{an^2}$$

where P and P_0 are the vapor pressures of the solution and pure solvent respectively. N is the mol-fraction and *a* and C are constants.[4]

Due to the fact that it is claimed[5] that all equations connecting the vapor pressure of water with the temperature apply to saturated solutions of salts, it may be well to give a short account of the attempts made to deal with the variation of the pressure of saturated vapor (in contact with the liquid) with the temperature. These are characterized by the fact that on compression or rarefaction the volume undergoes considerable change while the pressure remains constant, until one or the other of the phases has entirely disappeared.

If the pressure of the saturated vapor depends only on the temperature, some general relation between the pressure and the temperature such as:

$$P = f(T)$$

must exist. The form of the function will probably depend on the nature of the substance, but no general law has as yet been found. The first attempt in this direction was made by Dalton, who proposed the simple law that the vapor pressure increases in a geometrical progression as the temperature increases in an arithmetical. This assumes that the relation between the pressure and temperature is of the form $p = b\alpha^T$ or $\log p = C^T + c$. This formula, however, holds only for small limits of temperature,—near the point at which the constants were determined.[6]

Young[7] proposed the formula $P = (a + bT)^n$, the three constants of which are determined experimentally. Another equation suggested by Roche[8] from theoretical considerations belongs to the type

$$P = b\alpha^{\frac{T}{m + nT}}$$

Finally, a more general form was suggested by Biot[9]: $\log p = a + b^T + C\beta^T$

Regnault found that Young's formula might be used to represent the results of experiments within a limited range of temperature, but that be-

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[1] Van Laar: Z. physik. Chem. **72**, 727 (1910).

[2] Z. physik. Chem. **72**, 723 (1910); **82**, 599 (1913).

[3] Hildebrand and Eastman: J. Am. Chem. Soc. **37**, 2452 (1915).

[4] Porter: Trans. Faraday Soc. **11**, 48 (1915).

[5] Woitaschewsky: Z. physik. Chem. **78**, 110 (1912). See also Compt. rend. **176**, 1552 (1923).

[6] Preston: "Theory of Heat," 3rd Ed. p. 393 (1919).

[7] Nat. Phil. **11**, 400.

[8] See Dulong and Arago's Memoir, Mém. de L'Institut **10**, 227.

[9] Preston: "Theory of Heat," p. 118 (1919).

yond this range it had to be abandoned. The formula of Roche, on the other hand, represents the whole series of experiments with considerable accuracy, but not quite as precisely as the more general formula of Biot.

Rankine[1] later suggested the expression:

$$\log p = a - b/t - C/T^2$$

where *a*, *b* and C are empirical constants, and T is the absolute temperature corresponding to the vapor pressure, p. This type of formula is in frequent use as it represents the whole series of Regnault's experiments fairly well. A closer approximation may be obtained, however, by applying the relation due to Bertrand[2] namely:

$$P = G\left(\frac{T-a}{T}\right)^n$$

Kirchhoff[3] in 1858, and Rankine in 1866, independently suggested the formula,

$$\log p = A + \frac{B}{T} + C \log T$$

(This equation as well as that of Young can be obtained from theoretical considerations)[4] The work of Nernst and others in connection with the heat theorem has drawn considerable attention to the expression first proposed by Hertz[5] which has the following form:

$$\log p = K_1 + K_2 \log T + \frac{K_3}{T}$$

This equation has been applied by Knudsen[6] in the case of the vapor pressure of mercury, and was thoroughly tested by Smith and Menzies[7].

A formula based partly on the theorem of corresponding states was proposed by Nernst[8]. This equation is based on the assumption that the molecular heat of the vapor at absolute zero is greater by 3.5 than the molecular heat of the liquid. Recent investigations on the specific heat at low temperatures show this to be not true[9].

It is seen, therefore, that all attempts to express the vapor pressure of a liquid in equilibrium with its vapor as a function of the temperature has been without recognized success. No rational law holding from the supercooled region below the triple point has been formulated. It is true, however, that the temperature ratio law of Ramsay and Young[10] holds for the whole range, from very low pressures up to the critical[11].

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[1] New Phil. Journal Edinburgh, July (1849).

[2] Bertrand: "Thermodynamique," p. 93 (1887).

[3] Pogg. Ann. 103, 185 (1858).

[4] Callendar: Enc. Brit. 10th Ed. p. 397.

[5] Wied. Ann. 17, 199 (1882).

[6] Ann. Physik, (4) 29, 179 (1909).

[7] J. Am. Chem. Soc. 32, 1434 (1910); Lewis: Physical Chemistry, 1, 93 (1920).

[8] This formula is discussed fully in Nernst: "Thermodynamics and Chemistry," (1907).

[9] Sackur and Gibson: "Thermodynamics," p. 218 (1917).

[10] Phil. Mag. 20, 515 (1885); 21, 33 (1886); 22, 37 (1886). For a very recent application of this principle, see: Lorenz: Z. anorg. allg. Chem. 138, 104 (1924); 143, 336 (1925). For its relation to Bertrand's vapor-pressure equation see Porter: Phil. Mag. 13, 724 (1907).

[11] Moss: Phil. Mag. 16, 356 (1903); 25, 453 (1907).

Many of the above equations derived for pure liquids in equilibrium with their own vapor have been applied to saturated solutions with varying success. Speranski[1] applied Bertrand's equation and found that it expresses accurately the experimental vapor pressure of saturated solutions of several salts. He also showed[2] that it holds for solutions of chloroform, benzene and liquid ammonia. The vapor pressure of potassium chloride, however, is more accurately expressed by the equation of Hertz[3]..

Relations connecting the vapor pressure with the solubility are rather scarce. The only one that came to my attention is that of Speranski[4] which has the form,

$$\log p = a \log C + b$$

where *a* and *b* are empirical constants and C is the weight of the salt in gms. which is required to saturate 100 gms. of water. It holds for $CuSO_4 . 5H_2O$ and Na_2SO_4 within the experimental error, but fails completely in the case of potassium chloride and potassium nitrate.[4]. Thus, all formulae suggested connecting the vapor-pressure and the temperature hold only for saturated solutions and then only for a few salts and within a short range of temperature; the equation connecting the vapor-pressure and the solubility is valid only in the case of a few salts. No function has been formulated as yet which expresses the vapor-pressure of aqueous solutions of non-volatile solutes, as a function of the temperature and the solubility, an equation which would express the experimental data within reasonable precision of most, if not all salts.

Degree of Saturation

Various methods are used to express the concentration of solutions. Each one of the methods has its field of usefulness. All of them, however, are arbitrary. The "volume-normal" system in expressing concentration while advantageous and correct for analytical purposes is both disadvantageous and illogical whenever any phenomenon is to be studied in which the influence of the solvent on the solute is involved. The only theoretical justification for the use of this system was based on van't Hoff's discovery[5] of the analogy between the osmotic pressure in dilute solutions and the gas law. Later, in order to bring the experimental values of the osmotic pressure in a closer conformity with the gas laws, the "weight-normal" system was introduced.[6]

Since then, however, the analogy between osmotic and gas pressures was definitely established to be a myth.[7] The theoretical foundation on which

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[1] Z. physik. Chem. 70, 519 (1910); J. Russ. Phys. Soc. 41, 91 (1910).

[2] Z. physik. Chem. 78, 86 (1912).

[3] Pavlovich: Z. physik. Chem. 84, 169 (1913).

[4] Z. physik. Chem. 78, 86 (1912); Another equation was recently proposed by Moudain-Mouval: Compt. rend. 178, 1164 (1924).

[5] Z. physik. Chem. 1, 481 (1887).

[6] Morse and Frazer: Am. Chem. J. 34, 1 (1905); 37, 324, 425, 458 (1906); 38, 175 (1907); Morse: "The Osmotic Pressure of Aqueous Solutions" p. 97 (1914); Findlay, "Osmotic Pressure" (1913); Bancroft: J. Phys. Chem. 10, 320 (1910).

[7] Lewis: J. Am. Chem. Soc. 30, 660 (1910); Kendall: 43, 1391 (1921); Hildebrand; "Solubility," p. 24 (1924).

these two systems were based was, thus shown to be groundless. Of the two, however, the "weight-normal" is to be preferred for the following reasons:

In the first place, the atomic weight is subject to constant revision, and therefore, varies from year to year. In the second place, the true molar weight except in a few cases, is not known, and the formula which is employed expresses only a surmise as to the composition of the ultimate molecule, or more frequently is merely the simplest expression which represents the stoichiometric proportions of the elements involved[1]. In the third place, the volume-normality changes with the temperature, so that to change from one temperature to another requires the knowledge of the density of the solution, which is seldom accurately known.

The mol fraction method of expressing concentration, because of Raoult's law assumes a theoretical significance. This law, however, is valid only in a few cases, for the so-called "ideal solutions." But even the ideal solution cannot be accurately defined by Raoult's law[2].

One thing is obvious and that is that the mol fraction is not a function of the intermolecular forces which exist in the solution and determine its properties. Whereas, when two properties of a solution are expressed as a function of each other with the object in view of gaining some knowledge about these intermolecular forces, both properties must be functions of these forces in so far as it is possible to determine.

The similarity between the process of solution and evaporation has been frequently pointed out. Nernst[3] went so far as to derive an expression for the lowering of the solubility similar to that of Raoult for vapor-pressure lowering. Whatever the theoretical basis for this and similar relations may be, it is plausible to assume that both the vapor pressure lowering and solubility are functions of the same solution forces. The composition expressed in terms of the solubility will, therefore, be a function of the solution, as much as the vapor pressure lowering. And all relations expressing any property of the solution as a function of the concentration expressed in this manner will be essentially fundamental.

The degree of saturation is the composition of a solution expressed in terms of the solubility. Thus, if the concentration of a solution is given as n gms. (or mols) per W gms. (or mols) of *solvent* and the concentration of a saturated solution as N gms. (or mols) per W. gms. (or mols) of solvent, the degree of saturation, S, is then given as,

$$S = n/N$$

The ratio of two degrees of saturation S_1, and S_2 at a given temperature will be:

$$S_1/S_2 = n_1/n_2$$

This ratio is, obviously, identical with the ratio of two concentrations expressed in gms. (or mols) per 1000 gms. of water. It is however, not identical with the ratio of two mol-fractions.

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[1] Lewis and Randall: "Thermodynamics," p. 33 (1923).

[2] Hildebrand: "Solubility," p. 27 (1924).

[3] Nernst: Z. physik. Chem. 6, 19 (1890).

This method of expressing concentration is not advocated for practical or for theoretical use. The disadvantages of this system are self-evident. In the first place, its accuracy is limited to that of the available data for the solubility. In most cases, this is very poor or not available at all. Furthermore, it cannot be applied to solutions the components of which are miscible in all proportions.

Nevertheless the theoretical importance of this method, especially in the study of the theory of solutions, is not invalidated by these shortcomings. It is hoped that the relation between the vapor pressure lowering and the degree of saturation derived in this paper will prove this point.

Vapor Pressure Lowering and the Degree of Saturation

Using the concept of the degree of saturation, the following relation is obtained:

$$\log \Delta P = K\left[\frac{1}{T} - a\left(1 - \frac{\log S}{b}\right)\right] \qquad (1)$$

where ΔP is the vapor pressure lowering, T, the absolute temperature, S, the degree of saturation, i.e. $S = n/N$, where n is the number of gms. or mols in a given weight of solvent and N is the number of gms or mols necessary to saturate the same weight of solvent, i.e. the solubility, and K, a, and b are constants.

This equation is derived on the basis of the following three postulates and is mathematically exact if the postulates are experimentally true.

Postulate 1: The coefficient, $\left[\frac{\partial P \log \Delta P}{\partial(\frac{1}{T})}\right]_S$ = constant = K, i.e. when log of the vapor pressure lowering, ΔP at a given degree of saturation, S, is plotted against the reciprocal of the corresponding absolute temperature a straight line is obtained. The slope of this line is K.

Postulate 2: The value of the coefficient is independent of the degree of saturation.

Postulate 3: The coefficient $\left[\frac{\partial K \log S}{\partial(\frac{1}{T})}\right]_{\Delta P = 1mm}$ is constant, i.e. when the log of the degree of saturation is plotted against the reciprocal of the absolute temperature at which the vapor pressure lowering is 1 mm. a straight line is obtained.

Assuming for the moment the validity of these postulates, relation (1) is derived as follows:

According to postulate 1

$$\left[\frac{\partial \log \Delta P}{\partial(\frac{1}{T})}\right]_s = K \qquad (2)$$

which on integration gives

$$\log \Delta P = K\left(\frac{1}{T}\right) + I \qquad (3)$$

where I is an integration constant.

When $\Delta P = 1$mm. $$I = K/T \tag{4}$$
where T, is the absolute temperature at which the solution of the given degree of saturation has a vapor pressure lowering of 1 mm.

According to postulate 3, when log S is plotted as ordinates and 1/T as abscissa, where T is the absolute temperature at which $\Delta P = 1$ mm. we obtain a straight line, the equation of which is,

$$\frac{\log S}{b} + \frac{(\frac{1}{T})}{a} = 1 \tag{5}$$

where *a* and *b* are the intercepts with log S and the 1/T axis respectively. Equation (5) can be written as

$$1/T = a\left(1 - \frac{\log S}{b}\right) \tag{6}$$

substituting this in (4) we get,

$$I = -Ka\left(1 - \frac{\log S}{b}\right) \tag{7}$$

This substitution is possible because of postulate 2. When (7) is substituted for I in (3) the final function is obtained.

$$\log \Delta P = K\left[\frac{1}{T} - a\left(1 - \frac{\log S}{b}\right)\right]$$

It is readily seen from the above simple mathematical derivation that relation (1) is exact if the three postulates are experimentally valid.

Experimental Proof of the Three Postulates

The experimental data used in testing the above three postulates were taken from Landolt and Börnstein's Tables and from Seidell's Solubilities.

The degrees of saturation corresponding to each temperature and vapor pressure lowering were obtained by dividing the concentration given in gms. per 100 gms. of water, by the proper solubilities similarly expressed. Smooth curves were drawn through the experimental points obtained by plotting the log of the degree of saturation, S, against the log of the vapor pressure lowering ΔP. The log ΔP for any given degree of saturation was read off from this series of isotherms and plotted against the reciprocal of the corresponding absolute temperature. The curves thus obtained are shown in Figs. 1 and 2.

It will be seen from these figures that the curve of each substance is a straight line which is a striking corroboration of Postulate 1, in view of the fact that 31 salts of various types are considered.

It may be of interest to point out that there is a break of the log $\Delta P - 1/T$ curve at the reciprocal of the absolute temperature corresponding to the transition point of two hydrates.

In order to prove Postulate 2, i.e. that the slopes of the log $\Delta P - 1/T$ curves are independent of the degree of saturation, a family of curves were obtained by plotting the values of log ΔP at different degrees of saturation against the reciprocal of the corresponding absolute temperature. In all cases, the slope of these curves is independent of the degree of saturation. The values of K,

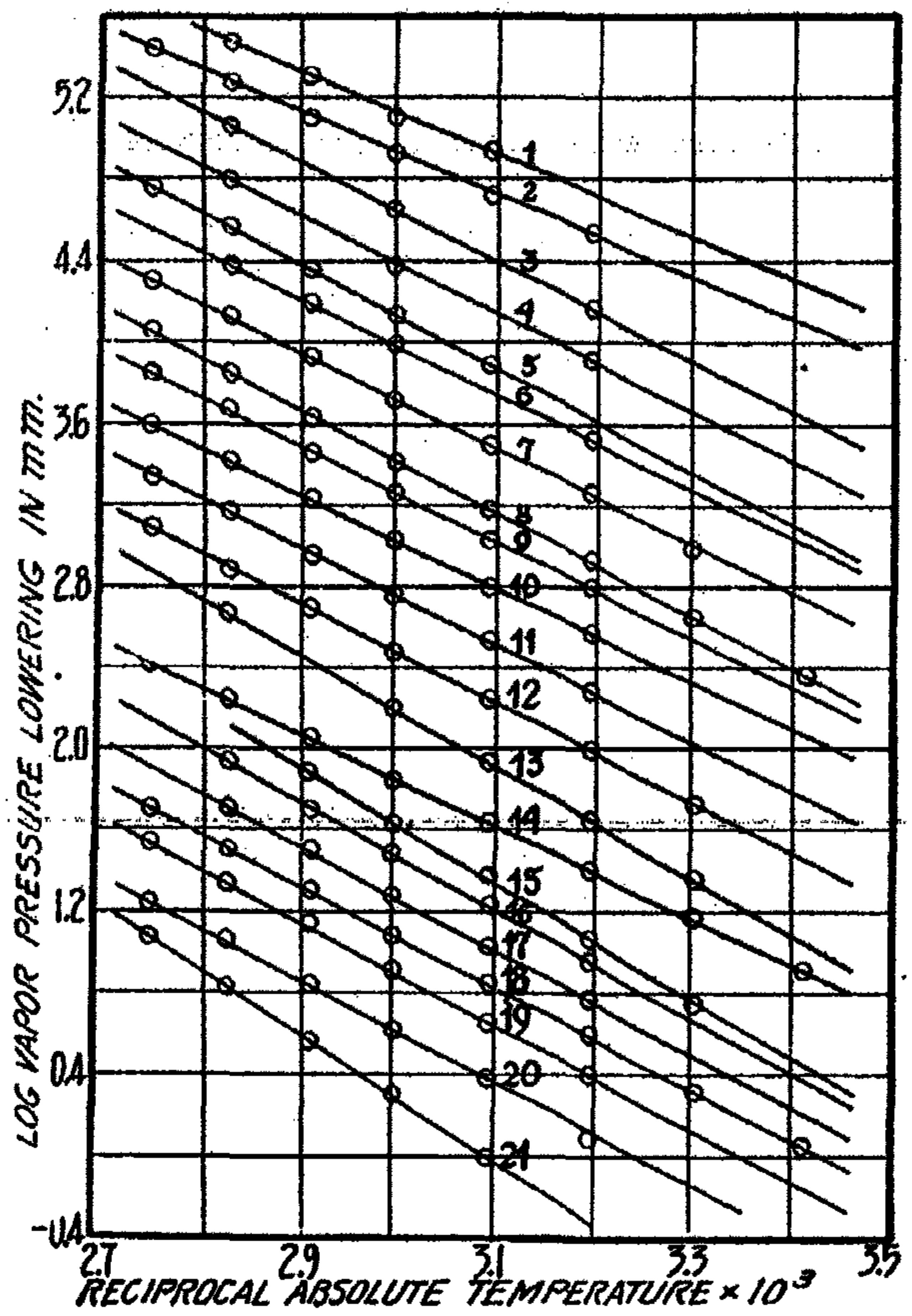

FIG. 1

Abscissas, reciprocal of absolute temperature x 10^3. Ordinates, log of the vapor pressure lowering in mm; there is a different origin of this axis for each curve.

LEGEND OF FIGS. 1 AND 2

No. of Curve	Name of Substance	log S		log ΔP scale	No. of curve	Name of Substance	log S	log ΔP scale
1	Na_2SO_4	0.4	Subtr.	4.8	18	KCl	0.4	O. K.
2	$Na_2CO_3 . H_2O$	0.4	"	3.9	19	$NiSO_4 . 6H_2O$	0.3	Subtr. 0.2
3	$MgCl_2 . 6H_2O$	0.5	"	3.3	20	KI	0.4	Add 0.6
4	$BaBr_2 . 2H_2O$	0.4	"	3.2	21	KNO_3	1.0	" 0.4
5	$BaCl_2 . 2H_2O$	0.3	"	3.2	22	NH_4Br	0.4	Subtr. 2.5
6	$CaCl_2 . 2H_2O$	0.9	"	2.8	23	KBr	0.6	" 2.6
7	$(NH_4)_2SO_4$	0.5	"	2.7	24 a	$NaBr . H_2O$		
8	Na_2NO_3	0.5	"	2.1	24 b	$NaBr . 2H_2O$	0.3	" 1.6
9	K_2CO_3	0.5	"	1.9	25 a	$ZnSO_4 . H_2O$		
10	K_2CrO_4	0.5	"	2.2	25 b	$ZnSO_4 . 6H_2O$	0.5	" 2.1
11	CsCl	0.8	"	1.8	26 a	$LiBr . H_2O$		
12	RbCl	0.5	"	1.3	26 b	$LiBr . 2H_2O$	0.6	" 0.8
13	$NaI . 2H_2O$	0.4	"	0.5	27	$BeSO_4 . 4H_2O$	0.4	" 1.2
14	NaCl	0.4	"	0.7	28	$SrBr_2 . 6H_2O$	0.4	" 0.3
15	$CoSO_4 . 7H_2O$	0.2	"	0.2	29	$SrCl_2 . 6H_2O$	0.4	" 0.3
16	NH_4Cl	0.4	"	0.2	30	$NaClO_3$	0.5	" 0.3
17	LiCl	0.9		O.K.	31	$CuSO_4 . 5H_2O$	0.4	" 0.4

the slope of the line $\log \Delta P - 1/T$, for each substance were obtained graphically from such curves and are given in columns 2 and 6 of Table I.

According to postulate 3, when log S is plotted against the reciprocal of the absolute temperature at which a solution corresponding to the degree of saturation, S, has a vapor pressure lowering of 1 mm., the curve obtained is a straight line. To prove this statement, values of $(1/T)_{\Delta p = 1\text{mm.}}$ were obtained by plotting $\log \Delta p$ against $1/T$ for different values of log S. The intersections of these lines with the $1/T$ axis are the required $(1/T)_{\Delta p = 1\text{mm.}}$ values corresponding to log S of the particular $\log \Delta p - 1/T$ curve. When these intersections are projected downward a distance equal to log S of the corresponding $\log \Delta p - 1/T$ curve, as shown in Fig. 3, a curve is obtained which is the desired $\log S - 1/T$ curve.

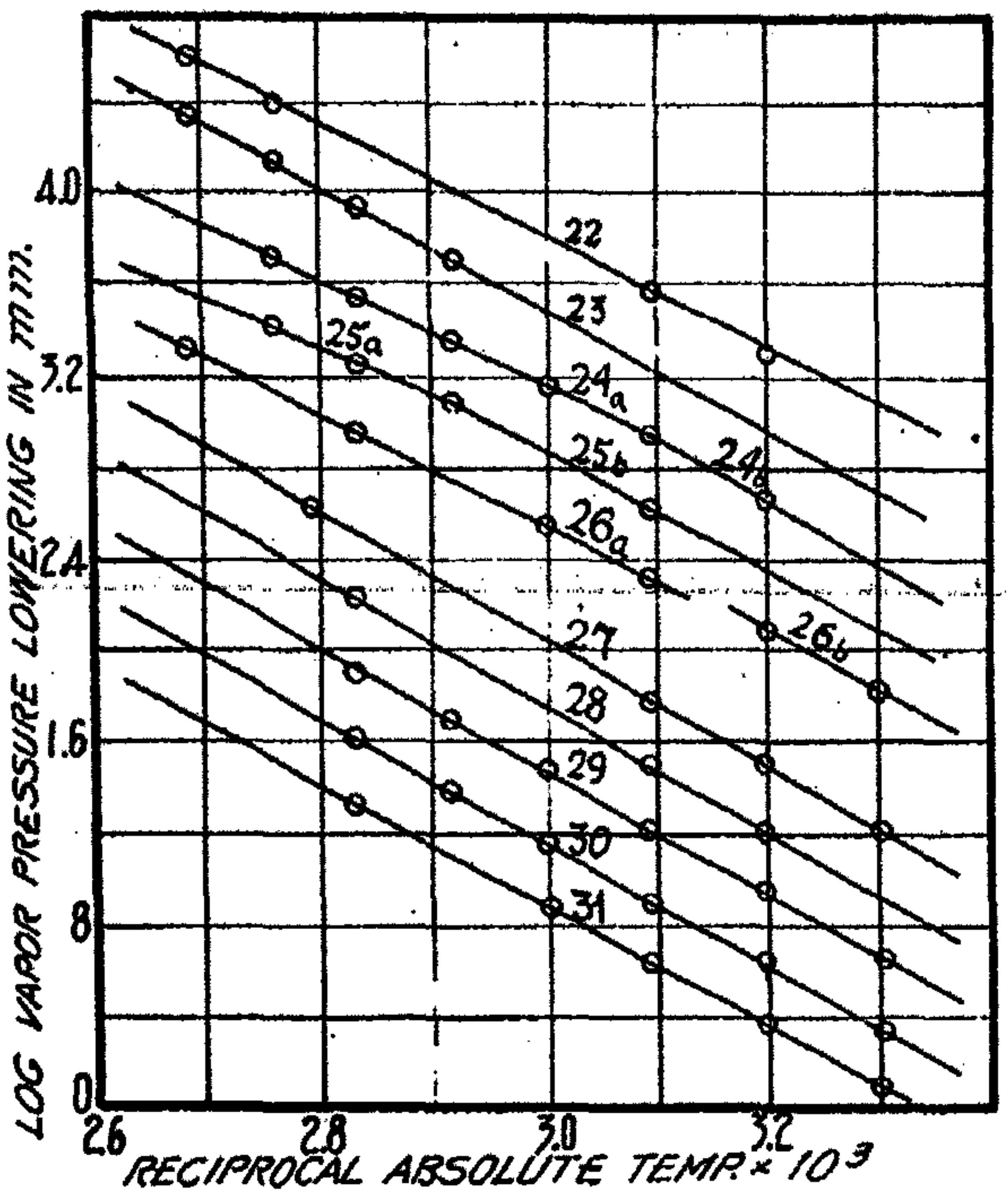

Fig. 2

Abscissas, reciprocal of absolute temperature x 10³. Ordinates, log of the vapor pressure lowering in mm; the origin of this axis is different for each curve.

Such curves for 31 salts are shown in Fig. 4. It will be seen that with the exception of $CuSO_4 . 5H_2O$, these curves are straight lines. The instances where there is a deviation from this rule are so few that it is plausible to assume that the experimental data in such cases are in error. This is conclusive proof of the validity of Postulate 3[1].

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[1] The experimental data for $Al_2(SO_4)_3$ and LiI are not in agreement with this postulate. The deviations, however, are so irregular that it makes one doubt the accuracy of the experimental data. We hope, however, in the near future, to publish new experimental data on the vapor pressure lowering of these salts and a few others.

The intersections of log S – 1/T curve with the 1/T and log S axes give the values of the constants a and b respectively. These values are given in columns 3, 4, 7 and 8 of Table I.

The values of the three constants, K, *a* and *b* given in Table I are not final. They are very sensitive to slight changes in the experimental data and will no doubt change as more accurate data should become available. It may even be predicted that more accurate data will bring out regular deviations from the three postulates; deviations which at present are masked by large experimental error. The degree of saturation as expressed in this paper is probably only the "apparent" degree of saturation and should be corrected for such effects as "self-salting-out." However, this, as well as other factors involved, are probably very small as evidenced by the fact that the values of ΔP calculated with equation (1) are in very close agreement with the experimental data. The comparative values of the experimental and calculated ΔPs are given in Table II. In order to save space, these values are given only

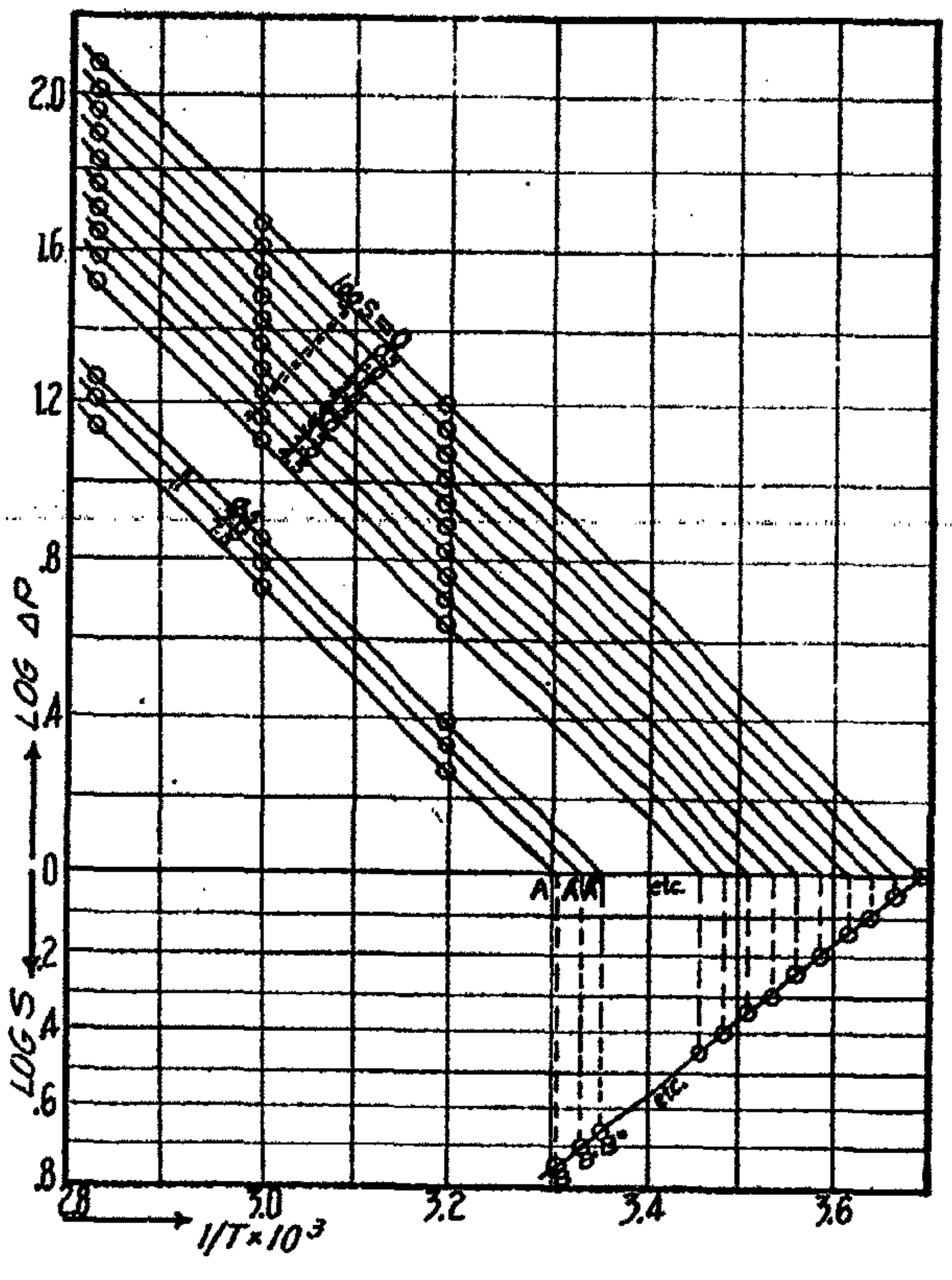

FIG. 3

Abscissas, reciprocal of absolute temperature x 10^3. Ordinates, upper part, log of the vapor pressure lowering of $BaBr_2 . 2H_2O$; the lower part, the log of the corresponding degree of saturation.

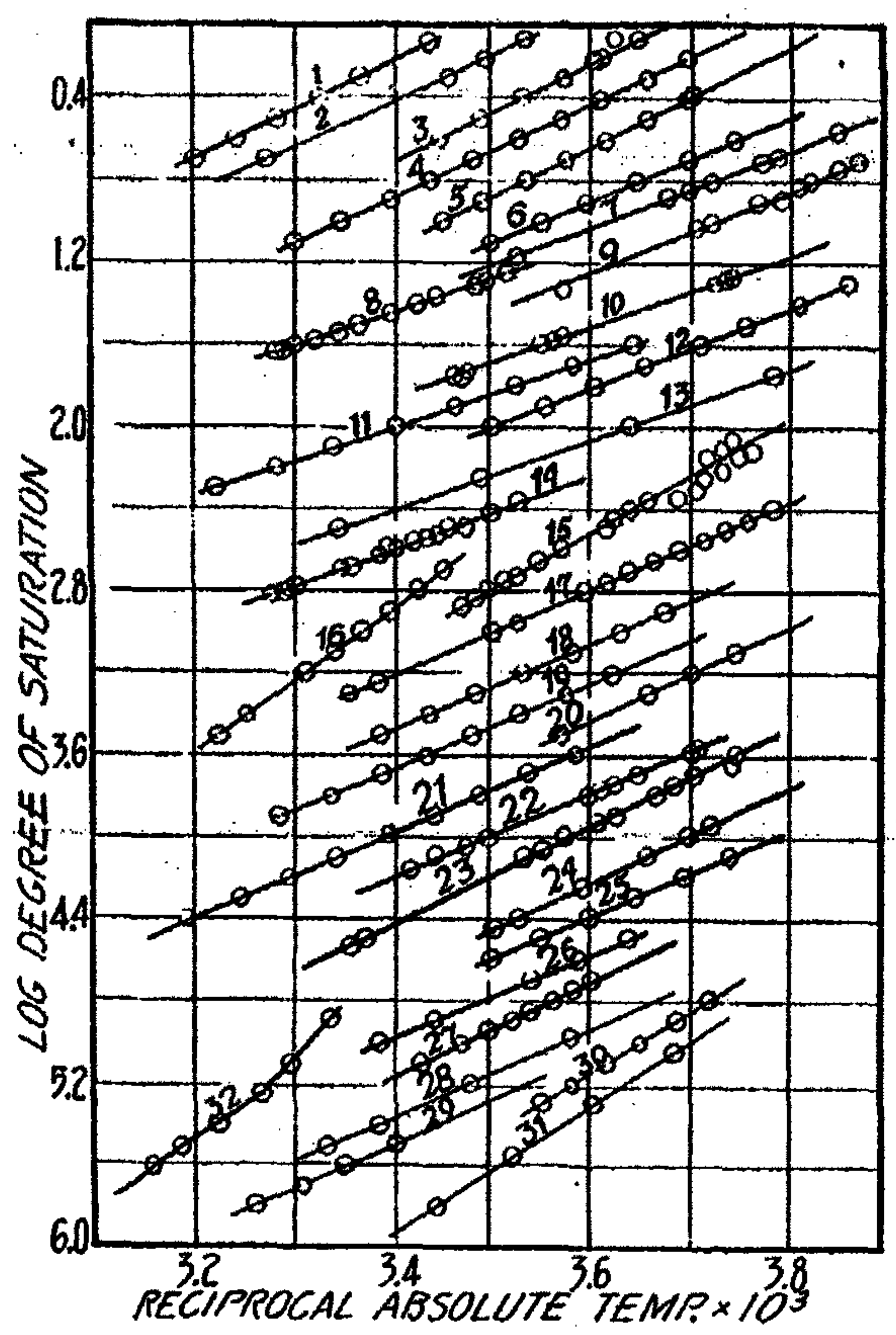

Fig. 4

Abscissas, reciprocal of absolute temperature x 10^3. Ordinates, log of the degree of saturation; the origin of this axis is different for each curve.

Legend of Fig. 4

No. of Curve	Name of Substance	log S Scale	No. of Curve	Name of Substance	Log S Scale
1	KCl	O. K.	17	NaCl	Add 2.4
2	$BrCl_2 . 2H_2O$	O. K.	18	$SrBr_2 . 6H_2O$	" 2.6
3	KBr	O. K.	19	$SrCl_2 . 6H_2O$	" 2.9
4	KI	O. K.	20	RbCl	" 3.0
5	NH_4Br	Add 2	21	Na_2SO_4	" 3.4
6	LiCl	O. K.	22	$Na_2CO_3 . H_2O$	" 3.4
7	$LiBr . H_2O$	O. K.	23	$NaI . 2H_2O$	" 3.3
8	$NiSO_4 . 6H_2O$	Add 1.20	24	$NaBr . 2H_2O$	" 3.7
9	$LiBr . 2H_2O$	" 2.0	25	$NaBr . H_2O$	" 3.8
10	$CaCl_2 . 2H_2O$	" 0.6	26	K_2CrO_4	" 4.4
11	$BeSO_4 . 4H_2O$	" 1.6	27	$(NH_4)_2SO_4$	" 4.4
12	K_2CO_3	" 1.2	28	$ZnSO_4 . H_2O$	" 4.7
13	$MgCl_2 . 6H_2O$	" 1.5	29	$ZnSO_4 . 6H_2O$	" 5.0
14	$CoSO_4 . 7H_2O$	" 2.4	30	NH_4Cl	" 4.8
15	$NaClO_3$	" 2.0	31	$NaNO_3$	" 4.8
16	KNO_3	" 2.2	32	$CuSO_4 . 5H_2O$	" 4.8

for three concentrations and a few temperatures. The agreement, however, is of the same order throughout.

Columns 1 and 2 are self explanatory. Column 3 gives the solubility expressed in gms. per 100 gms. of water. In columns 4, 7 and 10 are given the degrees of saturation obtained by dividing the concentration by the corres-

TABLE I

Values of the Three Constants

Name of Substance	K	$a \times 10^4$	b
LiCl	2570	3.945	8.025
$LiBr.H_2O$	2405	4.040	7.738
$LiBr.2H_2O$	2430	4.012	8.464
KCl	2500	3.594	8.985
KBr	2595	3.598	8.745
KI	2610	3.688	8.455
NH_4Cl	2625	3.625	10.63
NH_4Br	2500	3.682	8.940
NaCl	2308	3.690	7.937
$NaBr2H_2O$	2610	3.736	8.525
$NaBrH_2O$	2393	3.790	7.831
$NaI2H_2O$	2750	3.780	9.092
RbCl	2487	3.696	8.399
CsCl	2400	—	—
KNO_3	3200	3.495	12.52
K_2CrO_4	2350	3.593	7.315
$K_2CO_32H_2O$	2425	3.817	7.394
$Na_2CO_3H_2O$	2025	3.708	7.242
$NaNO_3$	2590	3.670	11.36
Na_2SO_4	2090	3.585	7.370
$(NH_4)_2SO_4$	2400	3.631	8.720
$NaClO_3$	2650	3.690	10.21
$CaCl_22H_2O$	2315	4.022	7.071
$BaCl_2.2H_2O$	2575	3.480	8.078
$BaBr_2.2H_2O$	2425	3.690	7.216
$SrCl_2.6H_2O$	2770	3.664	7.770
$SrBr_2.6H_2O$	2750	3.724	7.770
$MgCl_2.6H_2O$	2460	3.836	6.573
$BeSO_4.4H_2O$	2775	3.551	5.803
$NiSO_4.6H_2O$	2610	3.447	5.771
$CoSO_4.7H_2O$	3073	3.417	6.287
$ZnSO_4.6H_2O$	2575	3.543	9.032
$ZnSO_4.H_2O$	2085	3.622	7.592
$CuSO_4.5H_2O$	2685	3.263	16.80

TABLE II

Comparison of Calculated and Observed Values for Vapor Pressure Lowerings, △ P

Name of Subst.	t	Soly.	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$
KCl	30	37.0	26.76	1.4	1.490	53.51	2.9	2.88	80.28	4.2	4.35
	50	42.6	23.34	4.0	4.132	46.68	8.2*	8.245	70.02	12.6	12.41
							8.3			12.5	
	70	48.3	20.67	10.0[a]	10.27	41.35	21.0	20.31	62.03	31.1	30.9
				9.7			20.3			31.2	
	90	54.0	18.65	22.6	23.04	37.29	47.3	45.95	55.93	69.8	69.6
				21.8			45.7			70.2	
KBr	70	90.0	28.36	14.8	15.45	39.65	21.8	21.98	51.05	29.1	29.09
	80	95.0	38.00	23.1	23.46	36.85	33.8	33.6	47.37	45.2	43.95
	90	99.2	25.20	34.8	34.94	35.28	50.9	49.92	45.36	68.2	65.62
	100	104.0	5.836	11.2	11.65	10.33	20.8	21.33	19.40	41.5	41.9
KI	50	168	8.928	2.2	2.225	20.83	5.9	5.92	38.69	11.9	11.97
	60	176	8.524	3.8	3.706	36.93	20.0	19.69	53.97	30.2	30.53
	70	184	8.152	6.2	5.996	19.03	16.0	15.77	35.32	32.0	31.99
	80	192	7.812	9.5	7.40	33.85	49.3	50.0	18.23	24.7	24.43
KNO_3	50	85.5	5.798	1.5	1.488	17.40	4.1	3.965	28.99	6.2	6.309
	60	110.	4.541	2.4	2.368	13.31	6.6	6.309	22.19	10.0	9.965
	70	138.	3.621	3.8}[a]	3.685	10.86	10.2}	9.817	18.10	15.7	15.61
				3.6}			9.3}				
	90	202	2.451	8.5	7.98	7.372	23.1	22.23	12.25	35.2	35.4
							22.4		34.	34.2	

TABLE II (Continued)

Name of Subst.	t	Soly.	S	ΔP							

Name of Subst.	t	Soly.	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$
$K_2CO_3.2H_2O$	40	117.	17.09	3.6	3.51	68.38	20.0	20.07	94.03	29.6	30.6
	60	121.2	15.76	9.4	9.33	63.09	52.6	52.88	86.74	77.7	78.7
	80	139.8	14.30	21.1	21.44	35.76	65.5	67.69	57.21	118.	121.6
	90	147.5	13.56	30.5	30.48	54.24	170.0	173.2	74.58	252.	250.1
K_2CrO_4	40	66.95	37.26	2.8	2.77	59.76	4.8	4.75	104.6	9.1	9.03
	60	70.85	35.28	7.5	7.35	70.58	16.6	16.32	98.80	24.3	24.11
	70	73.01	34.24	11.6	11.55	54.79	19.8	19.62	95.88	37.5	37.35
	80	75.14	33.28	17.3	17.22	66.71	38.2	38.46	93.18	56.0	57.41
	90	77.02	32.46	25.0	25.33	51.93	42.8	43.22	90.89	81.3	81.09
NH_4Cl	40	45.78	No data available			54.60	7.7	7.81	109.2	14.6	14.45
	60	55.38				45.14	21.3	21.7	90.30	39.3	38.97
	80	65.58				38.13	50.6	50.58	76.25	93.4	94.17
	90	71.26				35.07	75.0	75.17	70.16	13.8	137.87
NH_4Br	40	88.5**	16.95	2.6	2.66	33.90	5.5	5.37	56.51	9.1	8.56
	50	94.18	15.93	4.4	4.39	31.85	9.1	9.02	53.09	15.2	15.21
$(NH_4)_2SO_4$	30	77.29**	19.41	1.2	1.20	38.82	2.4	2.39	51.76	3.2	3.211
	50	84.52	17.74	3.5	3.44	35.49	6.9	6.82	47.32	9.3	9.12
	70	91.94	16.31	8.6	8.54	32.63	17.2	16.65	43.51	22.9	22.79
	80	95.32	15.74	12.9	12.93	31.47	25.9	25.94	41.97	34.5	34.59
	90	99.21	15.12	18.8	18.80	30.24	37.5	37.73	40.33	50.2	50.31

TABLE II (Continued)

Name of Subst.	t	Soly.	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$
NaCl	20	35.84**	27.90	1.1	1.096	55.8	2.3	2.303	69.75	2.9	2.92
	30	36.06	27.72	2.0	1.995	55.46	4.2	4.201	69.34	5.4	5.33
	50	36.66	13.64	2.8	2.781	40.92	8.9	9.07	81.82	19.1	18.97
	60	37.07	13.49	4.5	4.474	67.43	25.12	25.18	80.94	30.9	30.78
	70	37.52	26.65	14.45	14.79	66.63	39.26	39.72	79.98	48.3	48.37
	90	38.54	12.97	15.9	15.90	38.92	50.4	51.50	77.82	108.5	108.5
$NaBr.2H_2O$	40	105.8**	35.27	6.0	6.1	26.45	8.4	8.49	17.63	13.4	13.46
	50	116.0	58.01	6.3	6.29	38.67	10.1	10.0	19.43	22.7	22.2
$NaBr.H_2O$	80	118.36	16.90	24.9	24.91	25.35	39.8	39.9	50.70	89.3	89.33
	90	120.76	24.85	59.0	59.02	33.14	82.7	82.6	49.70	132.0	131.5
$NaNO_3$	30	94.9	10.53	1.4	1.404	21.17	2.4	2.447	84.30	7.9	7.83
	40	102.	9.805	2.4	2.403	39.22	7.8	7.73	58.83	11.0	10.93
	60	122	8.195	6.4	6.546	32.78	21.	20.94	65.57	37.3	37.24
							20.2b			36.5b	
	80	148.	27.02	49.9	49.31	40.54	70.4	69.26	54.05	88.8	88.2
				49.4c			69.7c			88.2c	
$Na_2CO_3.H_2O$	40	49.7	20.12	2.0	2.07	40.24	4.3	4.244	60.35	6.7	6.46
	60	46.4	21.55	5.6	5.46	43.10	11.1	11.19	64.66	17.2	17.03
	70	45.78	21.84	8.1	8.31	43.68	17.0	17.05	65.53	26.0	26.06
	90	45.4	22.22	18.0	17.77	44.44	37.4	36.42	66.66	55.3	55.38

TABLE II (Continued)

Name of Subst.	t	Soly.	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$
Na_2SO_4	50	46.84**	32.03	3.3	3.33	42.7	4.6	4.52	106.75	11.4	11.25
	60	45.57	32.92	5.3	5.29	43.88	7.3	7.125	109.70	18.3	18.03
	80	43.69	34.33	12.5	12.59	45.77	17.0	16.75	114.45	42.7	43.35
	90	42.85	35.01	18.5	18.48	46.68	24.9	24.75	116.40	62.3	62.37
$NaClO_3$	30	126.	22.12	2.5	2.527	48.68	5.4	5.37			
	40	140.	19.84	4.3	4.377	43.65	9.3	9.33	No data available		
	60	172.	16.13	11.5	11.48	35.49	25.2	24.79			
	80	189.	13.22	27.4	26.98	29.10	59.7	57.27			
LiCl	40	90.6	8.840	4.0	3.96	13.20	6.4	6.59	27.63	16.9	16.72
	60	103.	7.768	10.6	10.55	11.65	17.2	17.63	24.27	44.8	43.95
	70	109.	7.340	16.5	16.44	11.01	26.8	27.3	22.93	69.3	70.40
	80	115.	6.960	25.0	24.91	10.43	40.3	41.40	21.73	103.0	104.70
$LiBr.2H_2O$	30	191.	7.854	2.8	2.849	15.71	6.2	6.29	23.56	10.1	9.995
$LiBr.H_2O$	40	205.	7.316	4.8	4.799	14.63	10.3	10.54	21.95	16.7	16.8
	50	214.	7.010	7.2	6.654	21.03	26.7	26.53	28.04	38.0	38.02
	60	224	13.39	24.8	24.945	20.09	41.5	41.78	26.80	59.7	59.84
	80	245	12.24	56.2	57.94	18.36	96.	75.4	24.49	139.	138.2

TABLE II (Continued)

Name of Subst.	t	Soly.	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$
RbCl	30	97.60**	15.37	1.2	1.24	35.86	3.1	3.08	76.85	7.1	7.21
	50	109.3	13.72	3.6	3.54	32.02	8.9	8.938	68.63	20.5	20.70
	60	115.5	12.99	5.7	5.65	30.31	14.2	14.35	38.95	19.1	18.87
	70	121.38	12.36	8.9	8.867	28.83	22.2	22.42	61.78	51.5	51.44
	90	133.2	11.26	19.8	19.75	26.28	49.5	50.00	56.31	115.0	115.3
$BaCl_2.2H_2O$	50	43.67	22.90	1.9	1.915	68.60	6.7	6.47	91.60	8.9	8.86
	60	46.42	21.54	3.1	3.080	64.63	10.9	10.45	86.18	14.4	14.31
	70	49.47	20.22	4.8	4.84	60.64	17.1	16.33	80.99	22.5	22.63
	80	52.42	19.08	7.3	7.34	57.23	26.0	25.07	76.32	34.2	34.28
	90	58.74	18.01	10.8	10.79	54.03	38.5	36.9	72.05	50.7	50.76
$BaBr_2.2H_2O$	40	114.2	21.89	2.4	2.403	43.79	5.7	5.68	87.58	13.5	13.43
	60	123.2	20.29	6.4	6.419	40.59	15.1	15.07	81.18	35.8	35.64
	80	134.8	18.54	14.8	14.84	37.98	34.9	34.94	55.64	58.3	58.02
$CaCl_2.2H_2O$	60	137.0	7.30	7.7	7.28	10.95	12.6	12.4	21.9	31.1	30.76
	70	141.6	7.06	11.0	11.12	10.55	18.6	19.05	21.19	47.2	47.12
	80	146.95	6.80	16.0	16.56	10.21	27.5	28.12	20.42	70.5	69.99
	90	152.6	6.56	23.2	23.46	9.83	40.	39.99	19.66	103.	99.33

TABLE II (Continued)

Name of Subst.	t	Soly.	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$
$SrCl_2.6H_2O$	30	58.71	17.04	1.00	1.003	34.07	2.4	2.49	51.11	4.1	4.227
	40	66.31	15.31	1.7	1.709	30.63	4.2	4.25	45.94	7.0	7.16
	50	72.4	13.81	2.8	2.82	27.63	6.8	6.99	41.44	11.5	11.87
	60	81.8	12.22	4.4	4.36	24.44	10.8	10.8	36.67	18.1	18.11
$SrBr_2.6H_2O$	50	135.8	14.73	4.2	4.29	29.46	10.9	10.69	44.19	17.9	18.11
	60	150.0	13.33	6.6	6.73	26.67	16.2	16.75	40.00	28.5	28.58
	80	181.8	11.00	15.5	15.41	22.01	37.8	38.36	43.97	100.	102.1
$MgCl_2.6H_2O$	40	57.49	17.4	3.2	3.07	34.78	8.6	8.27	60.88	19.4	18.48
	60	61.04	16.38	8.4	8.37	32.77	22.7	22.54	57.34	51.2	50.41
	80	66.12	15.13	19.	19.51	30.25	51.6	52.79	52.94	116.1	117.9
$BeSO_4.4H_2O$	30	43.78	34.18	0.8	7.94	68.34	2.6	2.57	102.8	5.2	5.13
	40	46.30	32.03	1.4	1.403	64.05	4.4	4.54	96.06	8.9	9.07
$NiSO_4.6H_2O$	30	43.45	57.53	1.0	1.026	103.6	2.5	2.530			
	50	50.18	49.82	2.8	2.811	89.68	7.0	7.005			
	65	54.81	45.60	4.4	4.25	82.10	10.9	10.61	No data available		
	80	63.14	39.59	9.5	9.55	71.26	23.6	23.86			
	90	67.88	36.83	13.4	13.37	66.30	33.2	33.42			

Table II (Continued)

Name of Subst.	t	Soly.	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$	S	$\Delta P_{obs.}$	$\Delta P_{calc.}$
$CuSO_4.7H_2O$	40	48.85	51.18	1.6	1.57	92.12	4.3	4.210	No data available		
	50	55.2	45.29	2.7	2.60	81.52	7.2	6.995			
	60	60.4	41.39	4.3	4.29	74.50	11.4	11.52			
	70	65.7	38.05	6.5	6.95	68.48	17.3	18.65			
$CuSO_4.5H_2O$	30	25.0	40.00	0.5	.492	60.00	0.6	.602	80.00	0.7	0.698
	40	28.5	35.09	0.9	.883	52.64	1.1	1.09	70.12	1.3	1.257
	50	33.3	30.03	1.4	1.504	45.05	1.9	1.867	60.05	2.2	2.152
	60	40.0	25.00	2.3	2.45	37.50	3.1	3.005	49.99	3.5	3.475
	80	55.0	18.18	5.5	6.004	27.27	7.2	7.27	36.27	8.4	8.490
$ZnSO_4.6H_2O$	15	50.77	29.55	0.3	0.328	39.39	0.4	0.436	49.23	0.5	0.549
	50	76.86	19.52	2.0	2.00	26.02	2.7	2.707	32.52	3.4	3.392
	70	89.03	16.85	5.1	5.106	22.46	6.8	6.827	28.08	8.5	8.55
$ZnSO_4.H_2O$	80	86.6	17.32	7.7	7.73	23.10	10.3	10.34	28.87	12.9	12.87
	90	83.7	17.92	11.5	11.47	23.	15.2	15.19	29.86	19.1	19.13

[a] The data given in the lower row are by Nicol; the rest of the data are by Emden.

[b] These figures are by Tamman.

[c] These figures are by Nicol; the rest of the data are by Emden.

** Solubilities from Landolt and Bornstein.

ponding solubility given in column 3. In columns 5, 8 and 11 the experimental vapor pressure lowerings are given, and the corresponding calculated values are given in columns 6, 9 and 12.

Conclusion

In conclusion, it is of interest to point out that the constant, *a*, in equation (1) is the reciprocal of the absolute temperature at which a saturated solution has a vapor pressure lowering of 1 mm. This is seen from Figs. 2 and can be readily proven theoretically. This is important, because if the vapor pressure lowering of a saturated solution of 2 (or better 3) temperatures is known, then the line $\log \Delta P_1 - /T$ can be drawn. The slope of this line is K and its intersection with the $1/T$ axis is a. The third constant of the equation can be obtained if only one other value of ΔP and the corresponding degree of saturation are known.

Two generalizations follow directly from equation (1), which can be written in the form,

$$\log \Delta P = \frac{Ka}{b} \log S + K\left(\frac{1}{T} - a\right) \qquad (8)$$

For a saturated solution, since $S = 1$ and $\log S = O$, this equation reduces to,

$$\log \Delta P_s = K\left(\frac{1}{T} - a\right) \qquad (9)$$

Substracting (9) from (8), We obtain,

$$\log \frac{\Delta P}{\Delta P_s} = \frac{Ka}{b} \log S$$

or dropping the logs $\quad \dfrac{\Delta P}{\Delta T_s} = S^{\frac{Ka}{b}}$

This equation can be stated in words in the form of two generalizations.

1. The ratio of the vapor pressure lowering at any degree of saturation over the vapor pressure lowering of a saturated solution at a given temperature is independent of the temperature.

2. The value of this ratio is a simple function of the degree of saturation. These two generalizations will be more fully discussed and experimentally proven in an early publication.

Summary

(1) It was suggested that the degree of saturation is a fundamental method of expressing concentration and should be used in the study of the theory of solution wherever possible.

(2). Using this method of expressing concentrations, a relation is arrived at which gives the vapor pressure lowering, ΔP, as a function of the absolute temperature, T, and the degree of saturation, S, or indirectly the solubility. This equation has the form, $\log \Delta P = \left[K \frac{1}{T} - a\left(1 - \frac{\log S}{b}\right)\right]$ where K, *a* and *b* are constants, and holds for 31 salts.

(3) The values of the three constants for 31 substances are given.

(4) Two generalizations are directly deducible from the equation:

Generalization 1: The value of the ratio of the vapor pressure lowering at any degree of saturation over that of a saturated solution at a given temperature is independent of the temperature, i.e. $\frac{\Delta P}{\Delta P_s}$ is the same for all temperatures.

Generalization 2: The value of this ratio is a very simple function of the degree of saturation, i.e. $\frac{\Delta P}{\Delta P_s} = S^{\frac{Ka}{b}}$ where K, *a* and *b* are the three constants in the above equation.

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MECHANISM OF THE PHOTOCHEMICAL REACTION BETWEEN HYDROGEN AND CHLORINE. II*

BY ABRAHAM LINCOLN MARSHALL

In a previous communication[1] it has been shown that the amount of reaction induced in a mixture of hydrogen and chlorine by a given number of hydrogen atoms is strongly dependant on the total pressure of the system, increasing rapidly with increased pressure. In this connection it seemed advisable to reinvestigate the photochemical hydrogen chlorine reaction over a wide pressure range. This paper will present the results of a preliminary study of the problem. The results are of interest not only in this particular connection but as applied to "chain reactions" in general. It has been definitely established that the number of molecules of hydrogen chloride formed per quantum of light absorbed increases rapidly with increased pressure. The range of pressures investigated was from 0.001 cm., to 6 cm. and the quantum yield in this range increased from about 20 to over 25,000 molecules. At present very little can be said concerning its dependence on the relative pressures of hydrogen and chlorine but this subject will be dealt with in a subsequent communication.

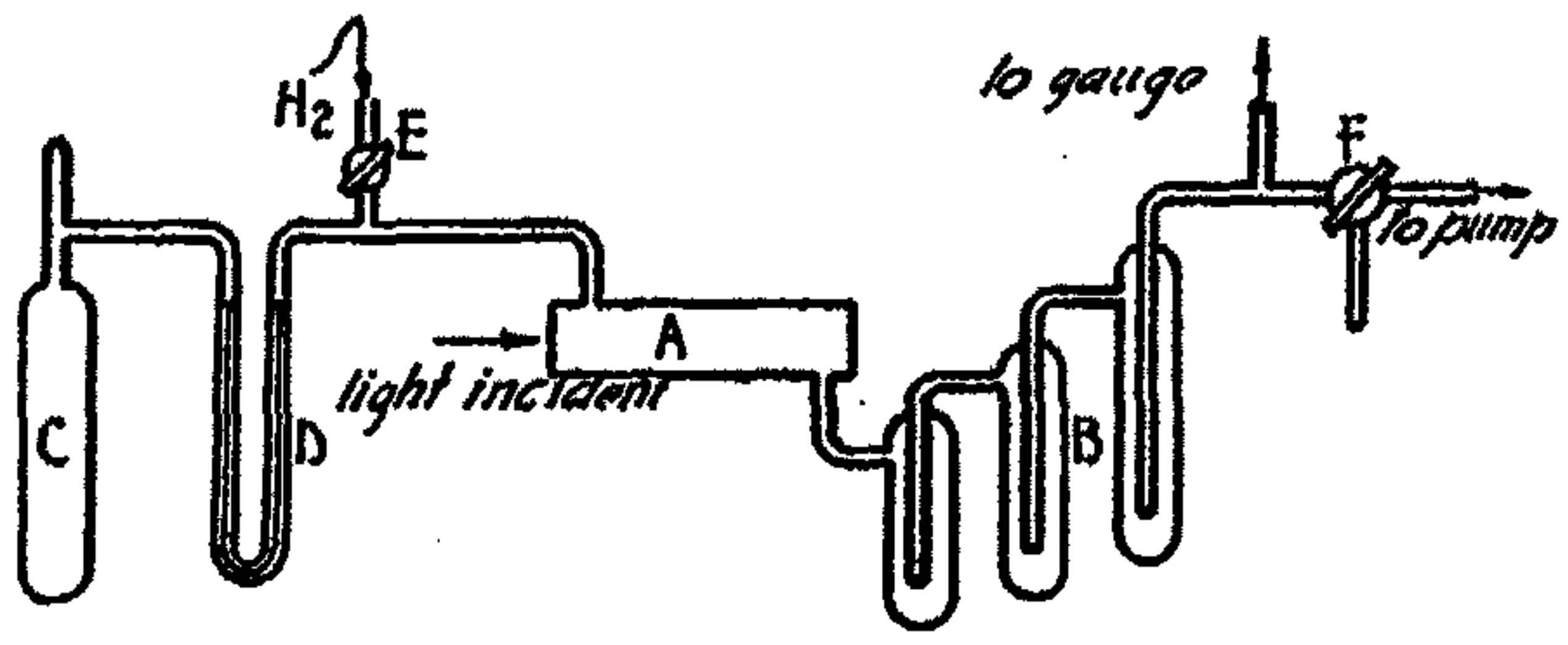

Fig. 1

Experimental

The method used was similar in many details to that already described. It consisted in drawing a mixture of hydrogen and chlorine thru a quartz reaction vessel where it was illuminated by a quartz mercury arc. The whole apparatus (Fig. 1) was swept out by a stream of chlorine for two weeks before use in order to ensure complete absence of impurities from the walls of the vessel which would inhibit the reaction.

Liquid chlorine was collected in C after being twice redistilled at liquid air temperatures, the middle fraction having been collected each time. The amount of chlorine passing thru the system in a given time was determined by the size of the capillary E and the temperature of the liquid chlorine in C. The capillary D when cooled by liquid air was used to stop the flow of chlorine.

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* Contribution from the Laboratory of Physical Chemistry, Princeton University.

[1] J. Phys. Chem. 29, 842 (1925).

Carefully purified hydrogen, dried over potassium hydroxide, was admitted at E in amounts regulated by this stopcock. After illumination the gases were passed thru liquid air traps at B to remove chlorine and hydrogen chloride. The pressure of the residual hydrogen was then measured on a McLeod gauge, the gas then passing thru the stopcock F to a mercury condensation pump. It was possible to regulate roughly the rate of flow of the gases by control of the stopcock F and this method was used to obtain the higher pressures employed.

Three check experiments were usually made at each pressure. The apparatus was then filled with hydrogen from D and the gases caught in the liquid air traps, blown out in turn into a solution of potassium iodide in order to determine their composition.

At the time these experiments were performed, I had no method for measuring the pressure in vessel A during the course of the reaction. In order to calculate the chlorine pressure in the reaction chamber and from it the number of quanta absorbed, it has been assumed that the hydrogen pressure measured on the guage was the same as that of the partial pressure of hydrogen in A and that the chlorine pressure could be calculated from this by multiplying it by the ratio of the number of cubic centimeters of chlorine leaving the chamber to that of the number of cubic centimeters of hydrogen.

Calculation of Light Absorption

In order to calculate the number of quanta absorbed in any experiment, it was necessary to know the amount of energy incident on the system and the average extinction coefficient of chlorine for this energy.

Coblentz, Long and Kahler[1] give a value for the energy radiated from a 220 volt Cooper-Hewitt quartz mercury arc at a distance of 40 cm. measured perpendicularly from the center of the lamp axis. This lamp was consuming 400 watts energy and a current of 3 amps. The value given by them is 0.0017 g. cals. per square centimeter per second in the wave length range 0 to 1.4μ and 66% of this energy is in the range 0 to 0.45μ. In the same paper they also state that the decrease in energy with distance from the lamp follows the inverse square law for distances greater than 36 cm.

Harrison and Forbes[2] give measurements on the distribution of energy in the spectrum of a quartz mercury arc over the range 2300A° to 14,000A° and its variation with current and applied voltage in the lamp circuit. From Fig. 7 p. 16 of their paper one obtains the following data for the relative intensities of the spectral lines for a lamp consuming 3 amps. current and 25 watts per cm. power.

From these figures one obtains the same gross distribution as given by Coblentz. The lamp used in this investigation consisted of a 110 volt D.C. Hanovia quartz mercury arc and burned on 3 amps and 180 watts. The total

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[1] Bureau of Standards Scientific Papers, No. 330.

[2] J. Optical Soc. 10, 1 (1925).

TABLE I

λ	Galvanometer deflection
11290A°	18
10148	34
5790	104
	Total 156
4359	62
4078	48
3663	98
3350	6
3132	58
2967	8
2536	19
2300	11
	Total 310

energy radiated would thus be slightly less than 50% of that quoted by Coblentz for a Cooper-Hewitt lamp of twice the length. This amounts to 0.0008 g. cals., cm.,$^{-2}$ sec.$^{-1}$ in the range 0–1.4μ at 40 cm. from the arc. In these experiments the area of the vessel was 19.6 cm.^{2} and the lamp was 76 cm. from the middle of the reaction chamber which was 15 cm. long. Assumed the inverse square law the total energy incident on the reaction vessel per hour amounted to..

$$0.0008 \times \left(\frac{40}{76}\right)^2 \times 19.6 \times 3600$$
$$= 15.6 \text{ g. cals., hr.}^{-1}$$
$$\text{or } 65.7\ (10)^7 \text{ergs hr.}^{-1}$$

The distribution of energy in absolute units amongst the various wave lengths is given approximately in Table II. The value of ϵ given in the column three is the extinction coefficient of chlorine given by von Halban and Sie-

TABLE II

λ	Energy in Ergs $\times 10^{-7}$	ϵ
5790A°	14.8	0.1
4359	7.5	1.64
4078	6.9	3.99
3663	14.0	27.17
3350	0.85	65.5
3130	8.3	21
2967	1.14	17
2536	2.7	1

dentopf[1]. From these values one can calculate the amount of energy of each wave length absorbed by chlorine by means of the formula

$$\epsilon = \frac{1}{Cd} \log \frac{J_0}{J}$$

which is the mathematical expression for Beer's law. C is the concentration in mols per liter, d the thickness of the absorbing layer in cm., J_0 the incident energy and J the energy transmitted.

Table III gives the calculated values for the energy absorbed by chlorine at a pressure of 0.024 cm. under the above conditions.

TABLE III

λ	$J_0 - J$
4078	0.7 (10)^5 ergs
3663	15.3 "
3350	2.8 "
3130	8.3 "
2967	1.0 "

The total energy absorbed is then 28.1 (10)^5 ergs and the only range of any importance is 3000—4000 A°. The total energy incident in this range is 31.2 (10)^7 ergs. Over this range one can now calculate an average extinction coefficient for chlorine which amounts to $\epsilon = 16.8$. The average wave length of absorbed light is 3500A° which gives a value of hv = 5.6 (10)$^{-12}$ ergs. Hence the total number of quanta incident on the reaction vessel in the wave length range 2967—4078A° per hour is

$$\frac{31.2\ (10)^7}{5.6\ (10)^{-12}} = 5.6\ (10)^{19} \text{ quanta}$$

From the method used in calculating the average chlorine pressure in the reaction vessel, it can easily be seen that the only results for which any great degree of accuracy can be claimed are those in which the hydrogen pressure greatly exceeds that of the chlorine which in turn is large compared to that of the hydrogen chloride.

The results obtained are presented in the three following tables. The first column gives the time of the experiment in minutes and the second and third the amount of chlorine passing thru unchanged and the amount of hydrogen chloride formed. These are expressed in c.c. of thiosulphate and alkali used. The fourth column gives the amount of hydrogen used in terms of the current flowing thru the hydrogen generator. The remaining columns are self-explanatory.

In the experiments given in Table IV the arc was 4.2 cm. from the reaction vessel. For the experiments at higher pressures, it was necessary to move the arc further away from the vessel. Table V gives the results obtained with the arc 55 cm. for the vessel.

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[1] Z. physik. Chem. 103, 7 (1922).

Table IV

$2\times(10)^{21}$ Quanta incident on Reaction Vessel per Hour

Time in Minutes	Cl_2 c.c. 0.266N	HCl c.c. 0.1086N	Amps.	H_2 pressure in cm.	c.c. gas per hour at N. T. P.		Cl_2 pressure in cm.	$\frac{J_0}{J}$	Molecules HCl formed per hour $\times 10^{-21}$	Quanta abs. per hour $\times 10^{-17}$	Molecules per quantum
					Cl_2	H_2					
60	32.6	0.40		.00017	97	23.6	.00070	1.0002	.026	4	65
60	32.6	0.12		.00017	97	23.6	.00070	1.0002	.0079	4	20
30	15.2	0.06		.00018	90.6	4.7	.00347	1.0012	.008	24	3.4
30	16.2	0.45		.00018	96.6	4.7	.00370	1.0013	.060	26	36
45	161.2	2.82	0.44	.0019	640	184	.0066	1.0023	.248	46	53
45	161.5	3.14	0.44	.0019	642	184	.0066	1.0023	.275	46	60
34	5.7	0.28	1.6	.0029	30	669	.00013	1.00004	.0325	0.8	406
36	70.0	3.13	1.6	.0029	348	669	.0015	1.0004	.343	8	429
26	53.1	1.65	1.6	.0029	365	669	.0016	1.0004	.254	8	318
20	41.9	0.98	1.6	.0029	374	669	.0016	1.0004	.195	8	244
60	49.70	5.63		.0038	148	55.5	.0101	1.035	.37	700	5.3
60	51.3	4.23		.0038	153	55.3	.0105	1.036	.28	720	3.9
36	125.8	4.4	1.7	.0061	625	711	.0054	1.0018	.483	86	134
30	125.9	3.84	1.3	.0051	750	544	.0070	1.0025	.50	50	100
30	16.7	0.36	5.0	.012	99	2090	.012	1.00016	.0474	3.2	150
40	23.9	0.87	6.0	.05	107	2510	.052	1.0007	.086	14	62

TABLE IV (Continued)

Time in Minutes	Cl_2 c.c. 0.266N	HCl c.c. 0.1086N	Amps.	H_2 pressure in cm.	c.c. gas per hour at N. T. P. Cl_2	c.c. gas per hour at N. T. P. H_2	Cl_2 pressure in cm.	$\frac{J_0}{J}$	Molecules HCl formed per hour $\times 10^{-21}$	Quanta abs. per hour $\times 10^{-17}$	Molecules per quantum
40	93.8	44.4	2	.244	420	836	.123	1.042	4.3	840	53
60	0.87	6.4		0.5	2.6	164	.0079	1.0026	.42	52	81
60	1.17	5.5		0.5	3.5	178	.0098	1.0033	.36	66	55
20	29.5	77.5	11	0.70	264	4600	.0402	1.014	15.3	280	546
22	32.9	85.6	11	.70	267	4600	.0407	1.014	15.3	280	546
20	29.3	79.2	11	.70	262	4600	.0400	1.014	15.6	280	558
27	4.1	127.6	11	1.4	27.2	4600	.0083	1.0027	18.7	54	3470
20	2.56	95.2	11	1.4	22.9	4600	.0070	1.0025	18.9	50	3780
20	2.6	92.4	11	1.4	23.2	4600	.0071	1.0025	18.3	50	3660
20	0.50	89.6	15.6	2.1	4.5	6520	.00145	1.0005	17.7	10.0	17,700
20	0.42	87.6	15.6	2.1	3.75	6520	.00121	1.00041	17.4	8.2	21,300
20	0.44	85.6	15.6	2.1	3.93	6520	.00127	1.00042	16.5	8.4	19,500
30	0.21	24.0	20	3.5	1.2	8360	.00050	1.00013	3.16	2.6	12,200
36	0.1	41.6	20	3.5	0.5	8360	.00021	1.00007	4.56	1.4	32,600
30	0.1	33.0	20	3.5	0.6	8360	.00025	1.00008	4.34	1.6	27,200
20	0.01	102	12	3.8	0.09	5020	.000068	1.000023	19.16	.46	438,000

TABLE V

6.8 $(10)^{19}$ Quanta incident on Reaction Vessel per Hour

Time in Minutes	Cl_2 c.c. 0.266N	HCl c.c. 0.1086N	Amps.	H_2 pressure in cm.	c.c. gas per hour at N. T. P. Cl_2	c.c. gas per hour at N. T. P. H_2	Cl_2 pressure in cm.	$\frac{J_o}{J}$	Molecules HCl formed per hour $\times 10^{-21}$	Quanta abs. per $\times 10^{-17}$	Molecules per quantum
15	6.15	96.0	20.6	5.8	73.3	8620	.0494	1.017	25.6	11.6	22,000
15	6.1	98.5	20.6	5.7	72.8	8620	.0465	1.016	26.3	10.9	24,100
15	5.2	102.8	20.6	5.8	62.1	8620	.0417	1.0145	27.4	9.8	28,000
20	26.5	226.4	21.4	5.7	316.0	8950	.201	1.068	42.5	46.3	9,200
17	12.55	119.2	18.0	3.9	132	7530	.0684	1.0235	27.7	16.0	17,300
15	10.50	108.4	18.0	3.9	125.3	7530	.0649	1.022	28.5	15.0	19,000
30	32.1	150.6	16.0?	4.0	191.5	6690	.114	1.039	19.8	26.5	7,460
24	33.8	99.6	16.0?	3.9	252	6690	.147	1.050	16.4	34.0	4,830
20	35.8	69.2	10.8	2.44	320	4520	.173	1.059	13.7	40.1	3420
20	34.5	73.6	10.8	2.58	308	4520	.176	1.060	14.5	40.8	3550
30	92.8	2.12	16	0.90	5.53	6690	.0744	1.025	.28	17.0	165
30	90.9	2.64	16	1.07	5.42	6690	.0866	1.030	.35	20.4	171

TABLE VI

Distance from lamp in cm.	Time in Minutes	Cl_2 c.c. 0.266N	HCl c.c. 0.1086N	Amps.	H_2 pressure in cm.	c.c. gas per hour at N. T. P. Cl_2	H_2	Cl_2 pressure in cm.	$\frac{J_0}{J}$	Molecules HCl formed per hour $\times 10^{-21}$	Incident Quanta $\times 10^{-19}$	Quanta abs. $\times 10^{-17}$	Molecules per Quantum
39	20	3.6	163	20	5.8	32.2	8360	.0223	1.0077	32.2	17.5	1.35	23,900
	16	3.72	137.6	20	5.8	41.6	8360	.0288	1.010	34	17.5	1.75	19,500
	16	5.56	154.4	20	5.8	62.2	8360	.0431	1.015	37.9	17.5	2.02	18,800
190	15	31.2	53.2	21	5.9	372	8780	.250	1.085	14.0	0.74	6.3	22,000
	15	33.6	48.0	21	5.7	400	8780	.260	1.09	12.6	0.74	6.7	18,800
	15	33.8	48.0	21	5.8	403	8780	.263	1.09	12.6	0.74	6.7	18,800
119.5	22	28.8	116	20	4.8	234	8360	.134	1.044	20.8	1.88	8.3	20,900
	15	24.6	62.8	20	4.9	293	8360	.172	1.059	16.6	1.88	11.1	15,000
62.5	15	6.15	96	20.6	5.8	73.3	8610	.0494	1.017	25.6	6.8	11.6	22,000
	15	6.1	98.5	20.6	5.8	72.8	8610	.0465	1.016	26.3	6.8	10.9	24,100
	15	5.2	102.8	20.6	5.8	62.1	8610	.0417	1.014	27.4	6.8	9.8	28,000

In Table VI the results are given for the variation in quantum yield with intensity of incident light at constant total pressure. The intensity was varied by altering the distance of the arc from the reaction system, the range covered being from 39 to 190 cm. Coblentz[1] has shown that over this range the inverse square law holds in calculating light intensity from the mercury arc. From the results given it can be seen that for a twenty-fold change in light intensity the quantum yield is unchanged. This is in direct contradiction to the results of Baly and Barker[2] who observed a sixty-fold increase in reaction velocity for a twenty-fold increase in light intensity for mixtures of constant composition. M. C. C. Chapman[3] also fails to check Baly's result over a six-fold increase in light intensity.

Summary

1. The photochemical hydrogen-chlorine reaction has been investigated by a dynamic method over the pressure range 0.001—6.0 cm. and the quantum yield found to increase from about 20 to over 25,000 molecules.

2. At a total pressure of 5.9 cm. it has been found that the quantum yield is independent of light intensity when the latter is increased by twenty times.

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Schenectady, N. Y.

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[1] Bureau of Standards Scientific Paper No. 330.

[2] J. Chem. Soc. **119**, 653 (1921).

[3] J. Chem. Soc. **125**, 1521 (1924).

THE ADSORPTION OF SOME VAPORS BY ALUMINA GEL*

BY J. H. PERRY

The recovery of vapors from gas mixtures is of fundamental importance wherever solvents are used commercially. As a basis for solvent recovery systems, the use of gels, particularly silica gel, is constantly finding greater and greater application. The properties of alumina of adsorbing certain vapors[1], particularly water vapor, has long been known,[2] its efficiency for this vapor having been rated next to phosphorus pentoxide.[3] The experiments herein described represent a general survey of the adsorption of ten vapors by alumina gel. This work was under way at the time an article by Munro and Johnson[4] appeared on the "Adsorption of Vapors by Alumina." The present work, although anticipated by these workers, was continued with substances, which, with two exceptions, (carbon tetrachloride and chloroform) were different than those used in the above paper. Since there seems to be little hope for an immediate opportunity of more detailed study of any of the vapors included here, it has been thought worth while to record these preliminary results already obtained as a confirmation (for carbon tetrachloride and chloroform), and an extension of the work of Munro and Johnson. The feasibility of using alumina gel for the recovery of vapors must await a more detailed study: of rates of gas flow, the optimum temperature of adsorption and a process of desorbing the gel. The optimum water content of the gel used is also of fundamental importance, as the results of previous workers on silica gel have proven.[5]

Preparation of the Gel

The gel used in the following experiments was prepared from an aqueous solution of C. P. aluminium sulfate by slow precipitation at room temperature with C. P. ammonium hydroxide. The aluminium hydroxide thus formed was washed with distilled water until no trace of sulfates could be detected in the filtrate. The resulting gel was filtered by suction and dried 60°C until a hard, glass-like material was obtained. This was broken up and screened. The material used passed a mesh sieve of the range 10-14 and was of uniform size. The gel was activated by passing dry, CO_2-free air

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*Contribution from the Cryogenic Laboratory, Bureau of Mines, Department of Commerce. Published by permission of the Director, Bureau of Mines.

[1] Johnson: J. Am. Chem. Soc., 34, 911 (1912).

[2] Dover and Marden: J. Am. Chem. Soc., 39, 1609 (1917).

[3] Marden and Elliott: Ind. Eng. Chem., 7, 320 (1915).

[4] Munro and Johnson: Ind. Eng. Chem., 17, 88 (1925).

[5] Patrick and McGavack: J. Am. Chem. Soc., 42, 946 (1920); Patrick and Long: J. Phys. Chem., 29, 336 (1925).

heated to 200°C through the gel which was heated in the same bath as the air. This form of activation was continued after each experiment until the gel came back to its original weight. The duration of the activation varied but little after each experiment and was about two and one-half hours. In any experiment where there seemed to be some decomposition of the vapor, either during the adsorption process or during the subsequent activation of the gel, that sample of gel was discarded and a new sample of the same gel was activated and used for the next experiment. The gel contained 29.98% water, determined by heating a sample of the material for several hours with an air-gas blast.

The general method of the experiments consisted in passing a vapor-air mixture through a U-tube, containing a known weight of the alumina gel, which was thermostated at 25°C. The process of adsorption was followed by weighing the saturator tube and the tube containing the gel at frequent intervals.

The vapor-air mixtures were prepared by passing dry, CO_2-free air through two spiral saturating tubes (of a construction similar to that employed in an air-lift pump) at a sufficiently slow rate to assure saturation of the air stream. The flow of air was controlled by the insertion of a capillary flow meter in the line before the drying and CO_2-removal tubes.

The results of these experiments are reported as grams of vapor per 10 grams of adsorbent. These data may readily be converted to cubic centimeters of vapor per gram of adsorbent as has usually been done in the work on silica gel and that on alumina gel by Munro and Johnson. The saturation values as given below are extrapolations estimated either from the data themselves or from the graphs.

All chemicals used were of C. P. grade or specially purified. The ethylene chloride, methylene chloride and ethyl methyl ketone were obtained from the Research Laboratory of the Eastman Kodak Company. Most, if not all, chloroform that can be bought, including the purest, contains ethyl alcohol, which prevents or retards decomposition. For this reason the chloroform used was purified in the following manner: It was agitated with pure concentrated sulfuric acid until the acid was no longer colored. It was then washed with sodium carbonate, then successively with alkaline permanganate, and distilled water, dried over sodium and distilled.

The chlorine derivatives used in this work are more or less oxidized by air with the production of acid, which would react with the alumina to produce aluminium chloride. The amount of this action is slight and would very likely be of no consequence. In an extended commercial utilization of alumina gel for these vapors, this action, which of course would be cumulative, would eventually destroy the usefulness of this adsorbent.

The Data

Grams vapor supplied in successive intervals	Grams vapor adsorbed in each interval	Grams vapor supplied in successive intervals	Grams vapor adsorbed in each interval
CCl_4		$CHCl_3$	
1.6952	0.6565	3.3536	1.9104
0.8420	0.2179	2.6641	0.6647
0.9918	0.3660	2.3765	0.6799
4.3950	1.2611	3.3944	0.2932
3.3122	0.5890		
3.0618	0.3028		
2.9141	0.0997		
CH_2Cl_2		$C_2H_4Cl_2$	
1.3224	1.0585	4.8916	1.4900
1.9760	1.0109	2.3780	0.5877
2.1128	0.7355	2.2015	0.4030
2.1389	0.3812	8.8637	0.7500
4.5969	0.2035	4.9810	0.2609
3.4035	0.0096	12.2553	0.0899

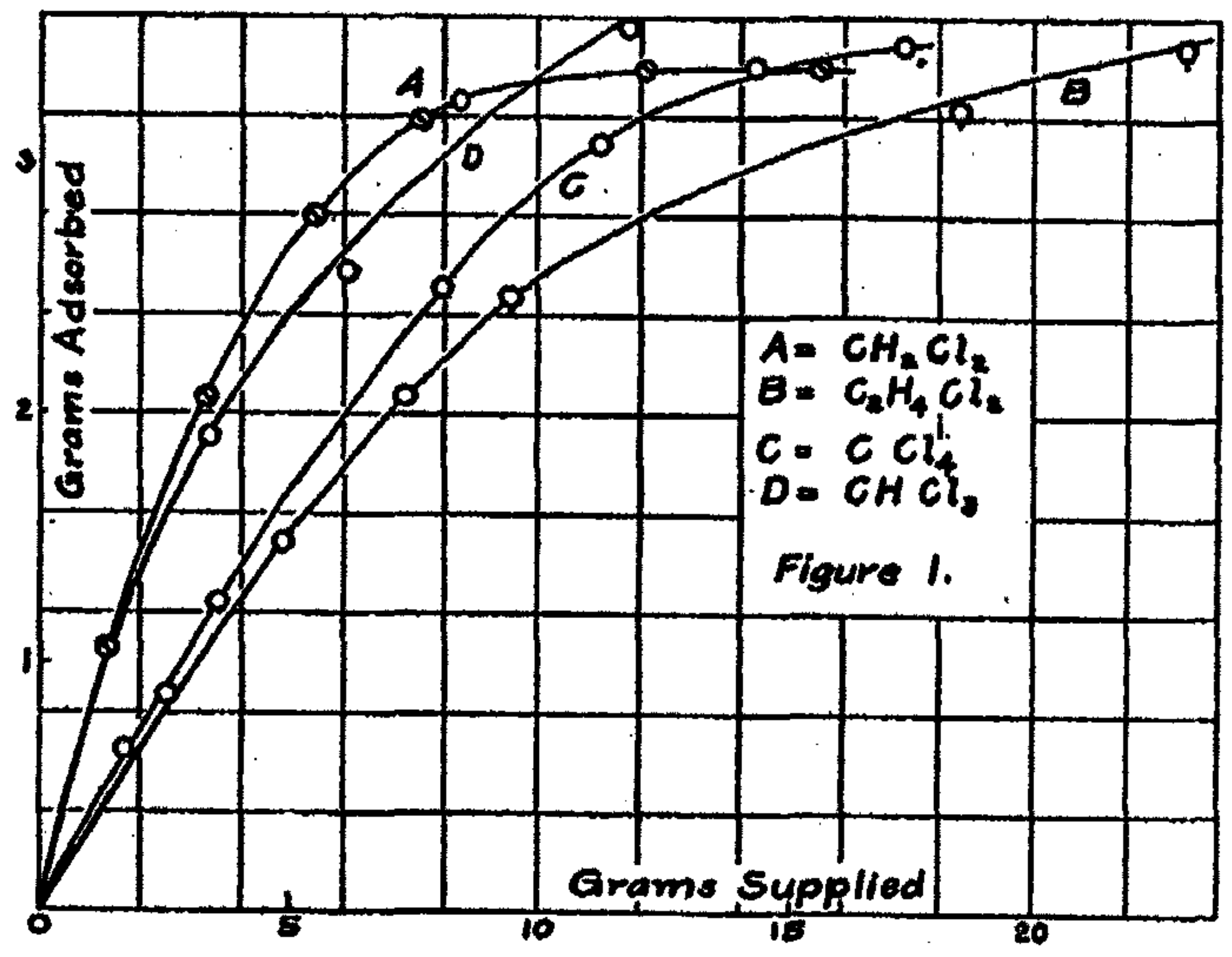

Fig. 1

Figure 1 shows the adsorption curves for carbon tetrachloride, chloroform, methylene chloride, and ethylene dichloride. The relative adsorption efficiencies of these four substances are readily apparent from the curves, that for methylene chloride being the most efficient. The saturation values of carbon tetrachloride and ethylene dichloride are 3.6 and 3.7 grams per 10 grams of gel respectively. The value obtained by Munro and Johnson for carbon tetrachloride was 3.08 grams per 10 grams of gel. The difference between the two samples of gel may be ascribed to the difference in the methods of activation, from which a different water content and hence a different structure would result.

The saturation values of methylene chloride and chloroform are 3.4 and approximately 3.8 grams per 10 grams of gel respectively. Munro and Johnson give the figure 2.51 grams per 10 grams of gel as the saturation value of chloroform.

Grams vapor supplied in successive intervals	Grams vapor adsorbed in each interval
Ethyl formate	
6.4991	1.6942
4.3810	0.4770
5.6817	0.2488
5.5443	0.0978
6.0816	0.0016

Grams vapor supplied in successive intervals	Grams vapor adsorbed in each interval
Ethyl methyl ketone	
6.9783	1.5354
7.1770	0.5913
4.5130	0.1818
5.0061	0.0830
5.3381	0.0209

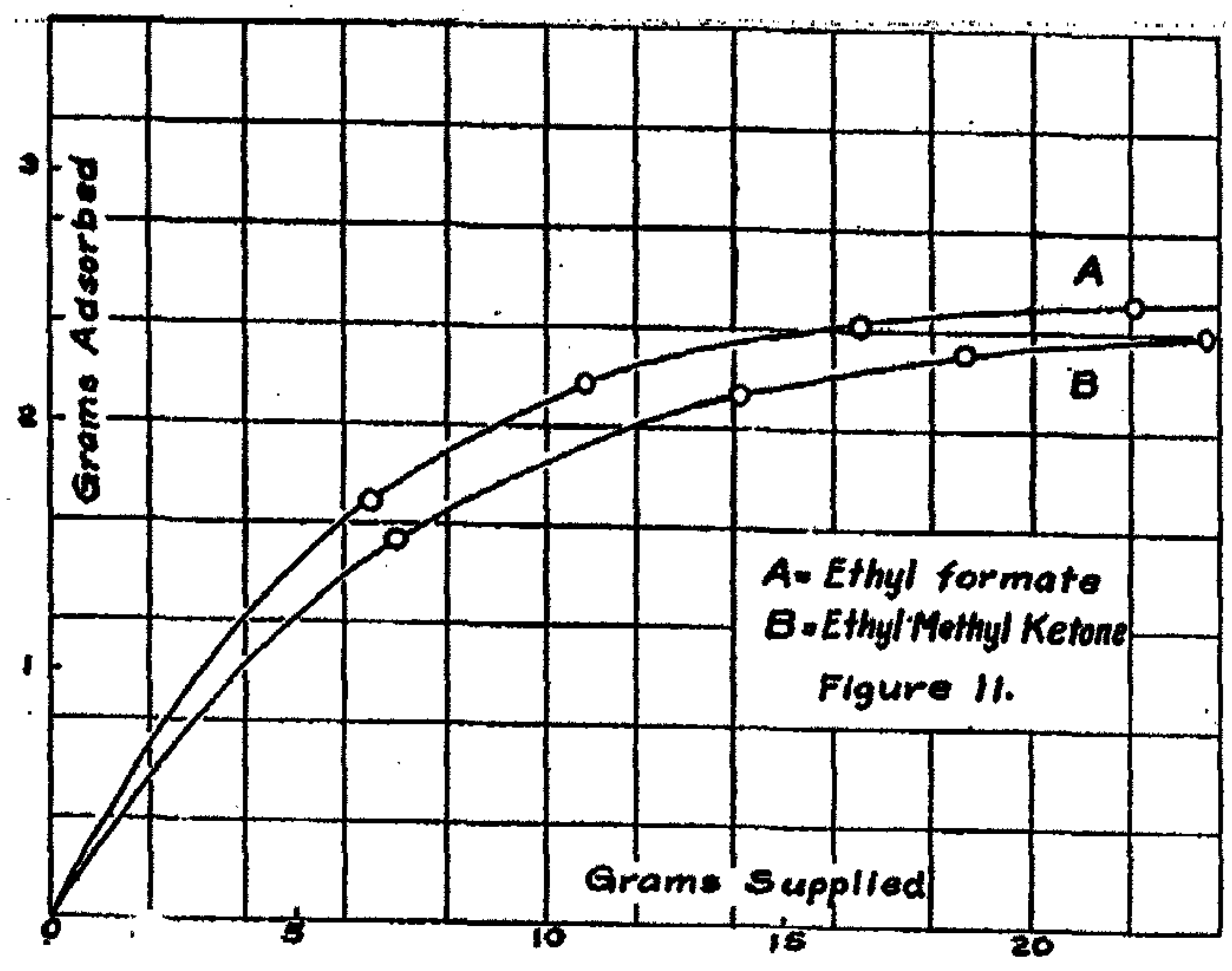

Fig. 2

It will be seen from Figure 2 that the adsorption curves for ethyl formate and ethyl methyl ketone are very similar. The adsorption efficiency is never 100% in either case but the saturation values are approximately the same for the two substances. The saturation value for ethyl formate being 2.70 grams per 10 grams of gel, while that for ethyl methyl ketone is 2.46 grams per 10 grams of gel.

In attempting the recovery of the adsorbed ethyl methyl ketone, by gradually raising the temperature while a current of dry, CO_2-free air is passed through the U-tube, the gel is colored a dark brown, almost black color. A brownish yellow liquid came over and was condensed in a cold bath.

This is evidently a case of a chemical reaction catalysed by the alumina gel. Alumina is therefore not suitable for the recovery of ethyl methyl ketone, although it is an excellent adsorbent for this vapor. A result similar to this has been obtained for acetone by Munro and Johnson.

Grams vapor supplied in successive intervals	Grams vapor adsorbed in each interval	Grams vapor supplied in successive intervals	Grams vapor adsorbed in each interval
1.1471	0.3663	0.4046	0.0721
2.0913	0.6058	0.6844	0.1557
1.8694	0.4308	1.8221	0.5278
3.8998	0.6776	2.3281	0.7788
5.1445	0.5637	2.9560	0.5605
19.4909	0.0838	2.2300	0.1774
		1.5840	0.0628

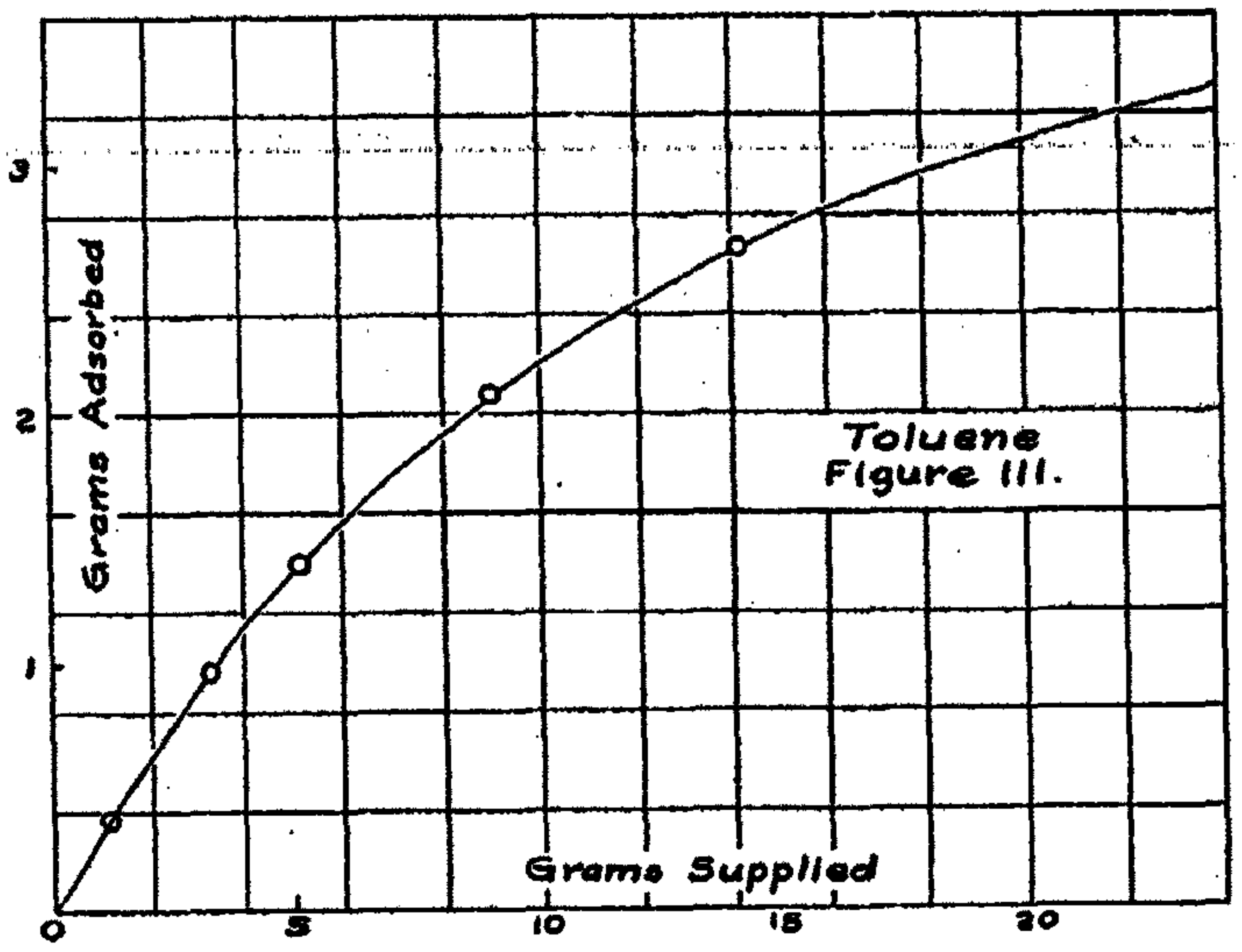

FIG. 3

In the curves for toluene and hexane, total adsorption is never obtained, the amount adsorbed is never equal to the amount supplied. The *efficiency* of adsorption of toluene is greater than that of hexane. The saturation value of toluene is 2.8 grams per 10 grams of gel.

Grams vapor supplied in successive intervals	Grams vapor adsorbed in each interval	Grams vapor supplied in successive intervals	Grams vapor adsorbed in each interval
Methyl acetate		Carbon disulfide	
0.9580	0.6353	4.4567	0.8759
1.8657	1.2671	5.9008	0.7596
1.3812	0.3365	9.3015	0.5573
1.6369	0.0722	9.3051	0.3186
2.2453	0.0903	8.2121	0.1691

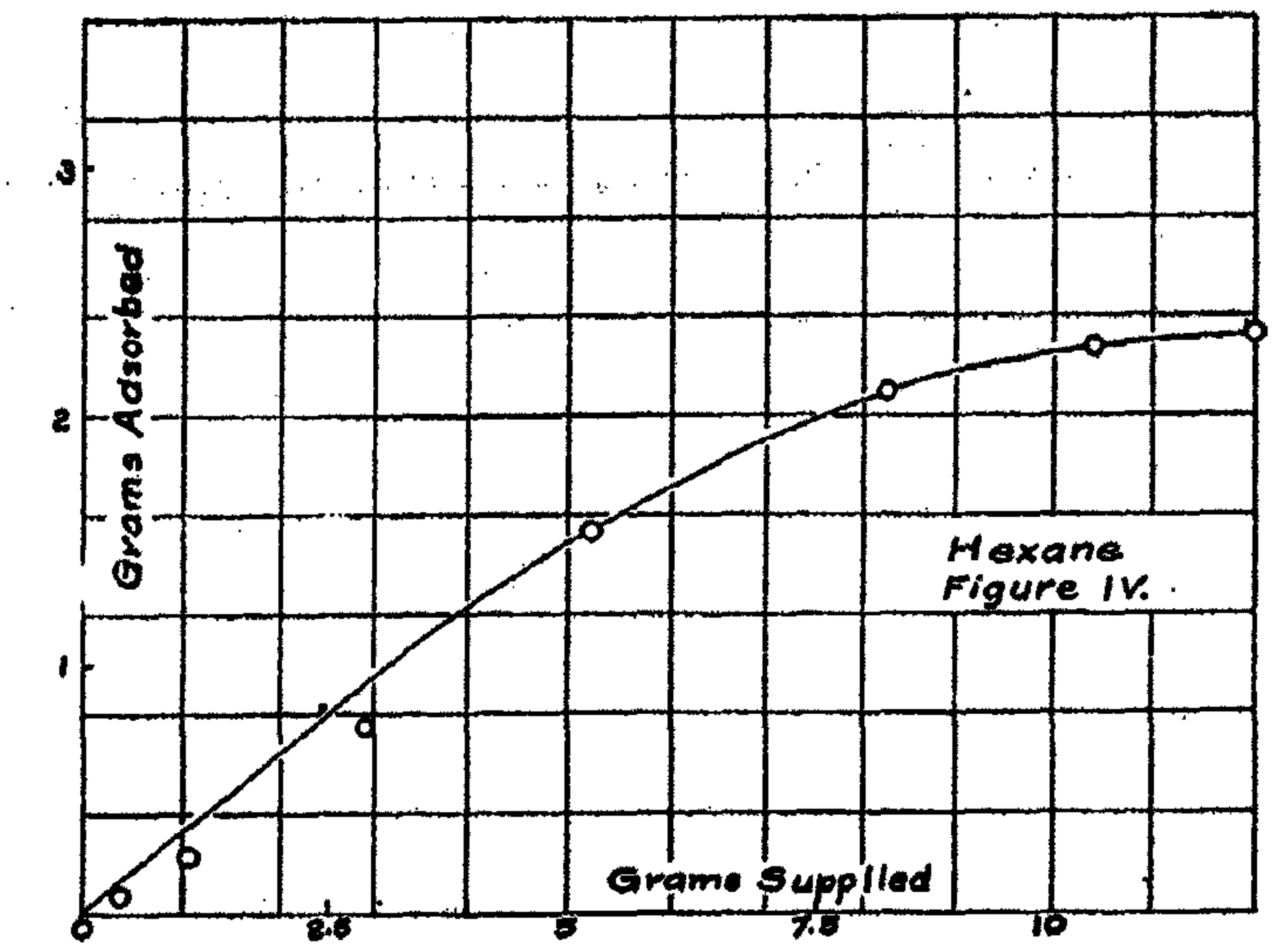

FIG. 4

The saturation values of hexane and of ethyl methyl ketone are almost exactly identical, namely 2.47 and 2.46 grams per 10 grams of gel.

The adsorption of methyl acetate in its initial stages is nearly 100% efficient but the efficiency rapidly decreases. This vapor is removed from the gel only with great difficulty, and hence this gel cannot be considered suitable for the recovery of this vapor from gas mixtures, although its adsorption is satisfactory. A similar difficulty has been encountered by previous investigators in the recovery of ethyl and amyl acetate vapors from alumina gel.[1] The saturation value for methyl acetate is 2.56 grams per 10 grams of gel.

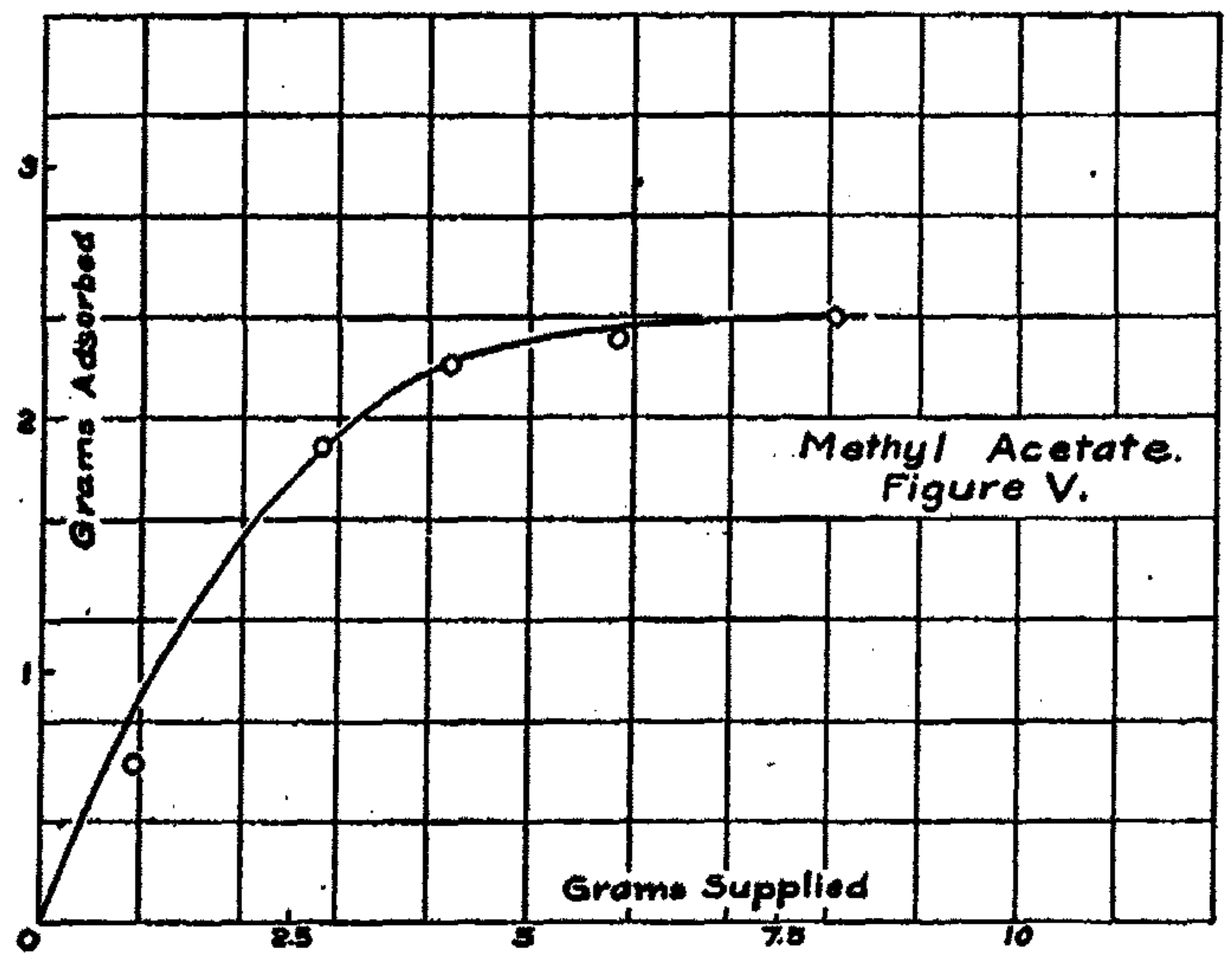

FIG. 5

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[1] Munro and Johnson: loc. cit.

Figure 6 shows the adsorption of carbon disulfide. The adsorption process is very satisfactory although never 100%. In the attempted recovery of this vapor the gel turned sulfur yellow in color, the gel having the appearance of sulfur particles. The saturation value for carbon disulfide is 2.96 grams per 10 grams of gel.

From some preliminary experiments started with benzene and ether, it has been found that the benzene or ether initially adsorbed on alumina gel from a mixture of water and benzene, ether vapors, was slowly displaced by the water vapor after the vapor mixture had been passed through the gel for some time. This is not surprising, since similar results have been found for silica gels. Williams[1] found that benzene previously adsorbed on silica gel from a mixture of water and benzene vapors is slowly displaced by the water upon continued passage of the mixture through the gel. Almquist, Gaddy, and Braham[2] have recently found a similar effect for the adsorption of water and N_2O_4 vapors on silica gels.

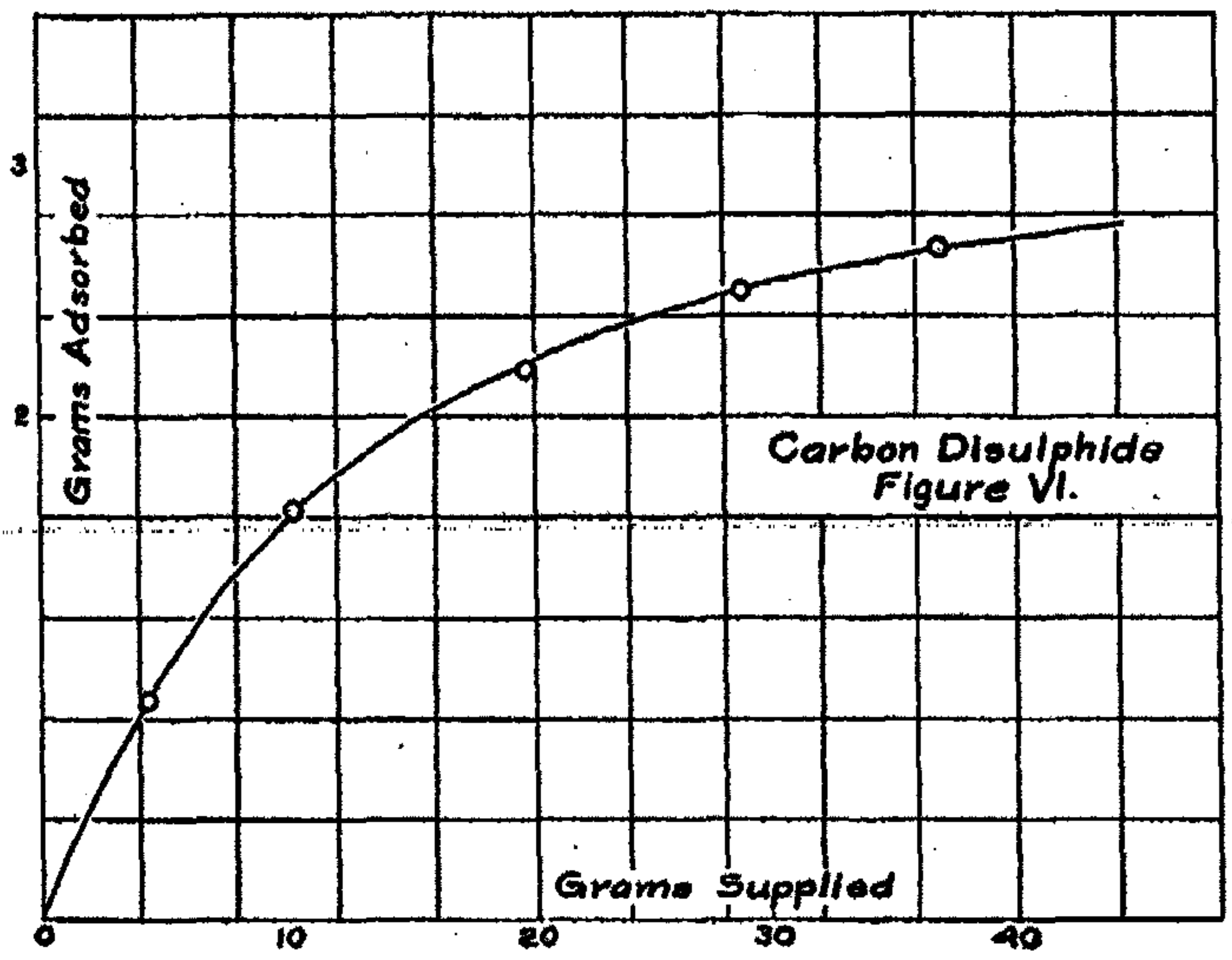

FIG. 6

The saturation values for the vapors investigated are given in the following table:

Substance	Saturation value (grams per 10 grams of gel used)	Substance	Saturation value (grams per 10 grams of gel used)
Carbon disulfide	2.96	Ethyl methyl ketone	2.46
Carbon tetrachloride	3.6	Hexane	2.47
Chloroform	3.8	Methyl acetate	2.56
Ethylene dichloride	3.7	Methylene chloride	3.4
Ethyl formate	2.7	Toluene	2.8

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[1] Williams: J. Soc. Chem. Ind. 43, 97T (1924).

[2] Almquist, Gaddy and Braham: Ind. Eng. Chem. 17, 599-603 (1925).

THE PHOSGENO-ALUMINATES OF SODIUM, STRONTIUM AND BARIUM[1]

BY A. F. O. GERMANN AND D. M. BIROSEL

It has been shown that the phosgene-soluble phosgeno-aluminates may be prepared most easily by the neutralization of phosgeno-aluminic acid ($COAl_2Cl_8$) with phosgeno-bases[2] (metallic chlorides). These bases are in general insoluble, so that after complete neutralization of the acid the soluble salt may be readily removed from the excess of base by decantation, and the salt purified by fractional crystallization. It was the object of the present investigation to extend our knowledge of phosgeno-salts by the preparation and characterization of some new members of the series, of which calcium phosgeno-aluminate is the only one so far definitely characterized[3].

Kendall, Crittenden and Miller[4] have investigated the melting point curves of the binary systems formed between aluminium chloride and a number of metallic chlorides. They identified the double salts: $NaCl.AlCl_3$ and $BaCl_2 \cdot 2AlCl_3$, but did not investigate the systems with calcium or strontium chloride. Baud[5] investigated a number of systems, one component of which was aluminium chloride, but Kendall points out that the method used by him is open to serious question. He reported a number of compounds not revealed by the fusion curves, and was unable to prepare the calcium compound prepared in phosgene solution by Germann and Gagos.

Preparation of Materials

Phosgene and aluminium chloride were purified as described in previous papers[6]. Sodium chloride was purified by precipitation from solution with hydrogen chloride gas, and dried by heating with the free flame in a platinum dish. The barium chloride used was the purest obtainable, and was dehydrated by heating to fusion in a platinum dish in a current of dry hydrogen chloride gas. Pure strontium chloride was dehydrated in the same way.

Procedure. Slightly modified Faraday tubes were used as reaction tubes, like that illustrated in Figure 1; a 10 mm. bore filling-tube near the arch, at A, being designed to permit the entrance of a weighing tube, for the introduction of weighed samples of the solid reagents, after which it was sealed to the apparatus containing the phosgene supply, and evacuated. Pure phosgene was then distilled in, and the tube finally sealed off at A. The aluminium

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[1] From a thesis submitted to Stanford University by D. M. Birosel in partial fulfillment of the requirements for the degree Chemical Engineer.

[2] Germann and Timpany: J. Am. Chem. Soc., 47, 2275 (1925).

[3] Germann and Gagos: J. Phys. Chem., 28, 965 (1924); Germann and Timpany: J. Phys. Chem., 29, 1423 (1925).

[4] J. Am. Chem. Soc., 45, 963 (1923).

[5] Ann. Chim. Phys., (8), 1, 8 (1904).

[6] Germann and McIntyre: J. Phys. Chem., 29, 102 (1925).

chloride dissolved immediately, while the other chloride reacted more slowly. The reaction was speeded up by maintaining the temperature of the leg containing the reagents in the neighborhood of 100°; in this way constant agitation of the solution was effected, due to boiling and distillation of the solvent to the cooler leg. After a week or more of this treatment, the solution was decanted from the excess of insoluble chloride into the other leg of the tube, pure solvent was distilled back, and the residue washed repeatedly. Finally, the leg containing the solution was cooled in liquid ammonia, and the other leg heated to drive out all phosgene; air was introduced by breaking off the tip at A, and the excess of insoluble chloride removed by breaking off the lower half inch of the Faraday tube at B. The glass and residue were placed in a stoppered weighing bottle, and weighed, after which the chloride was removed and the tare weighed. This furnished all the elements for calculating the ratios $AlCl_3 : NaCl$ and $AlCl_3 : SrCl_2$. The ratio in the case of the barium salt was unsatisfactory, hence the salt was analyzed after purification as described in the following paragraph.

The open end of the tube was then sealed off at B, the Faraday tube again sealed to the apparatus at A, evacuated, and once more sealed off at A. The solution of the phosgeno-salt was then crystallized by evaporation of a portion of the solvent, the mother liquor was drained off, fresh solvent introduced, and the salt thus recrystallized several times. When the salt was judged to be pure, the tube was opened at A, sealed to the evacuation apparatus, and the phosgene allowed to boil off at atmospheric pressure. The solid residue was warmed to the melting point, and all phosgene given up was pumped off. Following complete dephosgenation, the tube was opened, and the salt transferred to a bottle and kept in a desiccator. The complete vapor tension diagrams of the three systems with phosgene at 25° were determined, using the volumetric method to determine the compositions as used in previous work by one of us[1].

It has been mentioned that the data obtained in the synthesis of the barium salt were unsatisfactory; this may be due to the fact that the solution of the barium salt separates into two liquid layers at room temperature, a heavy oily layer containing the salt, with a layer of liquid phosgene on top. At low temperatures (for example by cooling in liquid ammonia) the two layers coalesce; the system thus exhibits a lower critical solution temperature. Evidently the solution obtained at these lower temperatures is supersaturated, since, once the oily layer has been crystallized, it appears to be impossible to bring it back into solution by cooling—crystal nuclei appear to persist, and the solution crystallizes instead. The strontium salt also exhibits a lower critical solution temperature, as, on warming its solution to 50° or above, the solution first becomes turbid, due to the formation of an emulsion, then the emulsion breaks, and a heavy oily liquid settles to the bottom: on cooling, the two layers coalesce. In a previous paper of this series[2] it was

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[1] J. Phys. Chem., 28, 965 (1924); 29, 102 (1925).

[2] Germann and Gagos: J. Phys. Chem., 28, 965 (1925).

pointed out that magnesium yields a liquid phosgeno-aluminate insoluble in phosgene: we have attempted to determine the composition of this magnesium salt by synthesis, but the results have been no more satisfactory than those in the case of the barium salt. Satisfactory results were, however, obtained in those cases where the product was soluble: in order to show the applicability of the method, calcium phosgeno-aluminate, whose composition has been thoroughly established, was synthesized quantitatively, and the results incorporated with those for the strontium and sodium salts.

Barium phosgeno-aluminate, $BaAl_2Cl_8$.Mol. Wt., 475. Melting point, 295.0°. Analysis, found: Cl, 59.56%; Al, 11.37%; Ba, 28.75%. Theory for $BaAl_2Cl_8$: Cl, 59.72%; Al, 11.36%; Ba, 28.92%.

Calcium phosgeno-aluminate, $CaAl_2Cl_8$; Melting point, 280° with loss of $AlCl_3$ by distillation; Mol. Wt., 377.7. Synthesis: $AlCl_3$ used, 3.5699 gm.; $CaCl_2$ used, 4.5555 gm; $CaCl_2$ excess, 3.0877 gm. Ratio $CaCl_2:AlCl_3 = 1:2.023$.

Strontium phosgeno-Aluminate, $SrAl_2Cl_8$. Melting point, 325°; Mol. Wt., 425.2. Synthesis: $AlCl_3$ used, 5.6023 gm.; $SrCl_2$ used, 5.9760 gm.; $SrCl_2$ excess, 2.7671 gm. Ratio, $SrCl_2:AlCl_3 = 1 : 2.08$.

Sodium phosgeno-aluminate, $NaAlCl_4$. Melting point, 155.5°. Mol. Wt., 191.8. Synthesis: $AlCl_3$ used, 3.9228 gm.; NaCl used, 3.4548 gm.; NaCl excess, 1.7804 gm. Ratio, $NaCl : AlCl_3 = 1 : 1.028$.

25° *Isotherms.* In Table I are assembled the experimental results relating to the vapor tension measurements for the system $BaAl_2Cl_8-COCl_2$, in two concordant series. Table II contains similar data for the system $SrAl_2Cl_8-COCl_2$, and Table III the vapor tension data for the system $NaAlCl_4-COCl_2$. The character of the 25° isotherms is shown in Figures 2, 3 and 4.

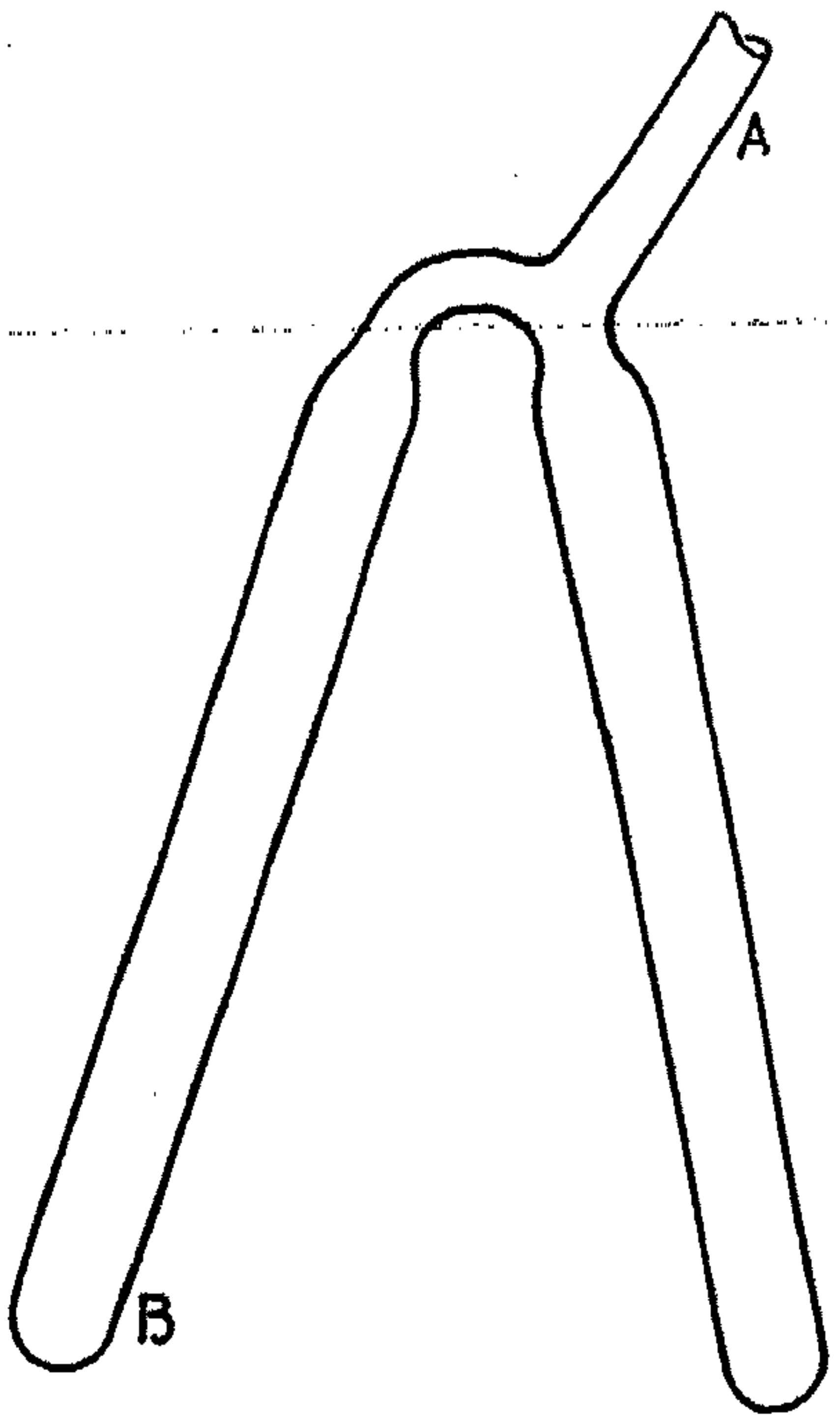


FIG. 2

Isotherm of $BaAl_2Cl_8$ Solution. The constant vapor tension of this system up to 49% of $BaAl_2Cl_8$ at 1405 mm., the vapor tension of pure phosgene, indicates that the salt is practically insoluble in phosgene at this temperature, and that the salt layer contains 51% of phosgene; these figures are probably accurate to less than 1%. The salt solution is capable of a large degree of supersaturation; in the experimental work cooling was resorted to to induce crystallization. The saturated solution contains 52.5% of $BaAl_2Cl_8$, as shown by the intersection at C in Figure 2. At E there is a second break in the curve, when the dry crystals begin to effloresce; this point is at 64.5% $BaAl_2Cl_8$,

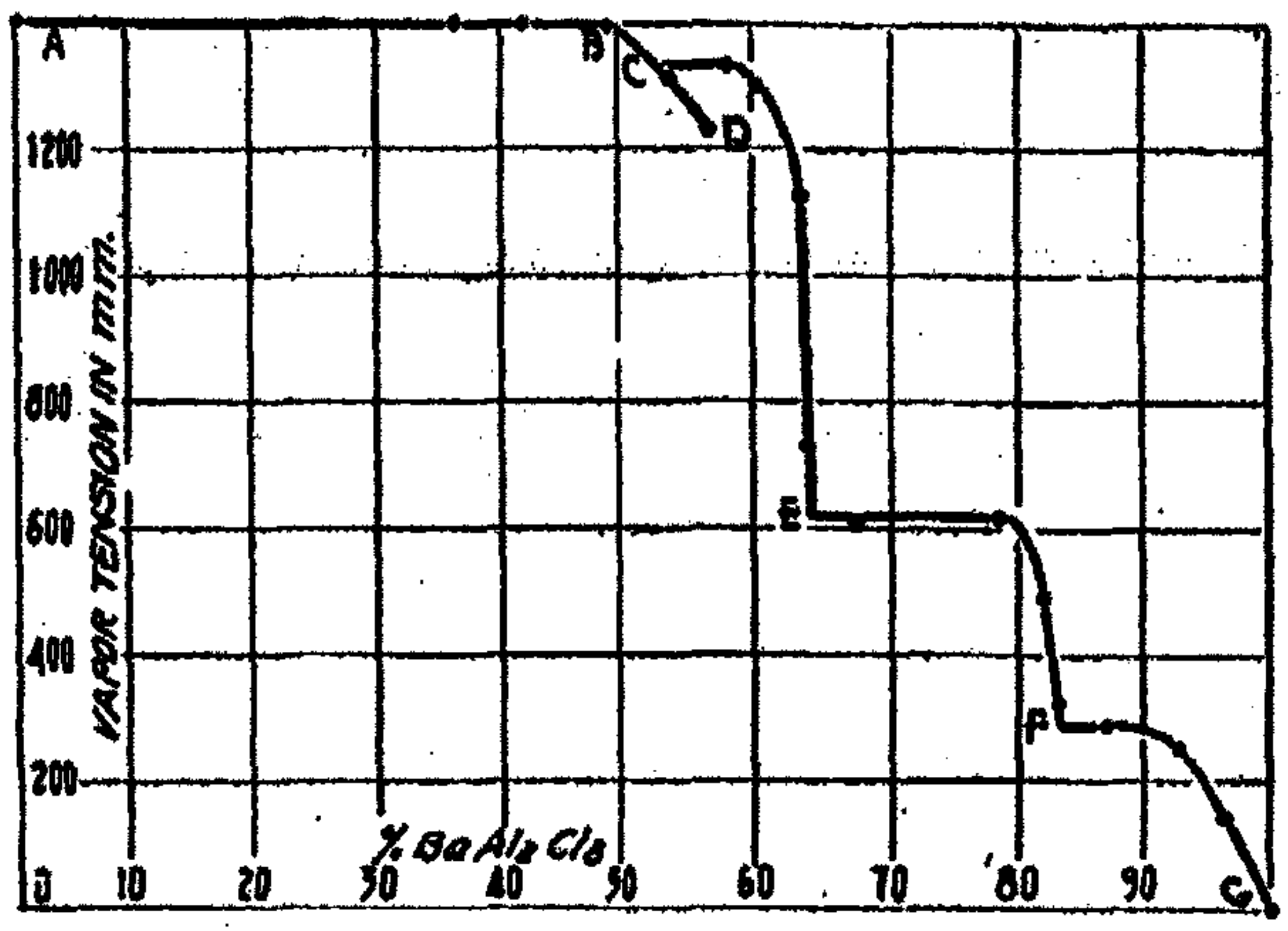


Fig. 2
Vapor Tension Curve 25° for the System $BaAl_2Cl_8-COCl_2$

TABLE I

Vapor Tensions of the System $BaAl_2Cl_8.COCl_2$ at 25°

Series A.		Series B.	
% $BaAl_2Cl_8$	Vapor tension	% $BaAl_2Cl_8$	Vapor tension
0 %	1405 mm.	0 %	1405 mm.
9.0 (2 layers)	1405 mm.	36.3 (1 layer)	1401
9.6 "	1405	41.7	1401
10.3 "	1405	49.0	1401
20.3 "	1405	54.0	1316
45.1 (1 layer)	1402	57.0	1232
47.2	1401	58.4 (crystals)	1338
50.4	1372	60.4	1305
52.9	1321	64.1	1130
53.1	1192	64.5	731
54.8 (crystals)	1343	67.6 (efflorescence)	611
57.3	1311	78.9	624
59.8	1241	82.0	498
63.1	1191	83.2	327
64.3	1024	87.4	293
64.5	741	93.1	258
68.3 (efflorescence)	557	96.6	148
76.4	611	100.0	0
82.5	550		
83.4	204		
92.2	282		
94.9	187		
98.0	135		
99.7	42		
100.0	0		

TABLE II

Vapor Tensions of the System $SrAl_2Cl_8.COCl_2$ at 25°

% $SrAl_2Cl_8$	Vapor tension	% $SrAl_2Cl_8$	Vapor tension
0 %	1405 mm.	64.7 %	934 mm.
16.2	1398.5	67.1	913
17.4	1395.5	69.4	853
18.9	1395.5	70.4	608
22.0	1395.5	70.8	318
23.4	1393	75.0 efflorescence	539
24.9	1391	78.6	541
27.5	1385.5	80.0	321
30.6	1375	80.3	147
35.2	1348.5	80.5	47
39.3	1297	80.6	14
42.2	1248	81.0	0
46.2	1151	85.5	176
48.7	1079	87.2	166
50.9	1008	89.2	174
53.3	925	91.6	170
55.5	849	94.5	153
57.6	756	97.0	147
59.3	696	99.5	116
61.0	632	100.0	0
63.2 crystals	942		

TABLE III

Vapor Tensions of the System $NaAlCl_4.COCl_2$ at 25°

% $NaAlCl_4$	Vapor tension	% $NaAlCl_4$	Vapor tension
0 %	1405 mm.	35.3%	1305 mm.
8.95	1400	37.9	1270
9.44	1399.5	40.7 crystals	1287
10.33	1398.5	44.2	1286
11.08	1398	48.9	1285
13.06	1397	58.9	1282
14.47	1396.5	67.5	1276
17.4	1393.5	79.0	1268
20.7	1389	95.1	1221
24.7	1380.5	98.7	742
28.7	1362	98.9	429
30.6	1349	99.6	102
32.8	1331	100.0	9

TABLE IV

Vapor Tensions at 25° of Solutions of $SrAl_2Cl_8$, $NaAlCl_4$ and $BaAl_2Cl_8$ in $COCl_2$ from Curves

% Salt	$SrAl_2Cl_8$	$NaAlCl_4$	$BaAl_2Cl_8$
0%	1405 mm.	1405 mm.	1405 mm.
5	1403.9	1402.2	
10	1402.2	1399.2	
15	1399.6	1395.5	
20	1396.5	1390.5	
25	1390.5	1378.5	
30	1377.5	1353.5	
35	1350.0	1308.0	
40	1286.5	1240.0	
45	1185.0		
50	1140		1390 mm.
55	867		1290
60	664		1150

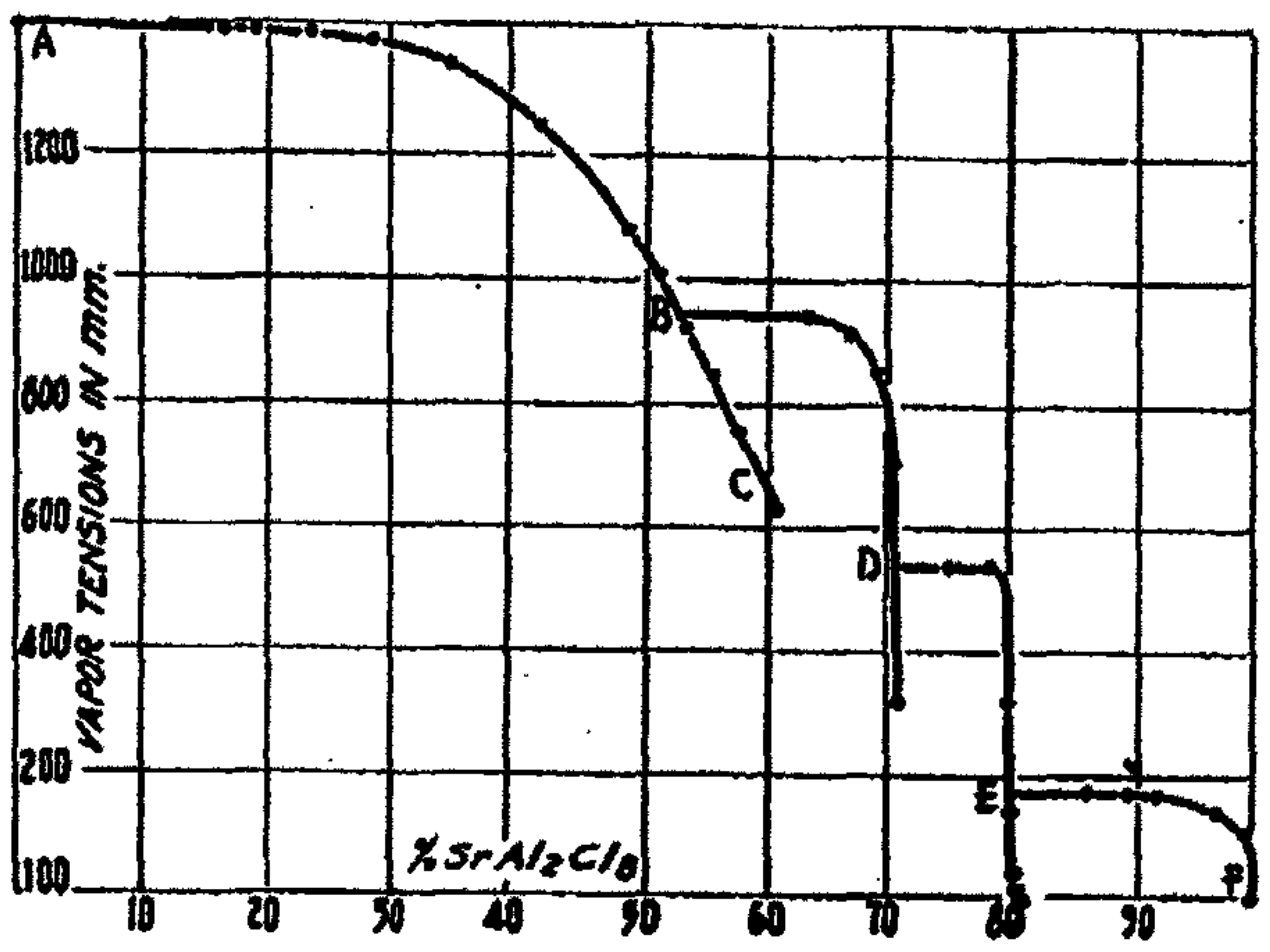


FIG. 3
Vapor Tension Curve 25° for the System $SrAl_2Cl_8$—$COCl_2$

corresponding to 3.03 molecules of the barium salt and 8.00 molecules of phosgene; the compound $3BaAl_2Cl_8 . 8COCl_2$ contains 64.30% $BaCl_2Cl_8$. At F there is a third break in the curve, at 83.2% $BaAl_2Cl_8$; this corresponds to 1.032 molecules of the barium salt and 1.000 molecule of phosgene; the compound $BaAl_2Cl_8.COCl_2$ contains 82.77% $BaAl_2Cl_8$.

Isotherm of $SrAl_2Cl_8$ Solution. Strontium phosgeno-aluminate has the highest solubility in phosgene at 25° of any salt so far investigated. On concentrating the solution, it becomes syrupy, and finally becomes gummy, or on cooling forms a glass. Figure 3 shows the vapor tension curve of this solution up to 60% (curve ABC), when crystallization was brought about by sudden cooling of a thin film of the solution. The intersection at B gives the solubility of the salt at this temperature as 52.3%. The horizontal portion of the curve BD represents the constant vapor tension of the saturated solution during evaporation and deposition of crystals, while the vertical portion gives the adsorption isotherm of the crystals. The composition of the crystals is given by the intersection at D, namely 70.5% of $SrAl_2Cl_8$, corresponding to five molecules of the strontium salt and nine molecules of phosgene; the compound $5SrAl_2Cl_8.9COCl_2$ contains 70.49% of $SrAl_2Cl_8$. These crystals lose only part of their phosgene of crystallization, and yield a second phosgenate at E which for some reason resists decomposition with remarkable vigor, the interval between the pressure readings at 80.3% and 81.0% (see Table II), representing the portion of the curve below the intersection at E, being no less than 48 hours. In fact, it was thought that the end of the curve had been reached, and that the residue was completely dephosgenated; so that when a pressure of nearly two hundred millimeters was registered the next day, there was a strong suspicion that a leak had developed in the one stop-cock giving access to the vapor tension apparatus; a sample of this gas was therefore pumped off, collected, and analyzed; it proved to be 100% phosgene; a second proof that no leak was involved is given by the fact that, as the percentages are arrived at from the weight of salt used and the *volume* of phosgene pumped off, the volumes being converted to weights by multiplying by the density of the gas, the density of the gas pumped off up to the point E was found to be extraordinarily high, whereas after completion to the point F on the curve the density value was perfectly normal. Once the decomposition was started, it appeared to go on readily, apparently catalyzed by the ansolvide, $SrAl_2Cl_8$. The composition of the product at E is given by the point of intersection as 80.3% of the strontium salt, which corresponds to one molecule of $SrAl_2Cl_8$ and 1.055 molecules of phosgene; the compound $SrAl_2Cl_8.COCl_2$ contains 81.12% of $SrAl_2Cl_8$.

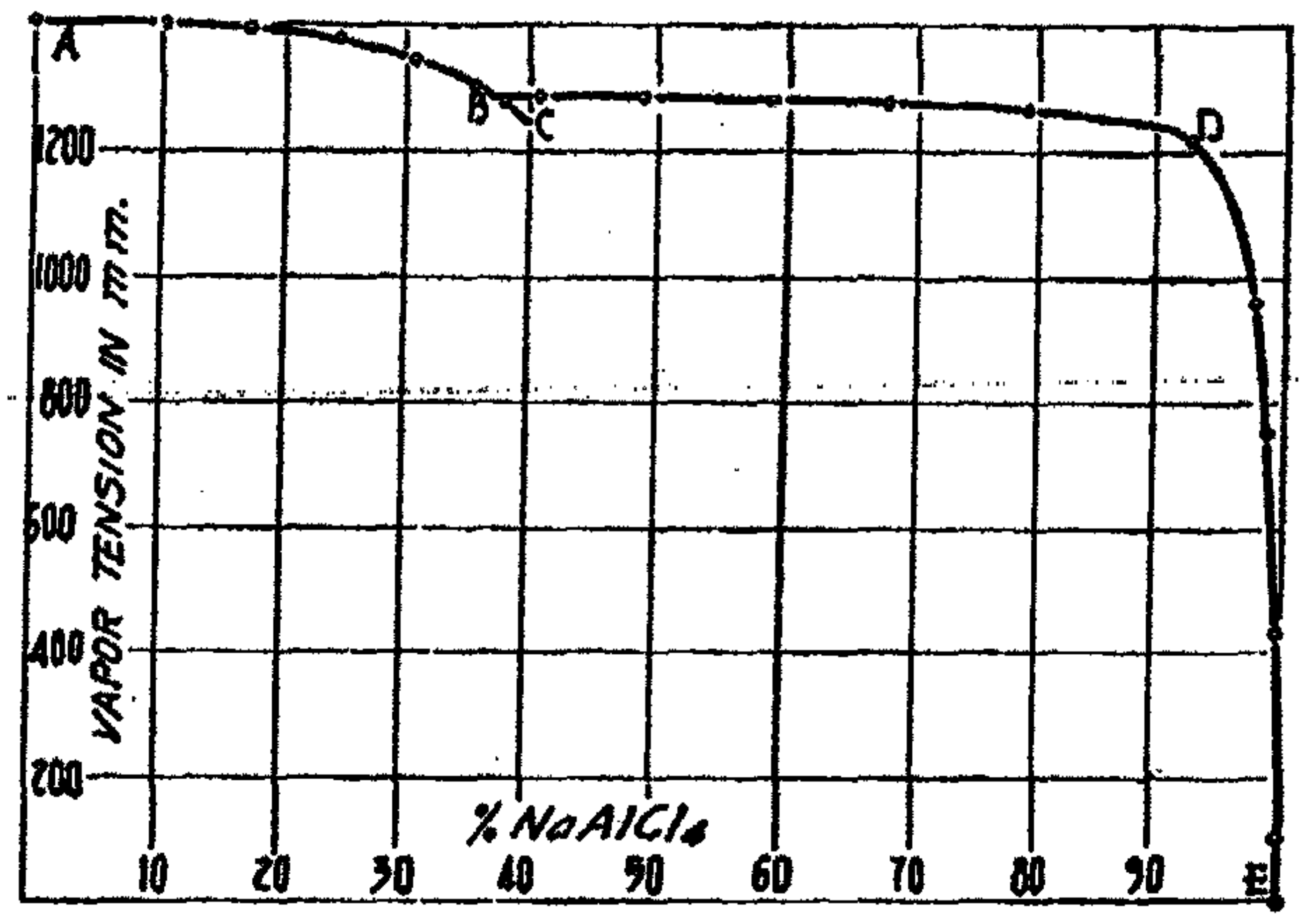


Fig. 4
Vapor Tension Curve 25° for the system $NaAlCl_4-COCl_2$

Isotherm of $NaAl_2Cl_4$ Solution. The solution of the sodium salt presents the simplest possible isotherm for this type of solution, that is for the solution of a non-volatile crystallizable salt in a volatile solvent. There is but one break in the curve, at the point B (Figure 4), where crystals begin to separate, showing a solubility of 36.5% $NaAlCl_4$. The solution is capable of slight supersaturation. No solvates are stable at 25.

Molecular Weights. It is possible to calculate the molecular weights of the phosgeno-aluminates of sodium and strontium from the vapor tension data. Using the formula $m = \frac{g\,Mp'}{p - p'}$, where m is the molecular weight of the solute, M that of the solvent, p the vapor tension of the solvent, p′ that of the solution, and g the weight of solute in 1 gram of solvent. We arrive at molecular weights for the strontium salt ranging regularly from 7130 at 2.5%, to 4530 at 15%, and for the sodium salt from 2545 to 2565, the values passing through a maximum in the latter case, indicating that the upper part of the curve is imperfect. These values lead to a value of about 7650 for the strontium salt, and to a value probably in excess of 3000 for the sodium salt; and to molecular aggregates containing from fifteen to twenty molecules of the simple formulas used in this paper. The higher solvate of strontium phosgeno-aluminate contains five of the simple molecules in one of the solvated molecules, and the vapor tension data seem to indicate that three or four of these are banded together to give immense colloid-like aggregates. Whether these solutions give the Tyndall effect has not been determined. In contrast to these solutions, previous papers of this series have shown that the solution of aluminium chloride in phosgene contains molecules with only two atoms of aluminium, while the solution of calcium phosgeno-aluminate contains molecules with four atoms af aluminium. What the significance of these facts may be is not clear.

Summary

Some new phosgeno-aluminates have been prepared, and their solutions in phosgene studied. The solubility of the salts has been determined at 25°, and the isotherms of their solutions at 25° found. The vapor tensions of their solutions have been tabulated in Table IV at round values of the composition. The following solvates have been identified:

$3BaAl_2Cl_8.8COCl_2$, vapor tension at 25°, 625 mm.;
$BaAl_2Cl_8.COCl_2$, vapor tension at 25°, 290 mm.;
$5SrAl_2Cl_8.9COCl_2$, vapor tension at 25°, 950 mm.;
$SrAl_2Cl_8.COCl_2$, vapor tension at 25°, 175 mm.
$NaAlCl_4$ forms no solvate with $COCl_2$ at 25°.

Molecular weight calculations indicate that the phosgeno-aluminates of strotium and sodium contain from fifteen to twenty atoms of strontium or sodium per molecule.

In conclusion, we wish to acknowledge the liberal supply of phosgene placed at our disposal by the officers of the Chemical Warfare Service.

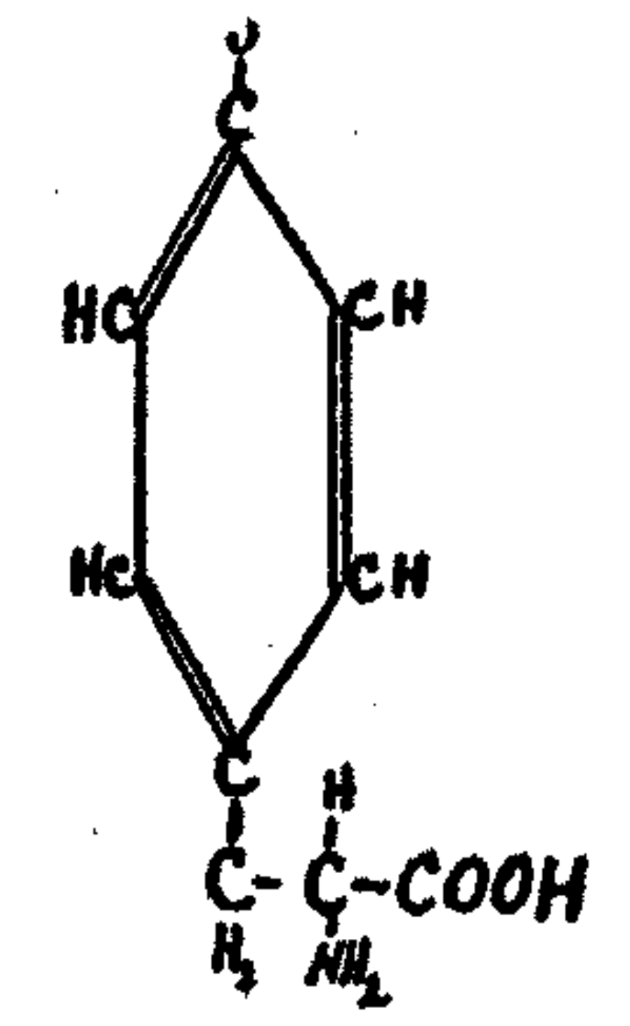
Stanford University,
California.

THE INFLUENCE OF THE pH UPON THE ULTRAVIOLET ABSORPTION SPECTRA OF CERTAIN CYCLIC COMPOUNDS

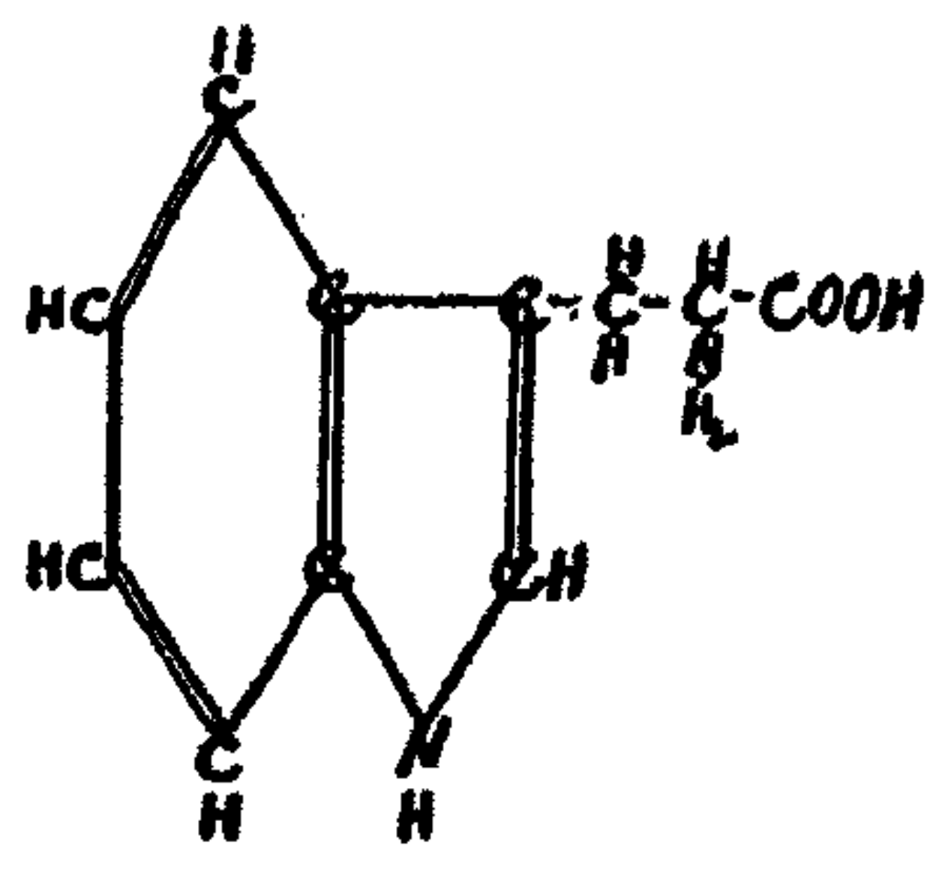
BY WILHELM STENSTRÖM AND MELVIN REINHARD*

Most cyclic compounds in water solutions give absorption bands in the ultraviolet. While studying this absorption for a mixture of amino acids we noticed that the absorption band shifted towards longer wave-lengths when the mixture was made alkaline[1] and therefore, decided to see how the change was related to the pH for tyrosine and tryptophane. For this investigation we used a Hilger ultraviolet spectroscope size C and a Hilger sector photometer.

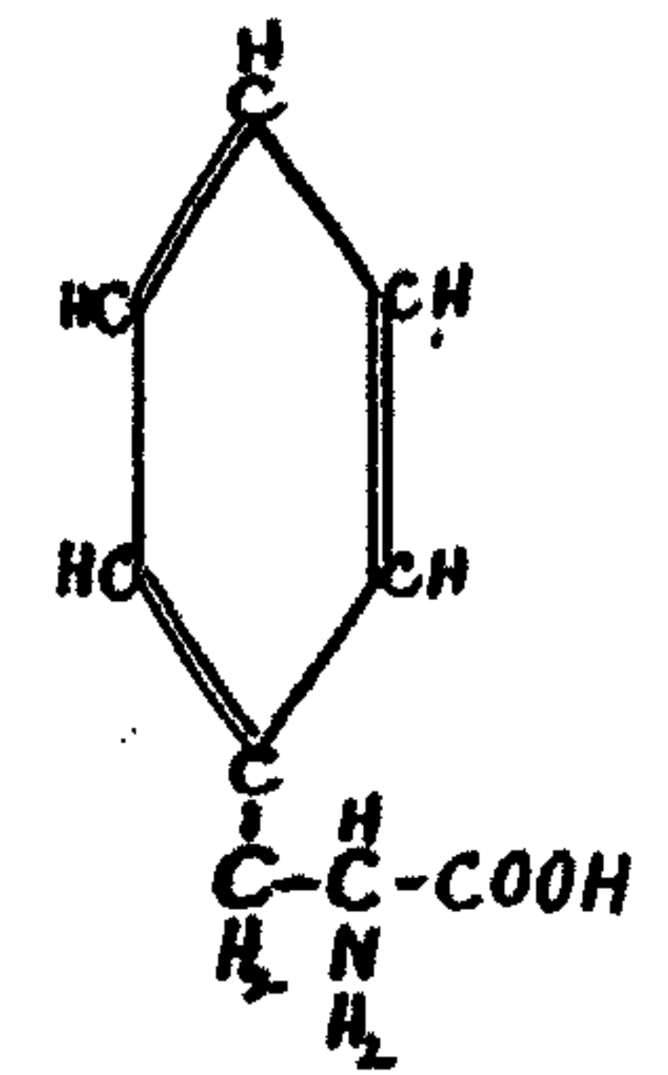
Tryptophane did not show any marked change in the absorption curve whether it was made strongly acid with HCl or strongly alkaline with NaOH. Tyrosine on the other hand, showed a decided shift of its absorption band when it was made alkaline with NaOH. (These observations are in accordance with the findings of P. A. Kober[2].) One important difference between these two amino-acids is that tyrosine has a hydroxyl group in the benzene ring while tryptophane has no such hydroxyl group. In order to find out if it was this group that was responsible for the difference in behavior just mentioned, we examined phenylalanine which differs from tyrosine only by not having the hydroxyl-group in the benzene ring. This substance did not show any shift of the absorption band when it was made alkaline. On the other hand the simplest compound with such a hydroxylgroup, phenol, gave the shift when made alkaline.



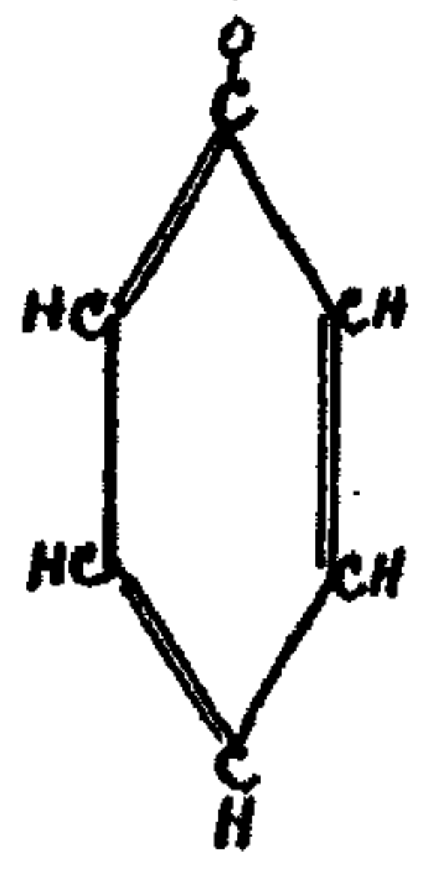
Tyrosine



Tryptophane



Phenylalanine



Phenol

It therefore, seems reasonable to conclude that this shift is related to the hydroxyl group in the benzene ring. The curves for phenol before and after the shift are shown in Fig. 1 A and B, those for tyrosine in Fig. 2 A and B.

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*From the State Institute for the Study of Malignant Disease, Buffalo, N. Y., Burton T. Simpson, M. D., Director.

[1] Stenström and Reinhard: Ultraviolet absorption spectra of blood serum and certain Amino Acids (not yet published). J. Biol. Chem.

[2] J. Biol. Chem. 22, 440 (1915).

In order to answer the questions: when does this shift take place and does it take place suddenly for a certain alkalinity or gradually when the alkalinity is increased, it was necessary to determine the absorption for different concentrations of the hydrogen ions. The pH was measured with the colorimetric method with phenolsulphophtalein, phenolphthalein and tropaeolin O indicators[1]. It would require a very great number of exposures to plot the complete curve for each step of pH and therefore, we decided to see how the wave-length changed at the points *a*, *b* and *c* (see Figs. 1 and 2) when the extinction coefficient (E) was kept equal to 1350 for phenol, equal to 1600 for tyrosine and equal to 700 for resorcinol which we also examined in this way. Fig. 3 gives the relation between the wave-length (ordinate) and the pH for phenol, Fig. 4 for tyrosine and Fig. 5 for resorcinol. The shift is very marked at *a* and *c* whereas at *b* it is small and irregular. The irregularities may however, be due to errors of the measurements. The shift starts at "a" at a considerably lower value of pH than at c. For phenol it starts at "a" for about pH = 8.7 and the sharp incline is over at pH = 9. The curve still slopes slightly at least up to pH = 11. At c the sharp incline starts at pH = 9. It is of interest to note that the dissociation constant for phenol is about 1.3×10^{-10}. $[\overset{+}{\mathrm{H}}]\,[\overset{-}{\mathrm{Phenol}}] = 1.3 \times 10^{-10}\,[\mathrm{Phenol}]$. Thus the number of phenol ions must increase from about 1% to 10% of the phenol molecules while the pH changes from 8 to 9. At pH = 10 there ought to be about the same number of phenol ions as of phenol molecules and for higher pH the number of phenol molecules becomes smaller and smaller. If we assume that in Fig. 1 curve A is produced by the phenol molecules and curve B by the

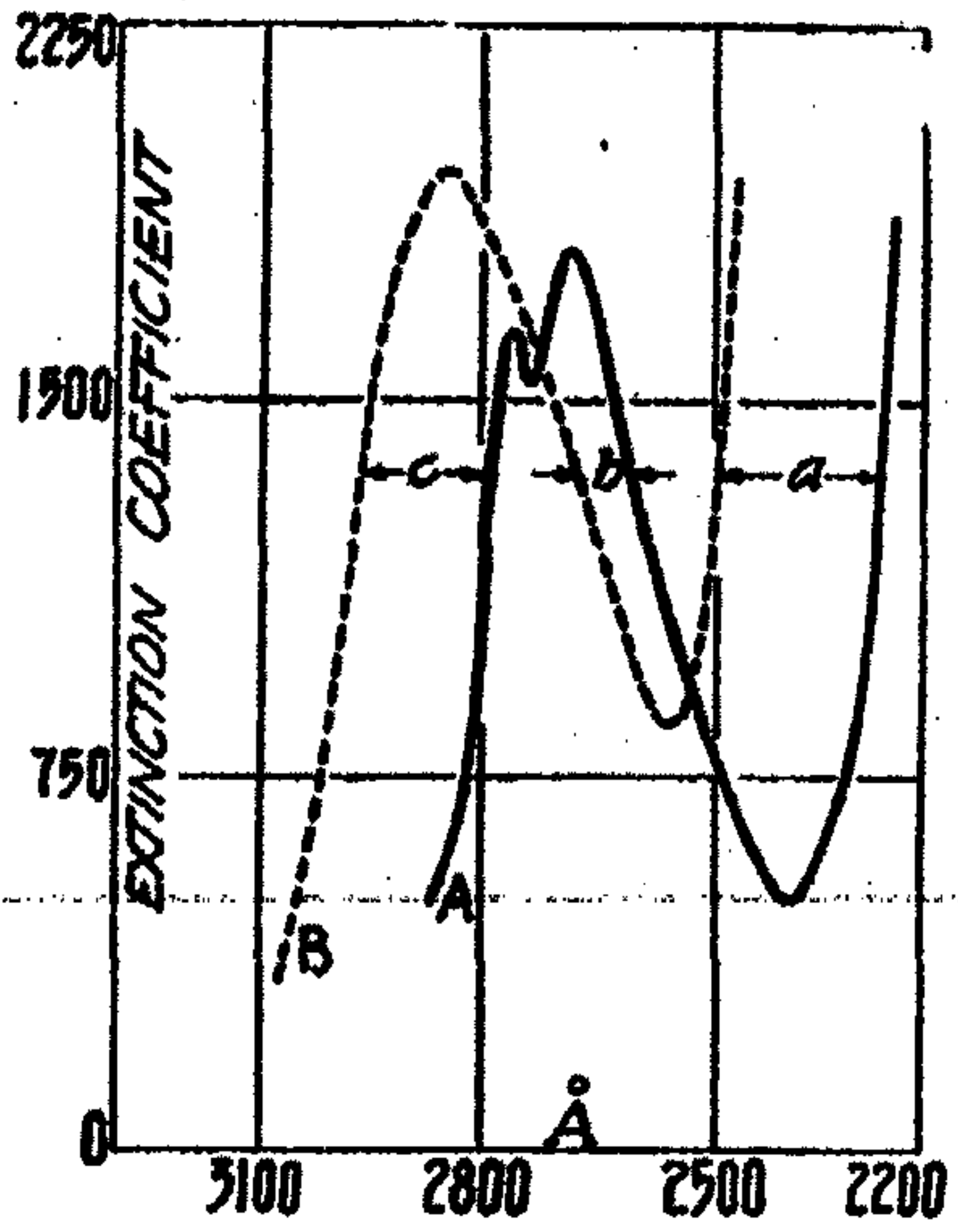

FIG. 1

A. Phenol in water. p<H4

B. Phenol in water + NaOH.pH 10.5

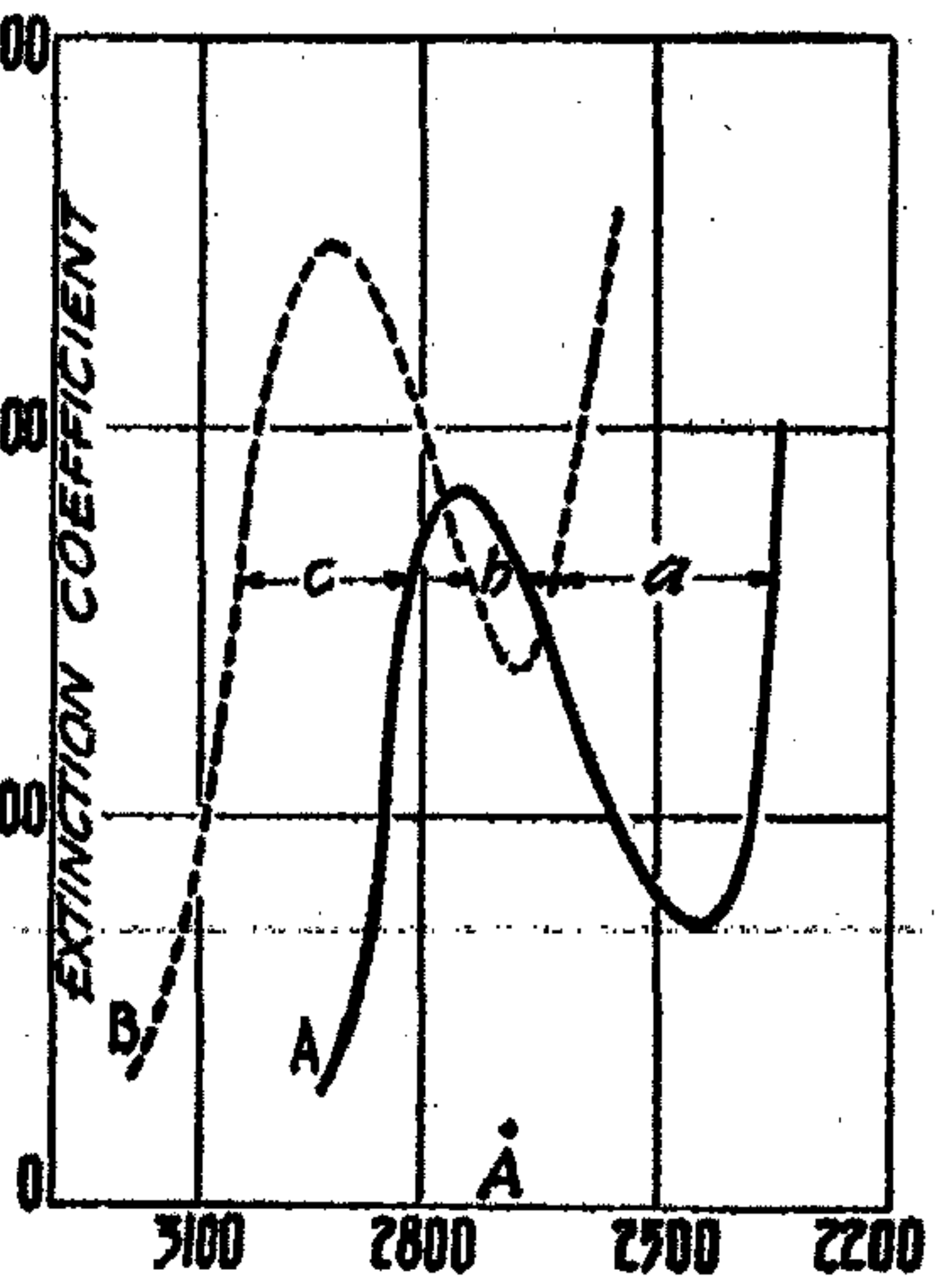

FIG. 2

A. Tyrosine in water pH<4.

B. Tyrosine in water + NaOH pH 12.7

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[1] Clark: "The Determination of Hydrogen Ions."

phenol ions then the shift is explained. The curves in Fig. 1 have a sharp incline at a and a small change in wave-length changes the absorption greatly. Therefore, a small addition of ions will increase the absorption or (which is the same) will give the same absorption at a longer wave-length than before. At c the extinction coefficient is only 50% greater for the ion than for the molecule and consequently no change can be noticed there until the relative number of ions has gone up considerably. In order to explain the shift in the curve for tyrosine in a similar way we must assume that the dissociation starts at the carboxyl group and later on also takes place at the hydroxyl group. The affinity constant for tyrosine is 4×10^{-9} while the shift starts first

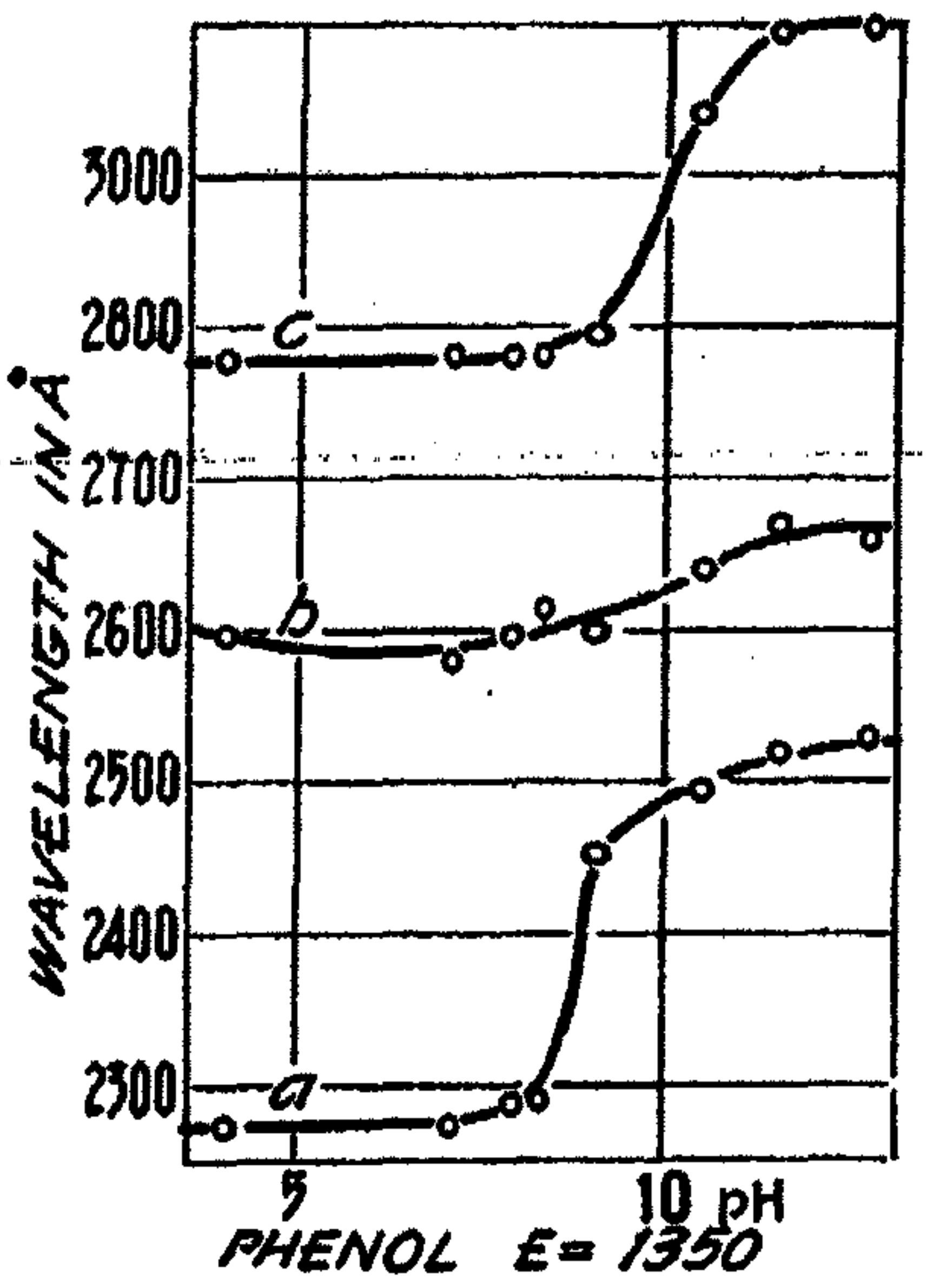


Fig. 3

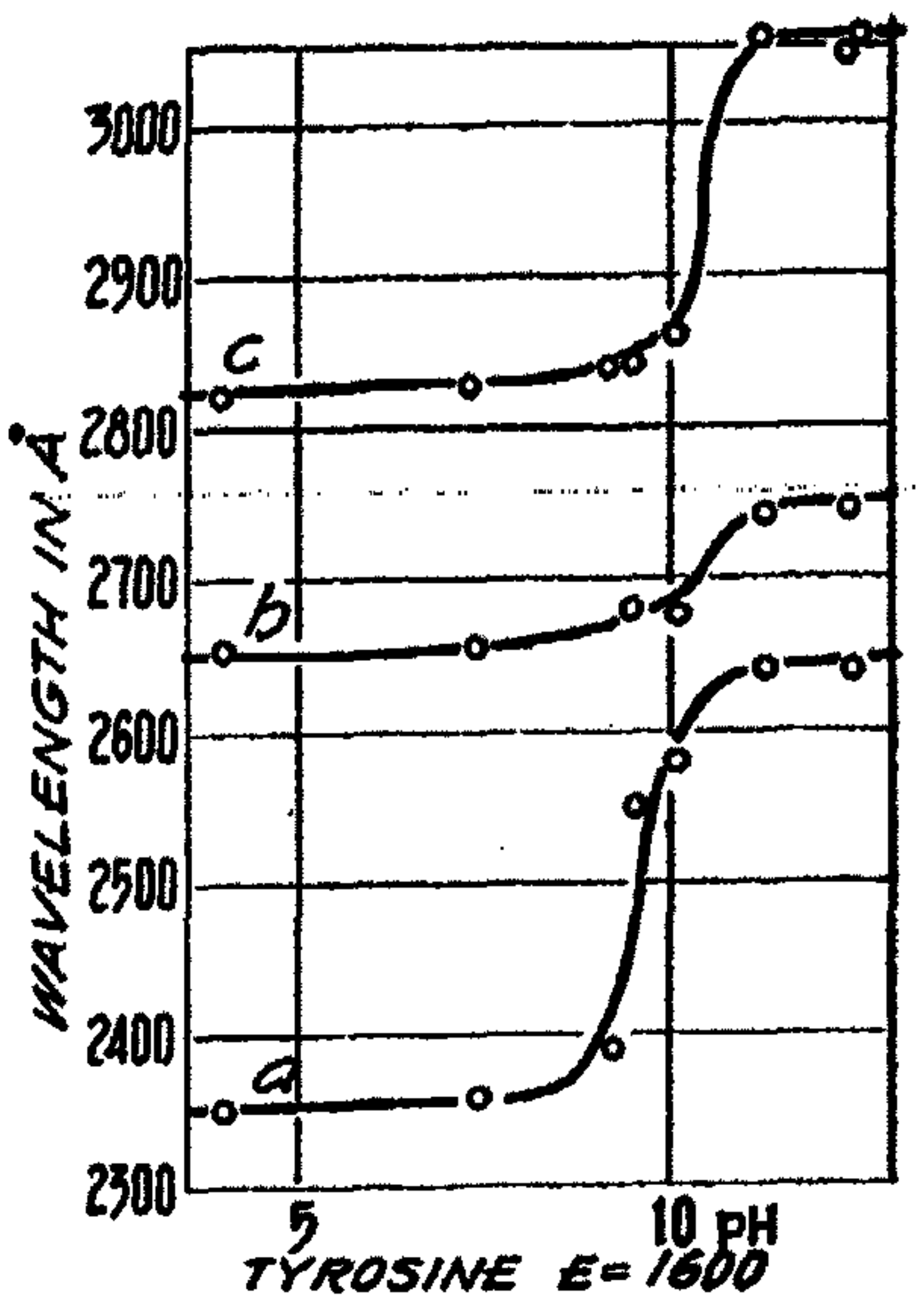
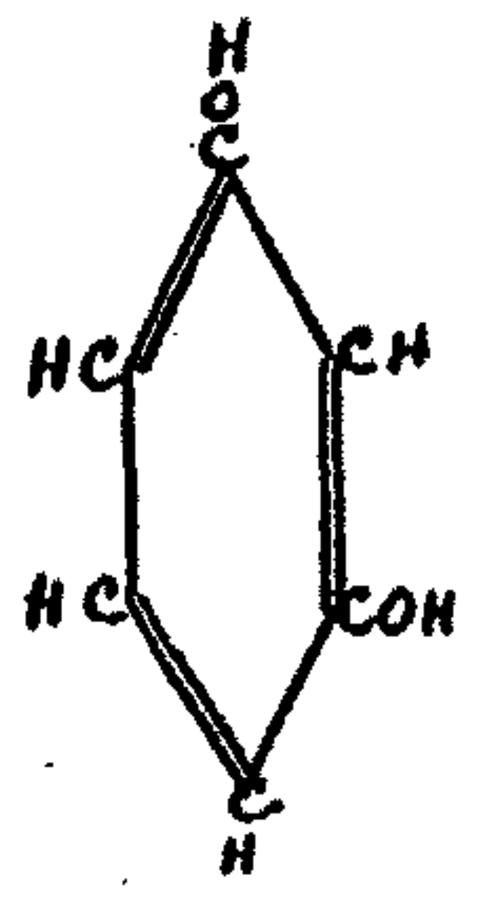


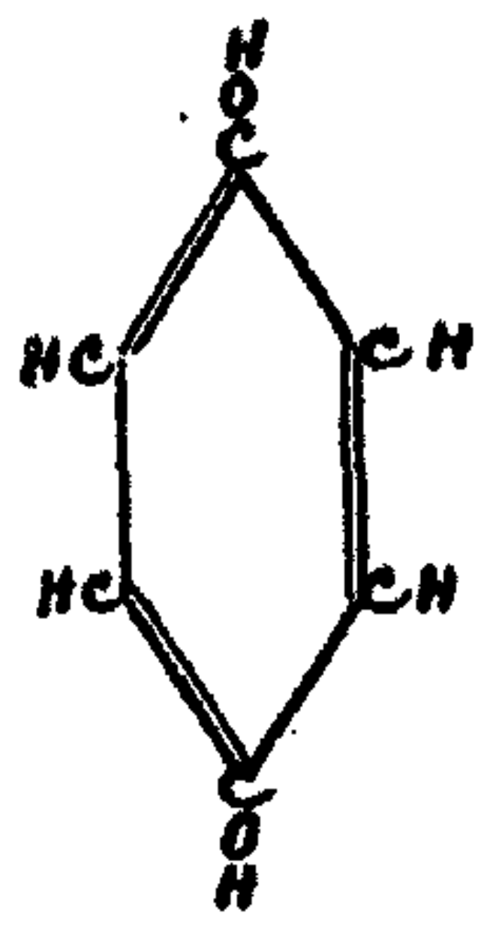
Fig. 4

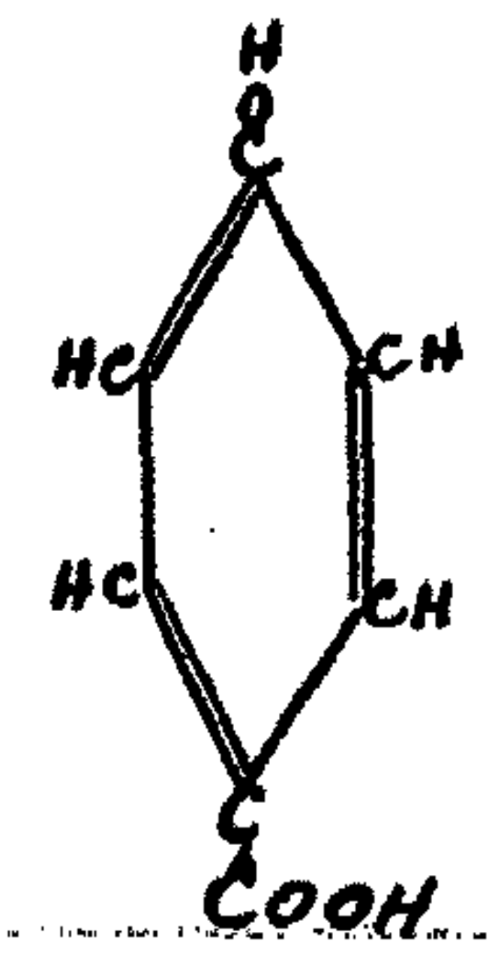
at pH = 9 (a) and ends at pH = 11.5 (c). If T is the concentration of tyrosine molecules and ions ionized at the carboxyl group only and T″ the concentration of tyrosine ions ionized at the hydroxyl group then $\frac{T}{T''}$ must be of the order of 10 for pH = 9 and 1/10 for pH = 11.5 (Judging from the relation between the absorption curve and the concentration of phenol ions and phenol molecules.) Therefore, the second affinity constant for tyrosine ought to lie between 10^{-10} and 10^{-11}; nearer 10^{-10}.

In order to test this theory further we examined the absorption of meta- and para-dihydroxybenzene (resorcinol and hydroquinone) paraoxybenzoic acid and salicylic acid, paraoxybenzaldehyde and benzoic acid at different pH. All of these compounds gave a shift when made alkaline enough except benzoic acid which does not contain the hydroxyl group (Hydroquinone was broken down.)

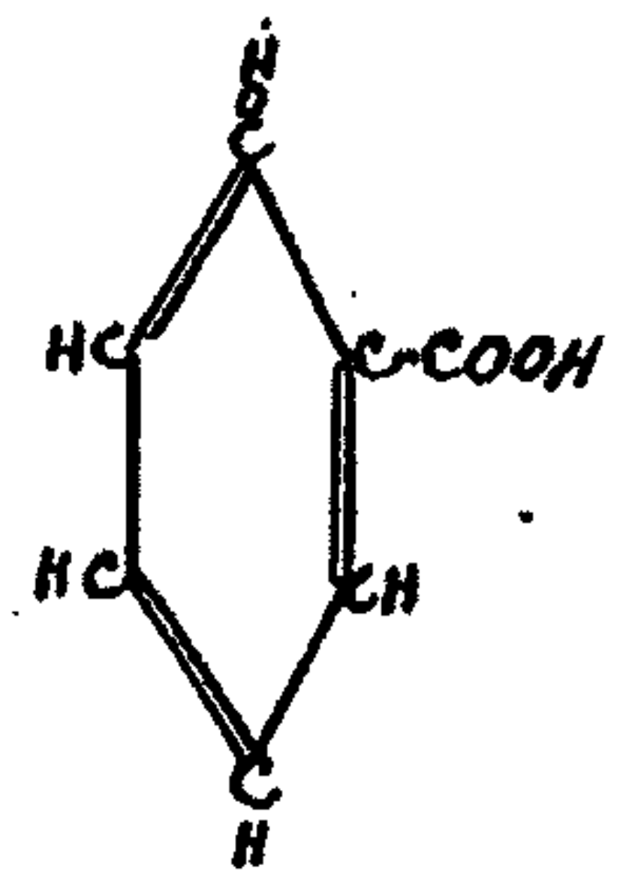
	Resorcinol		Hydroquinone		Paraoxy-benzoic acid.	
Affinity Const.	3.6×10^{-10}		1.1×10^{-10}		2.9×10^{-6}	
pH	<4	>13	<4	>13	<4	>13
λ at a	2350	2601	2390	molecule	2190?	2242
b	2570	2670	2640	destroyed	2345	2540
c	2830	3040	3050	3770	2740	3010
Extinc. coeff.	840	840	840	840	5800	5800

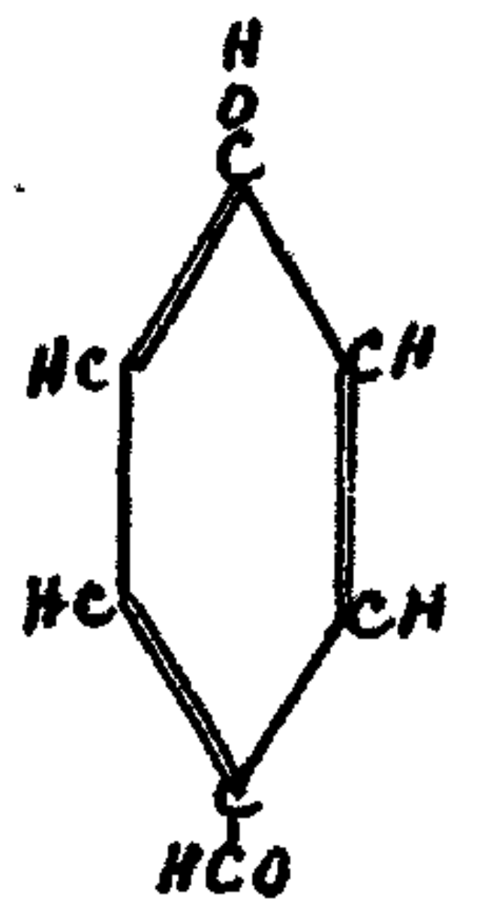


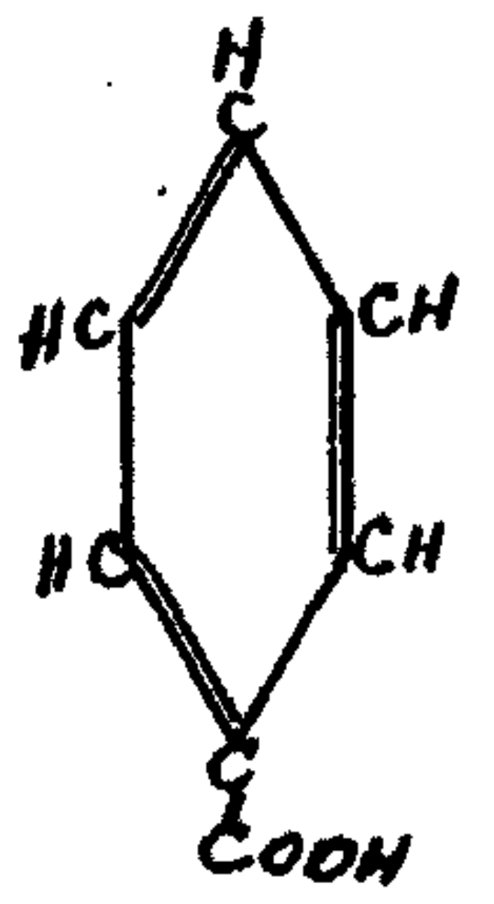




	Salicylic acid		Paraoxy benzaldehyde		Benzoic acid	
Affinity Const.	1.0×10^{-8} 1×10^{-13}				6×10^{-5}	
pH	<4	>13	<4	>13	<4	>13
λ at a	2460	2570	2305	2488	2535	2535
b	2850	2870	2500	2870	2608	2615
c	3100	3180	3070	3580	2822	2800
Extinc. coeff.	2400	2400	5100	5100	800	800







If our assumption is correct then it should be possible to determine the hydrogen ion concentration between certain limits for solutions of compounds with hydroxyl groups in the benzene ring with help of such curves as are shown in Figs. 3, 4 and 5, and also to determine the affinity constants in respect to the hydroxyl group.

A curve giving the shift for blood serum corresponding to the curve for tyrosine is reproduced in Fig. 6. It is of interest to notice that the shift starts first at pH = 12 in spite of the fact that it is probably the tyrosine constituent of the proteins which is responsible for this shift. It seems therefore, as if the tyrosine were joined in the proteins in such a way that the complete ionization at the hydroxyl group cannot take place until a pH = 12 has been reached.

Summary

1. It has been shown that the absorption bands in the ultraviolet somewhere between 2200 and 3600 A are dependent upon the hydrogen ion concentration for the following compounds: phenol, tyrosine, resorcinol, paraoxybenzoic acid, salicylic acid and paraoxybenzaldehyde in water solutions. It seemed to be independent of the pH within the experimental error for benzoic acid, phenylalanine and tryptophane in water solutions.

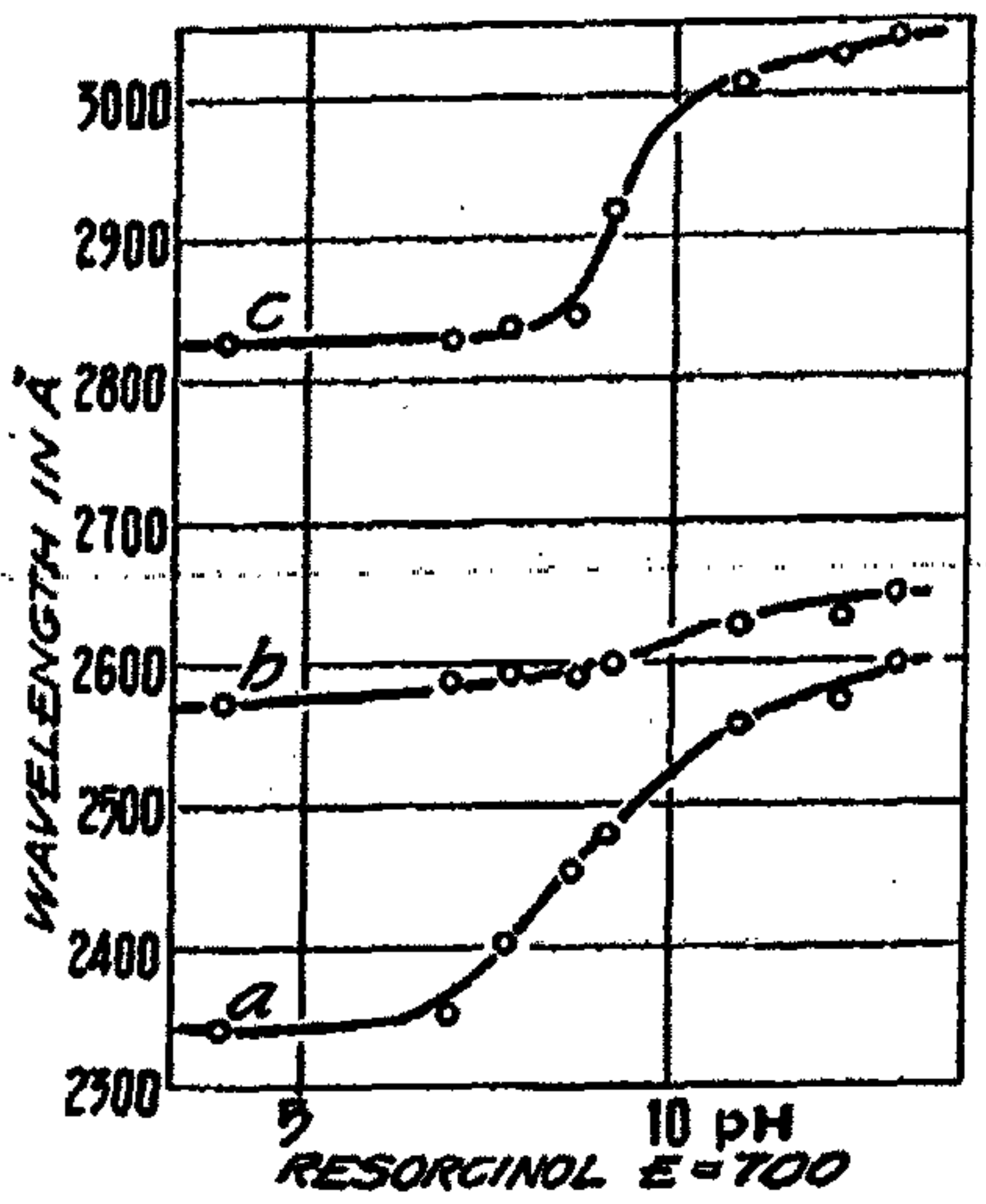


Fig. 5

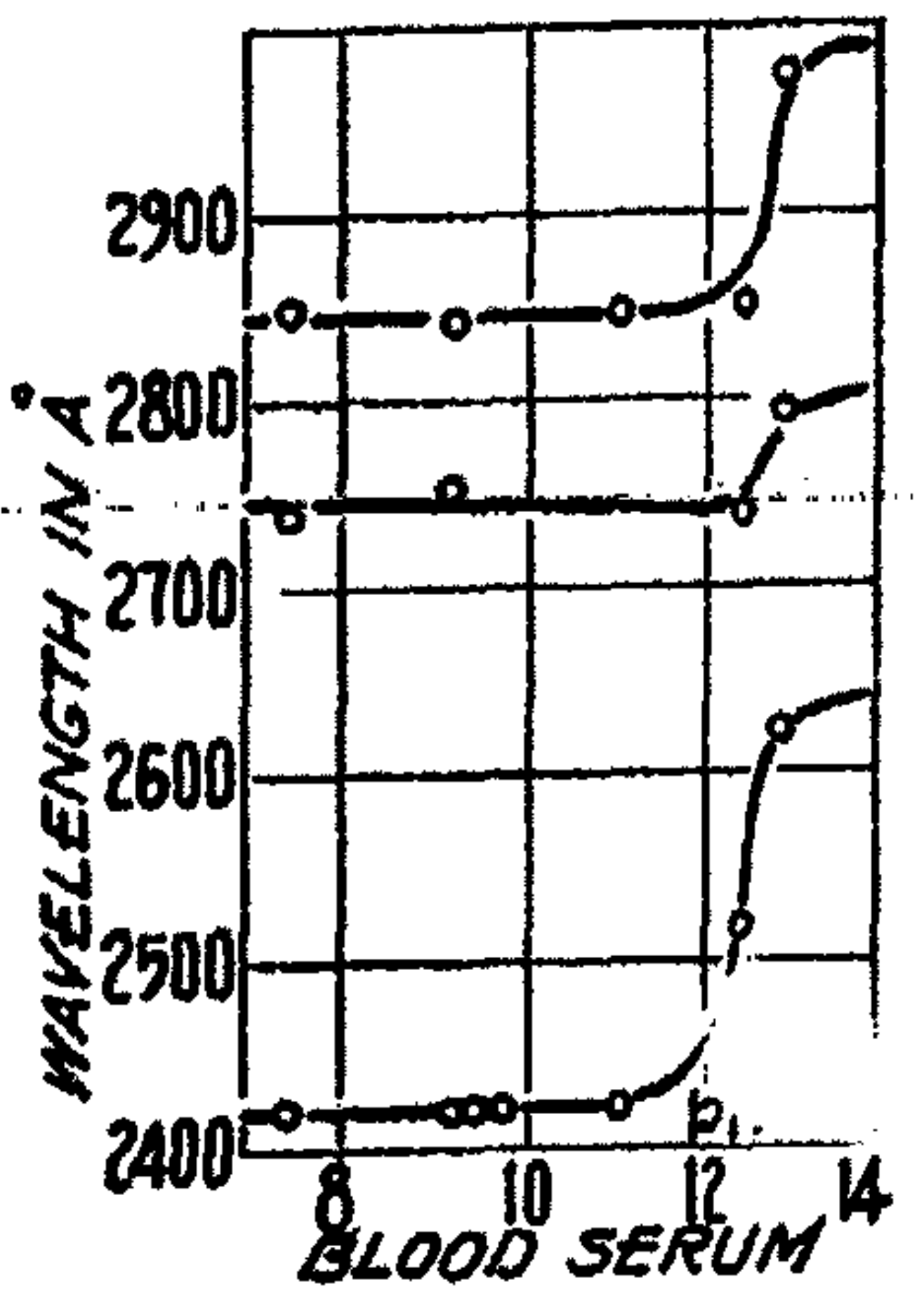


Fig. 6

2. The relation between the structure of the band and the hydrogen ion concentration can be outlined briefly thus: The band will shift towards longer wave-lengths and increase in intensity when a certain alkalinity has been reached by adding NaOH (other alkalies seem to have the same effect) to the water solution of the compound.

3. It seems to be compounds with a hydroxyl group in the benzene ring which show this shift. The affinity constant for this group in the compound seem to be related to the critical value of pH for the shift.

4. The relation between the pH and the wave-length for which a certain extinction coefficient is obtained has been determined and plotted for phenol, tyrosine and resorcinol (Figs. 3, 4 and 5.)

5. The shift can be explained as the change from a curve characteristic of the molecule to one curve characteristic of the compound ionized at the carboxyl group.

6. A curve showing the shift for blood serum has been plotted.

NEW BOOKS

Colloid Symposium Monograph. *Edited by Harry N. Holmes. 24 × 16 cm; pp. vii + 368. New York: Chemical Catalog Company, 1925. Price: $5.00.* This monograph contains the twenty papers presented at the second National Colloid Symposium held at Northwestern University in June 1924. The programme was: general principles of ion effects in colloids, by Leonor Michaelis; the electro-viscous effect in rubber sols, by G. S. Whitby and R. S. Jane; determination of particle size, by W. J. Kelly; an improved method of sedimentary analysis, by F. F. Renwick and V. B. Sease; sols with non-spherical particles, by Herbert Freundlich; studies with the kinoultramicroscope, by E. O. Kraemer; a new method for the determination of the distribution of size of particles in emulsions, by A. J. Stamm; properties of clays, by A. V. Bleininger; bentonite, by Jerome Alexander; plasticity in colloid control, by E. C. Bingham; the theory of adsorption and soil gels, by N. E. Gordon; the rôle of colloids in soil moisture, by G. J. Bouyoucos; polar emulsifying agents, by H. N. Holmes and H. A. Williams; iodine as an emulsifying agent, by H. N. Holmes and H. A. Williams; the orientation of molecules in the surfaces of liquids, by W. D. Harkins; the supercentrifuge, by L. H. Clark; the effect of surface energy on colloidal equilibrium, by H. O. Halvorson and R. G. Green; bacteria as colloids, by A. I. Kendall; the effect of ammonium salts upon the swelling of colloids and upon the growth of yeast, by E. I. Fulmer; physico-chemical studies of proteins, by W. A. Hoffman and R. A. Gortner.

The paper by Gortner is by far the longest and the most important. Gortner claims to have proved that the proteins which he has studied do combine in stoichiometrical proportions with alkali and with acid, forming sodium caseinate and casein hydrochloride for instance; but that these substances then adsorb alkali or acid as the case may be. There is no evidence that the caseinate ion is in true solution. The reviewer would have liked to have seen some rather more definite statement in regard to this point and also in regard to the alleged sodium caseinates. Most people have titrated casein with three indicators and have consequently got three caseinates. By this method one can find as many caseinates as one has indicators. Robertson made an electrometric study and found more caseinates. One would like to know whether Mr. Gortner believes in more than one sodium caseinate or whether his method is not sensitive enough to distinguish between them. It is to be hoped that we shall get this information in the second paper.

Gortner's results are very important; but they are presented in such a curious way that they are not convincing. Gortner does not plot acid or base taken up against final concentration of acid or base which he should do. He does not draw any curves, in Fig. 3 for instance, to show what the values would be in case of no adsorption. He works with one gram per 100 cc which seems inadequate. He assumes that there is no protein error and he apparently ignores hydrolysis. It does not seem to the reviewer that this paper proves anything, one way or the other. A systematic and complete study of casein or of durumin would have been more helpful than accumulating data on a large number of proteins. It would help the reader a good deal if the author had been more specific as to just what he means by equal, equivalent, normal, and molar phosphoric acid.

Wilder D. Bancroft

The Recent Development of Physical Science. *By W. C. D. Whetham. Fifth edition. 20 × 14 cm; pp. xvi + 313. Philadelphia: P. Blakiston's Sons and Co., 1924. Price: $3.00.* The previous edition of this book appeared in 1909 and consequently many sections have been rewritten so as to include the new work on radioactivity, the structure of the atom and the molecule, the quantum theory, and the principle of relativity.

After a discussion of atomic structure, the author says, p. 244: "Hitherto, wonderful as are the results described, they involve no breach with the old and well-tried principles of Newtonian dynamics. The paths of alpha particles, deflected by atoms of a gas, show the law of inverse squares, and the atomic corpuscles whirl round in their orbits as the planets round the sun. But, if we push our analysis further, we find that we are forced to assumptions which are not in accord with this familiar scheme of science. We are brought to contemplate conditions which we cannot explain on any known principles, conditions which, in the present state of knowledge, seem not only inexplicable but inconceivable to our minds. It may be that future years will see these difficulties resolved by human insight as so many others have been. But we must not overlook the possibility that the orderliness we perceive in nature may be merely the rediscovery of conventions we have ourselves inserted when framing the problems to be investigated. We choose mass and energy as convenient fundamental physical quantities. But, all unconsciously, this choice is made because mass and energy happen to remain constant throughout a series of physical and chemical changes—and then triumphantly we rediscover the persistence of matter and the conservation of energy. As Professor Eddington disturbingly suggests, every law of nature which seems to us rational may be a concealed convention which we have ourselves unconsciously inserted. Hence an unavoidable conclusion which yet seems to us irrational may be the sign of transcendent importance—the sign of a real law of nature at the last. If so, we seem almost brought back to Tertullian's *credo quia impossibile.*"

On p. 295 there is a paragraph which contains a distinctly new point of view. "Not only does the radiation from the sun cause a repulsion of small objects, but their radiation to each other will, as Professor Poynting has shown from the theory, lead to a mutual repulsion when the bodies are placed in a region of space where the effective temperature is lower than their own. Two meteorites at ordinary temperatures, say at 300° on the absolute scale, will in cold space repel each other with a force equal to their mutual gravitative attraction when their radii are about 3.4 centimetres, and, in the case of smaller bodies, the repulsion will overcome the gravitative effect. In this case, when the gravitational force is that between bodies of small mass, instead of that between some small body and the gigantic sun, a resultant repulsion is reached at much larger dimensions than those of the case formerly considered. It is evident that a swarm of meteorites of the right size might continue to revolve round a planet or sun without mutual forces and independently of each other. It is possible that this result has some bearing on the problem of Saturn's rings."

Wilder D. Bancroft

Introduction to General Chemistry. *By William Foster. 21 × 14 cm; pp. 649. Princeton University Press, 1924.* In the preface the author says that this textbook is the result of more than fifteen years of experience in teaching General Chemistry to large classes of college students. The chapters are entitled: some terms used by chemists; changes in matter; elements and compounds—the composition of the earth's crust; combination by weight—the atomic theory; nomenclature, symbols, formulae and equations; oxygen-combustion; the measurement of gases; hydrogen-calculations; valence-nomenclature; the kinetic theory of matter; water hydrates; molecular weights and atomic weights—molecular formulae; solutions; hydrogen peroxide—oxidation and reduction; chlorine; hydrogen chloride; energy and chemical change—thermochemistry; chemical equilibrium; ionization and electrolysis; some applications of the ionic theory; acids, bases, and salts—neutralization; the halogen family; the oxides and oxygen acids of chlorine; the classification of the elements—structures of matter; sulphur and hydrogen sulphide; oxides and oxygen acids of sulphur, selenium, and tellurium; the atmosphere—the helium family; nitrogen and ammonia; the oxides and oxygen acids of nitrogen; the phosphorus family; carbon and its oxides—carbides—cyanides; hydrocarbons—fuel and illuminating gases—flame; carbohydrates, alcohols, organic acids, esters, and soap; the food of plants and animals; silicon and boron; colloid chemistry; metal and alloys—metallurgy; the alkali metals; the alkaline earth metals; radioactive metals; copper, silver, and gold; the magnesium family; the aluminum and rare earth group; the tin family; the chromium family; manganese; the iron family; the metals of the platinum family.

The author says that the book is "teachable" and he ought to know. Other people who teach general chemistry have written testimonials saying that the book is "teachable" and they ought to know. The reviewer has never taught general chemistry and he probably does not know what is "teachable" or even what the word means. Speaking, however, as an interested outsider, it seems to him that metals should not come last, though that does happen practically everywhere except at Syracuse University. From the view-point of the student it seems foolish to put iron which he does know about on p. 578 and the oxides of chlorine on p. 254.

One would be justified in saying that there is an enormous amount of information in this book; but that is not the highest praise. It seems to the reviewer that the information is presented as a mass of facts. No ordinary student could read this book for pleasure and it is doubtful whether anybody could read it and come out with any clear mental picture.

The reviewer questions very much the wisdom of putting in as much physical chemistry. Something should be left for later courses. The chapter on thermochemistry might well be omitted and is it worth while to talk to freshmen about osmotic pressure? As the reviewer has said before, it is absolutely essential that the teacher of general chemistry should know his physical chemistry; but it is not essential that he should put all he knows into the introductory course in chemistry. This book is really the author's modification of Alexander Smith's views and Alexander Smith had a great reputation as a teacher; but some of us are glad to admit his teaching ability without accepting his judgment as to what should be taught.

A few errors caught the reviewer's eye in the parts with which he was familiar. Electrolysis of cupric chloride solution gives cuprous chloride at the cathode and not copper, p. 208. While the author does not say, p. 216, that potassium is set free in the electrolysis of potassium nitrate and reacts with water, the strain is too great and on the next page he says that nitrate is set free and reacts with water. It seems hardly adequate to define flame as the evolution of light when two gases combine, p. 389. The student would have profited by a few words as to the difference between the luminous and the non-luminous Bunsen flame and on the difference between these and the colored salt flames. The reviewer is sceptical as to the existence of sodium chromite, p. 559.

Wilder D. Bancroft

Lehrbuch der heterogenen Gleichgewichte. *By Gustav Tammann. pp. xii×358. Braunschweig: Friedr. Vieweg und Sohn, 1924. Price: 17 marks, bound.* The above book is frankly a digest of Roozeboom's "Lehrbuch der heterogenen Gleichgewichte" which, after his death, was continued by Büchner, Aten and Schreinemakers, and is issued by the same publisher.

Prof. Tammann has succeeded in including all the essential matter and at the same time has impressed it pleasantly with his own distinguished personality.

It is a pity that a chapter upon the reciprocal salt pair has not been added. If this book is translated into English—and it certainly should be—the reviewer ventures to suggest that the above omission should be rectified. The diagrams are numerous and, on the whole, are excellent. There are a few, like Fig. 132, page 162, which could be improved, "complexing" the whole diagram.

This book will, undoubtedly, take its proper place as the leading short text book on the subject.

F. A. Freeth

Principles of Electroplating and Electroforming. *By William Blum and G. B. Hogaboom. 23 × 18 cm; pp. xii+356. New York and London: McGraw-Hill Book Company, 1924. Price: $4.00.* The authors have introduced the new word "electroforming". It may be defined as the production or reproduction of articles by electrodeposition. It includes electrotyping, the reproduction of phonograph record matrices, and the manufacture of tubes and other objects by electrodeposition.

The chapters are entitled: introduction; methods of expressing conditions of operation; principles of chemistry; elementary principles of chemical analysis; principles of electricity; principles of electrochemistry; factors governing the character of the deposits; selection, specification and inspection of electrodeposits; preparation for electroplating; preparation for electroforming; electrical equipment: tanks and their equipment; copper deposition; nickel deposition; cobalt and iron deposition; deposition of zinc and cadmium; lead and tin deposition; silver deposition; gold and platinim deposition; deposition of alloys; experiments in electrodeposition.

This is of course the best book of its kind that has ever been written. It was a pleasure to find the authors emphasizing the importance of *significant figures*, p. 7, because many chemists err in this respect. If we desire to adjust the composition of a plating solution to within two percent, "it is just as accurate and far more convenient to state that the volume of a plating solution is 235 gallons as to call it 235.36 gallons, even though the calculations might indicate the latter volume."

One doubts whether the authors will succeed in getting people to say resistivity, p. 74, when they should. On p. 84 the authors give the reviewer's "axioms of electroplating" and on p. 106 is an admirable paragraph on throwing power. "Throwing power may be improved by *increasing either the conductivity or the cathode polarization*. The total drop in potential between the anode and the two parts of the cathode must be equal. If, however, the polarization is greater upon the near than upon the far point, this is equivalent to an increased resistance to the near point. *The lower the primary resistance to the near point* (*i.e.*, the better the conductivity of the solution), the greater will be the relative effect of the polarization. An increase in conductivity will not, however, improve the throwing power unless there is appreciable polarization. Any given change in operating conditions may produce opposite effects upon these two factors, and the actual results will depend upon which effect predominates. Thus, *e.g.*, warming a solution increases the conductivity but decreases the polarization. The latter effect is more pronounced, hence an elevation in temperature generally decreases throwing power."

On p. 104 we read that in numerous instances "defective plating could be traced very directly to an abnormal or undesirable structure of the steel or brass used in the base metal. In recent experiments it has been shown that when copper is deposited from the sulphate bath upon either cast or rolled copper which has been cleaned with nitric acid, the deposited metal consists of crystals which are extensions of the crystals present in the base metal."

Gold coatings may yield satisfactory service when the thickness is only 1.25 μ, p. 119, and in the dip-gold process the thickness may be only 25 μμ, p. 310. In chromium plating of dies the thickness is only about 2.5 μ and this stands up under hard service. It has been noticed, p. 129, that the powders which are most effective for cleaning electrodes are those which go into the interface between grease and water.

"The use of electrodeposited negatives is customary only when the original or "master" is of metal; or when it is necessary to go through several stages of reproduction. It is the most accurate method of reproducing a metallic surface. Unpublished experiments conducted at the Bureau of Standards have shown that it is possible to reproduce faithfully by the electrodeposition of nickel not only those engraved lines on a steel scale, which are about 0.0005 mm. in width, but also smaller scratches just at the limit of visibility with present microscopic methods. Electrolytic production of negatives is relatively slow and expensive and is therefore used only when accuracy is the prime consideration.

"The most important example of the use of electrodeposited negatives is in the phonograph industry. The original wax record is first coated with graphite, upon which copper is deposited to form a "master plate," which is a negative. From this plate one or more "mother plates" are made by electrodeposition. The plates are positives, and serve as the forms on which the final matrices or "stamping plates" are deposited. The fact that satisfactory results can be obtained even after several "generations" of plates have been made is good evidence of the accuracy of reproduction.

"In the use of metal forms, the principal difficulty is that of treating the surface so as to permit subsequent separation. The problem resolves itself into the production of a surface which will still be conducting, but which is not "clean", *i.e.* the deposited metal is not in sufficiently intimate contact with the metal of the mold to cause permanent adherence," p. 141.

On p. 91 the authors adopt the view-point of Briggs that a copper anode in sulphate solution forms cuprous ions and they show that a great increase in anode efficiency occurs if one bubbles in air at the anode so as to oxidize the cuprous ions chemically as fast as formed. On p. 222 it is stated that nickel plating can be done best at a pH of 5.5-6. When the British Association stopped at Sudbury last year, the man in charge of the electrolytic nickel refining told the chemists that the process was run at a pH of 5.5 and then asked us if we knew what was meant by pH.

There is an interesting paragraph on ageing on p. 232. "With many plating solutions, especially those of nickel, it is frequently found by platers that satisfactory results cannot be obtained until the solutions have been operated for one or more days. No definite explanation of this effect of "aging" has ever been established. In the case of cyanide plating solutions, the aging is undoubtedly connected with the formation of carbonates or of compounds intermediate between the cyanides and carbonates. No such explanation holds for nickel solutions, as there are no marked chemical changes produced during their normal operation. It seems at least probable that the beneficial effects of aging nickel solutions may be due to (*a*) an adjustment of the acidity (pH), (*b*) the formation (or precipitation) of colloids in the solution, or (*c*) a reduction in the content of dissolved air. It has been claimed by some that even an "aged" nickel solution, freshly filtered, does not operate well, but can be improved by the addition of a small amount of nickel hydroxide. Such an effect, if confirmed, may be due either to a neutralization of free acid or to the formation of a colloidal suspension of the basic nickel compound."

The reviewer is a little sceptical about "black nickel" being nickel sulphide, p. 250. The fact that there is sulphur in the deposit is hardly sufficient to warrant drawing this conclusion.

"In view of the cheapness and availability of iron, some surprise has been expressed that its deposition has not been more extensively applied for purposes other than refining. The reasons for this apparent neglect of iron deposition are not, however, difficult to find. Iron plating is not deserving of consideration for either protection or appearance, because of the ready corrodibility of iron, especially the electrolytic iron. Since a large part of the plating industry involves the coating of iron or steel with other metals for decoration or protection, there is little field for iron plating for such purposes. In the manufacture of printing plates there has been a demand in recent years for a surface more durable than copper. This demand has been met so successfully by the use of nickel that it is now not unusual to secure as many as 2,000,000 impressions from a nickel electrotype, a number which is greater than is usually desired except in unusual cases, such as the printing of government securities, cartons, bread wrappers, etc. For such demands or for printing on leather or rough cardboard, etc., it is admittedly desirable to secure harder surfaces. If this can be accomplished by means of iron deposition, possibly followed by case-hardening, there will be a distinct field for the process. Any such development must depend, however, upon a definitely superior service of the iron, and not upon its cheapness. On an ordinary nickel electrotype the actual cost of the nickel surface (which is usually less than 0.025 mm., or 0.001 in. thick) is much less than 1 per cent of the cost of the finished plate, so there would be relatively little economy in the substitution of iron for nickel," p. 256.

The discussion of the electrodeposition of alloys, pp. 317-323 seems inadequate to the reviewer because it is apparently based on the assumption that the two metals deposit as two phases. This is true for lead and tin, p. 318; but it is not true for brass which is the only alloy made commercially in this way.

Wilder D. Bancroft

Chemistry to the Time of Dalton. *By E. J. Holmyard. 19 × 13 cm; pp. 125. London and New York: Oxford University Press, 1925. Price: $1.00.* "An attempt has been made in the following pages to construct an intelligible account of the development of chemistry in its main outlines from the earliest times to the establishment of the Atomic Theory by John Dalton at the close of the eighteenth century. . . . My guiding principle throughout has been to emphasize the continuity of chemical thought and to show that the theory of evolution is applicable to the development of science no less than to the world of birds, beasts, and flowers," p. 5.

The chapters are entitled: chemistry in Greece, Egypt and Islam; chemistry in Europe until the fifteenth century; from Norton to Glauber; the phlogiston theory; Boyle and his contemporaries; Black, Cavendish, Scheele and Priestley; Lavoisier; Dalton.

"The technical operations of the ancient world—metallurgy, dyeing, glass-making, perfumery and the like—were empirical. In Greece they were carried out by the despised artisans and craftsmen, and in Egypt by the priests—eternally secretive—as well. The knowledge of nature which they implied came to the philosophers only by indirect paths and in fragments. The problem of the constitution of the Universe, with its irresistible appeal to Greek thought, had therefore to be attempted with the scantiest materials, and the theories which they elaborated bore no sort of relation to the slender basis upon which they were raised," p. 12.

"We shall find that Aristotle's theory of the *prima materia* and its corollary the mutual transmutation of the four 'elements' exercised an overwhelming influence upon chemical thought throughout the Middle Ages, until the bold spirit of Boyle broke free from its trammels. After Aristotle's death in 322 B. C. our centre of interest passes to the city of Alexandria in Egypt under the Ptolemies. Here for several centuries chemistry was studied mainly as an off-shoot of magic, although it is possible that advance was made in descriptive knowledge. It is to the Neo-Platonists of Alexandria that must be assigned most of the blame for transforming chemistry into a mystical science and for promulgating the syncretism and obscurantism which made the development of scientific method a matter of the utmost difficulty," p. 14.

Geber "has many claims to be considered the first to whom the title of chemist may legitimately be applied," p. 15. "The last Muslim chemist of importance is the versatile Aidamir-al-Jildaki, who died in Cairo probably in the year 1361 . . . . In general Al-Jildaki was a compiler and his books show little originality, although they are a rich mine of information on the development of chemistry in Islam.

"Meanwhile chemistry had passed into Europe through Spain and had already gained some celebrated disciples, so that we may now pause and briefly estimate the state of the science as it entered upon its conquest of a new continent. Out of the inchoate body of mystical doctrine which represented chemistry in the Alexandrian school the Muslims had extracted a definite scientific system in which experimental fact and theoretical speculation were for the first time brought into their true relationship. On the practical side a clear scheme of classification had been evolved and a wide range of substances had been carefully investigated and systematically characterized. The common laboratory methods of distillation, sublimation, calcination, solution, crystallization, and reduction had been improved and their general purposes were well understood. The chemistry of organic substances had been valiantly attacked and understood and the preparation of many of them had been described, including the extraction of essential oils by a primitive method of steam-distillation.

"On the theoretical side, chemistry had been raised to the dignity of a true science, on a level with those of mathematics and astronomy, and no longer confined to the basement as in the 'University' of Alexandria, where the different subjects of learning were lodged, in descending order of merit, at various levels in the building. The main theory of the period was that of the transmutation of the metals—a theory which had the great merit of unifying the science and which was, of course, scientifically true at the time and had not yet outlived its usefulness.

"Finally, the practical applications of chemistry were acknowledged to be an important factor of the whole, so that Europe was able to start its chemical studies with a firm basis of fact, a coherent body of doctrine, and a realization of the value of chemistry to everyday life, ready to hand. For this privilege of our ancestors let us haste to pay our homage to the followers of the prophet," p. 29.

In the chapter on "Boyle and his Contemporaries" the author says, p. 78: "Scientific method, not the product of any one age but always implicitly, if not explicitly, followed by most of the leaders of chemical thought, was beginning to be more clearly understood and more frequently applied by the rank and file. Although it must be admitted that many of the great discoveries in science appear to have been the result of happy accident or flash of genius, the laborious development of these discoveries in all their aspects and ramifications require a disciplined army of workers trained in the school of the so-called Baconian system."

"Joseph Priestley (1733-1804) was a man fortunately not blessed with too logical a mind. Passionately devoted to the study of chemistry, he made experiments hap-hazard, but was sufficiently accurate to appreciate the value of his results and to explain them in terms of current theory. As an experimenter he was brilliant, but he seems to have had no working plan, and strayed whither the fancy took him," p. 87.

Thomson gives some interesting details as to the opposition which Dalton's atomic theory encountered at the outset, p. 118. "There were, however, some of our most eminent chemists who were very hostile to the atomic theory. The most conspicuous of these was Sir Humphry Davy. In the autumn of 1807 I had a long conversation with him at the Royal Institution, but could not convince him that there was any truth in the hypothesis. A few days after, I dined with him at the Royal Society Club, at the Crown and Anchor, in the Strand. Dr. Wollaston was present at the dinner. After dinner every member of the club left the tavern, except Dr. Wollaston, Mr. Davy, and myself, who stayed behind and had tea. We sat about an hour and a half together, and our whole conversation was about the atomic theory. Dr. Wollaston was a convert was well as myself; and we tried to convince Davy of the inaccuracy of his opinions; but, so far from being convinced, he went away, if possible, more prejudiced against it than ever. Soon after, Davy met Mr. Davis Gilbert, the late distinguished president of the Royal Society; and he amused him with a caricature description of the atomic theory, which he exhibited in so ridiculous a light, that Mr. Gilbert was astonished how any man of sense or science could be taken in with such a tissue of absurdities. Mr. Gilbert called on Dr. Wollaston (probably to discover what could have induced a man of Dr. Wollaston's sagacity and caution to adopt such opinions), and was not sparing in laying the absurdities of the theory, such as they had been represented to him by Davy, in the broadest point of view. Dr. Wollaston begged Mr. Gilbert to sit down, and listen to a few facts which he would state to him. He then went over all the principal facts at that time known respecting the salts; mentioned the alkaline carbonates and bicarbonates, the oxalate, binoxalate, and quadroxalate of potash, carbonic oxide and carbonic acid, olefiant gas and carburetted hydrogen; and doubtless many other similar compounds, in which the proportion of one of the constituents increases in a regular ratio. Mr. Gilbert went away a convert to the truth of the atomic theory; and he had the merit of convincing Davy that his former opinions on the subject were wrong. What arguments he employed I do not know; but they must have been convincing ones, for Davy ever after became a strenuous supporter of the atomic theory."

Wilder D. Bancroft

Taschenbuch fur Gerbereichemiker und Lederfabrikanten. *By H. R. Procter. Translated by George Grasser. Third edition: 16 × 11 cm; pp. xv+263. Dresden and Leipzig: Theodor Steinkopff, 1924. Price: 90 cents.* The first German edition was a translation of the English edition; the second German edition was an anastatic reproduction of the first. The present edition has been revised and enlarged by Dr. Grasser who is therefore a good deal more than a translator.

Wilder D. Bancroft

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ON THE MECHANISM OF CATALYSIS BY ALUMINIUM OXIDE

BY M. C. BOSWELL AND H. M. DILWORTH

Experimental evidence and arguments have been presented by the senior author and his students, which lend considerable support to the theory that platinum black and partially reduced oxides function as catalysts by means of surface films of dissociated water, i. e. positively charged hydrogens and negatively charged hydroxyls.[1]

It seemed probable that the origin of the catalytic properties of aluminium oxide might likewise be found in a similar film on the aluminium oxide particles. Accordingly the quantitative experiments recorded in this paper were undertaken, with a view to determining whether this hypothesis appeared to be in harmony or not with the facts.

It was recognized at the outset that aluminium oxide differs markedly in constitution from partially reduced oxides. In the case of the latter, as has been pointed out in the above papers, there is an interior oxygen content which can be drawn upon either for the maintainance of the surface film on the particles, or for oxidation purposes directly if the surface film is destroyed. However, in the case of aluminium oxide, although there is a large interior content of oxygen, this is not, owing to the great stability of the oxide, available for any such purposes as those indicated above in the case of reducible oxides. Thus, if a surface layer of charged hydrogens and hydroxyls does exist on the particles of an aluminium oxide catalyst, it is not present in a reduced metal layer superposed on an underlying oxide layer, as in the case of partially reduced oxides, but must constitute a surface layer held in the exterior surface of the particles, thus:

$$\mathrm{Al_2O_3}\left|\begin{array}{l} | \\ | \\ \mathrm{H^+} \\ \mathrm{OH^-} \\ \mathrm{H^+} \\ \mathrm{OH^-} \\ | \\ | \end{array}\right.$$

The charged hydrogens and hydroxyls constituting the surface film would be in a state of tension due to the mutual attraction of opposite charges. The stability of this film, which will be shown presently, is probably due to this tension. Likewise the remarkable protection afforded by this film for the underlying interior oxygen in the case of partially reduced oxides, may be

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[1] Boswell: Trans. Roy. Soc. Canada, 16 III, 1 (1922); Boswell and McLaughlin: 17 III, 1 (1923); Boswell and Bayley: J. Phys. Chem. 29, 11, 679 (1925).

ascribed to this same tension in the surface film. Indeed the experimental observation of the extreme difficulty of removing all the water from glass surfaces (high temperatures in a vacuum being necessary) is probably connected with the existence of this film of charged hydrogens and hydroxyls. Likewise it seems not improbable that a similarly constituted film plays a not inconsiderable part in surface tension phenomena at the interface of water and solids. Also the catalytic action of the surfaces of glass and other solids is well known. This also probably has its origin in this surface film and the glass probably acts as a catalyst by a mechanism similar to, if not identical with, that to be outlined in this paper in the case of aluminium oxide.

The great difficulty of removing all water from aluminium oxide and other compounds not having an available oxygen content, is not found in the case of partially reduced oxides, whose interior oxygen is not wholly inaccessible. In the latter case the dissociated water layer is partially removed on raising the temperature quite moderately (450° in the case of partially reduced nickel oxide) whereas heating for hours in a blast lamp still leaves a water film on aluminium oxide particles. Presumably as the temperature of aluminium oxide is raised, more and more of the external layers of charged hydrogens and hydroxyls lose their charges and pass off as water. Whether the inner layers are, at the outset, held with the same tenacity as the outer ones, the former being more firmly held as the later are removed, or whether there is, at the outset, a progressively diminishing tension in the layers from the inside to the outside, the fact is that as the water is gradually removed, it becomes increasingly difficult to remove the water remaining. There is still a water film on the surface, even after heating at atmospheric pressure at 500°C. for twenty hours, followed by two days heating with a Meker burner. In the case of reducible oxides the loss of surface film by heating at a much lower temperature results simultaneously in the loss of catalytic properties, as would be expected, since this film is the seat of the catalytic activity. The more complete loss of surface film in the case of a partially reduced oxide is directly connected with the fact that in this case the interior oxygen gradually comes into play, liberating all the hydrogen on the catalyst as free water, thus destroying at once both the surface film and the catalytic activity characteristic of partially reduced oxides.

It is true that this completely reduced oxide may still function as a catalyst by means of hydrogen contained in the pure metal. However, such a catalyst is much less effective, as has been pointed out in the paper dealing with catalysis by nickel. In such a catalyst the hydrogen appears to exist in two forms—(1) dissolved hydrogen which can be pumped out under vacuum and (2) positively charged hydrogens alternating with negatively charged hydrogens. This belief in the existence of hydrogen in this latter condition in metals has also recently been expressed by Bennewytz and Gunther.[1]

Another marked difference between the two types of catalyst arising from this same cause is found in the fact that a partially reduced oxide has a re-

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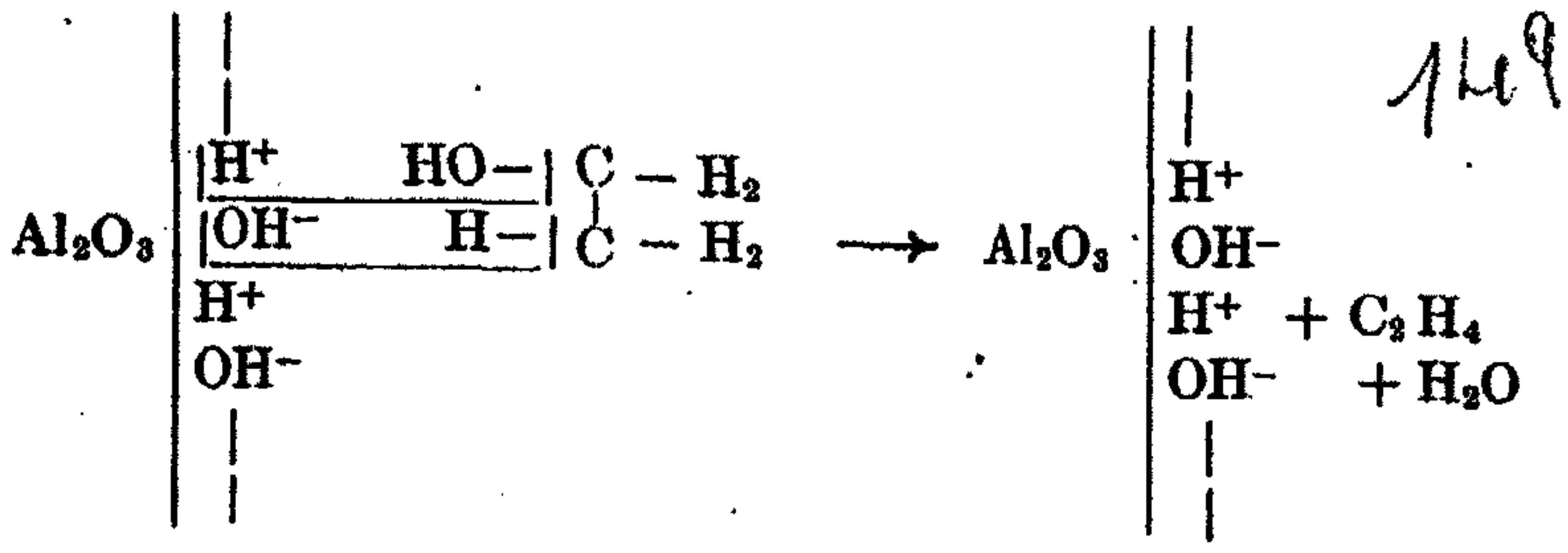
[1] Z. Physik. Chem. 111, 275 (1924)

duced metal layer overlying the unreduced oxide layer, and this reduced oxide layer probably carries the charged hydrogens and hydroxyls, whereas in the case of aluminium oxide the catalytic film of dissociated water lies wholly on the outer surface of each particle. This in all probability, gives rise to the marked difference in behaviour of the two catalysts.

Thus, aluminium oxide is commonly known as a dehydration catalyst, while the members of the other group of partially reduced oxides, are known as hydrogenation or dehydrogenation catalysts. In the latter case, as has been pointed out, the interior content of oxygen is vital to the restoration of the surface film, when it has been partially removed during the catalysis of hydrogenation of ethylene[1], or the union of hydrogen and oxygen[2]. Indeed the movement of oxygen from the interior to the surface film appears, from the experiments recorded by Boswell and Bayley[3], to take place so easily as to suggest that this movement may be vital to the whole mechanism of the catalysis of hydrogenation and oxidation. The absence of any available interior oxygen in aluminium oxide, thus pushes into the background the catalysis of hydrogenation and oxidation, and determines that, when aluminium oxide is heated in contact with say ethyl alcohol at gradually rising temperature, nothing happens until both the hydrogens and hydroxyls of the surface film act simultaneously, drawing hydroxyl and hydrogen respectively from the ethyl alcohol and thus forming ethylene and water.



$$\mathrm{Al_2O_3}\left|\begin{array}{l} | \\ | \\ \underline{H^+ \quad HO-}\,|\;C-H_2 \\ \underline{OH^- \quad H-}\,|\;C-H_2 \\ H^+ \\ OH^- \\ | \\ | \end{array}\right. \longrightarrow \mathrm{Al_2O_3}\left|\begin{array}{l} | \\ | \\ H^+ \\ OH^- \\ H^+ \quad + C_2H_4 \\ OH^- \quad + H_2O \\ | \\ | \end{array}\right.$$

The great tendency for the stable film to exist on the aluminium oxide, leads to the immediate re-formation of the original catalytic complex and so the cycle can continue. However, although the dehydration catalysis of aluminium oxide predominates over the catalysis of hydrogenation and dehydrogenation, yet these latter are, as is well known, not entirely suppressed. That is, the charged hydrogens and hydroxyls on the particles can under suitable conditions act independently, as well as simultaneously. This matter will be discussed later in this paper.

Thus, aluminium oxide is known as a catalyst chiefly for reactions involving the removal of both hydrogen and hydroxyl from a compound, the so-called dehydration reactions. The theory indicates that it should also catalyse the addition of both hydrogen and hydroxyl to unsaturated compounds. The experimental data shows that both the transformation of ethylene and

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[1] Boswell: Trans. Roy. Soc. Canada, 16 III, 1 (1922).

[2] Boswell and McLaughlin: Trans. Roy. Soc. Canada, 17 III, 1 (1923).

[3] To be published.

steam into ethyl alcohol, and of acetylene and steam into acetaldehyde, are catalysed by aluminium oxide. Likewise a catalyst of this constitution should catalyse the union of hydrogen and oxygen gases. This was found to be the case, the reaction setting in at 200°C. and proceeding rapidly at 250°C.

All the above reactions catalysed by aluminium oxide involve the elements of water, and in the two former either the addition or removal of water to or from the other reacting compound. Associated with this is the fact that aluminium oxide catalyst contains water, and the further fact that when this water content is diminished by heating at a high temperature the catalytic activity is likewise diminished. This all points to the conclusion that this catalyst functions by means of a surface film of water and that this film is the real seat of the catalysis. The marked stability of the film indicates that it is present in a special condition such as positively charged hydrogens and negatively charged hydroxyls, alternating with each other and completely enveloping each aluminium oxide particle. (See also paper on Platinum and Nickel.) This may be pictured thus:

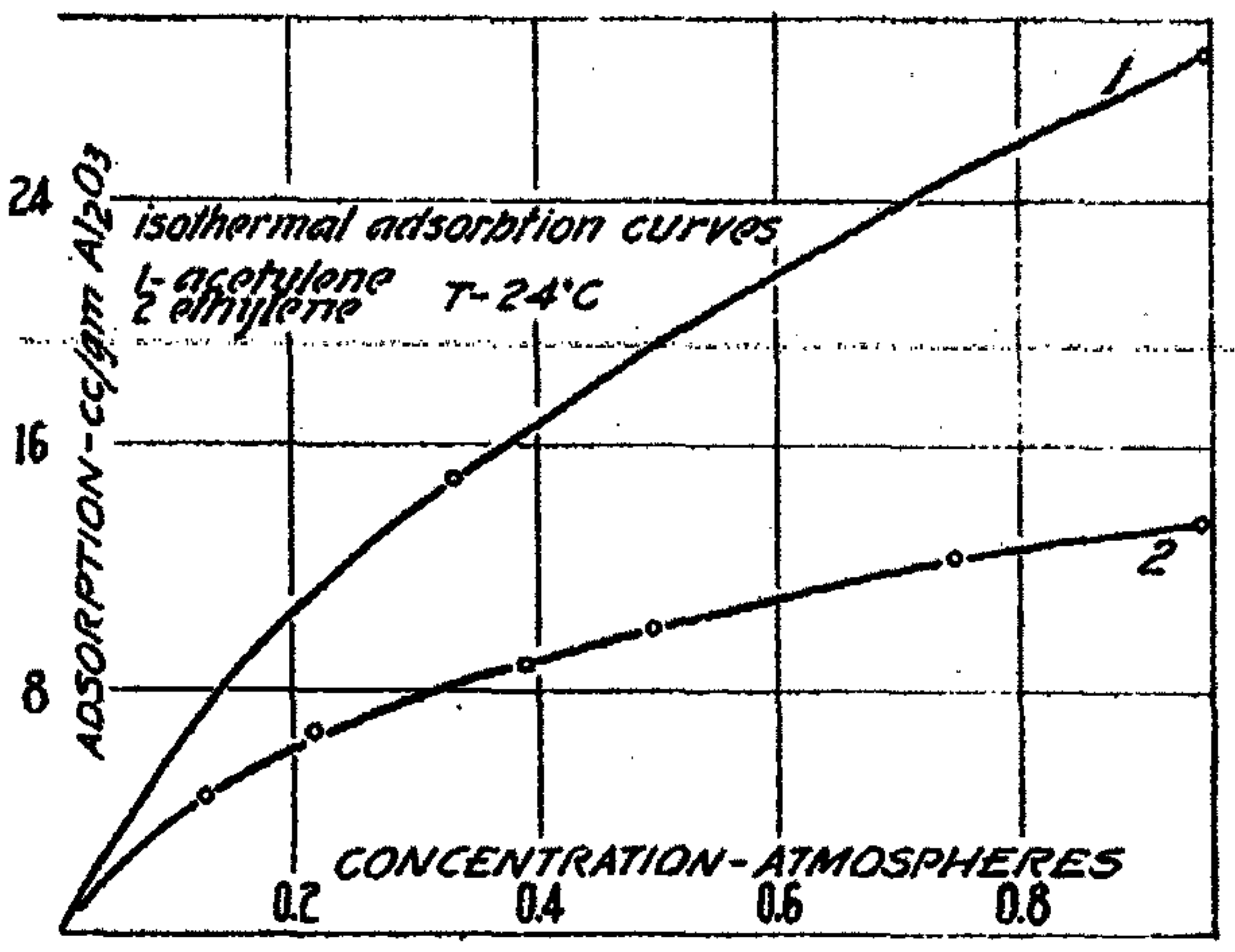


Fig. 1

$$
\begin{array}{c|lll}
 & | & | & | \\
 & | & | & | \\
 & H^+ . & OH^- . & H^+ \\
 & OH^- . & H^+ . & OH^- \\
Al_2O_3 & H^+ . & OH^- . & H^+ \\
 & OH^- . & H^+ . & OH^- \\
 & | & | & | \\
 & | & | & |
\end{array}
$$

As this is heated at gradually increasing temperatures the outer layers of dissociated water are removed as free water. The layers remaining are held with increasing tenacity, so that even at the temperature of the blast flame there is still some water left; at least one layer of charged hydrogens and hydroxyls remains. The catalyst has its maximum activity when used at a temperature of 350-400°C.

The chief catalytic use of aluminium oxide is for the transformation of alcohols into unsaturated hydrocarbons. A quantitative study was made of the gas changes involved in this reaction in the case of ethyl alcohol. The results recorded in the experimental part of this paper, show that besides the formation of ethylene and ether by the removal of one mol of water from one and two mols of alcohol, considerable quantities of carbon, ethane and hydrogen are also produced. The formation of these latter has also been observed by other investigators. However, the quantitative results recorded here offer a simple explanation of the mechanism of what has occurred on the surface of the catalyst. For instance it was found that 27 cc. hydrogen and 18cc. ethane were formed, while the total carbon remaining on the catalyst gave on combustion 61 cc. carbon dioxide and using up 71 cc. oxygen in the process. Several theories can be devised which will satisfy different portions of these measurements. But only two of these will fit the entire set of facts. One of these is: 36 cc. ethylene was simultaneously hydrogenated to 18 cc. ethane and dehydrogenated to 18cc. acetylene, $2\ C_2H_4 \longrightarrow C_2H_6 + C_2H_2$. The ethane was liberated, giving the 18 cc. ethane collected, while the 18 cc. acetylene was polymerized and adsorbed on the catalyst. An independent experiment with acetylene showed that this in reality occurs. Then a reaction independent of this hydrogenation-dehydrogenation reaction occurred, whereby 13.5 cc ethylene was transformed into 27 cc. hydrogen and free carbon. This hydrogen was liberated and collected while the carbon was adsorbed on the catalyst. The combustion of this adsorbed carbon to carbon dioxide would require 27 cc. oxygen and give 27 cc. CO_2. The combustion of the polymerized and adsorbed 18 cc. acetylene to carbon dioxide and water would require 45 cc. oxygen and give 36 cc. CO_2. Thus, based on this explanation of what has transpired a total of 72 cc. oxygen would disappear and 63 cc. carbon dioxide would be produced. Actually 71 cc. oxygen did disappear and 61 cc. carbon dioxide was obtained. The second explanation differs from this latter only with respect to the hydrogenation-dehydrogenation reaction. This may consist in the hydrogenation of ethylene to ethane and the dehydrogenation of alcohol to acetaldehyde, thus $C_2H_5OH + C_2H_4 \longrightarrow CH_3CHO + C_2H_6$ instead of the formation of one mol of ethane and one mol of acetylene from two mols of ethylene, as represented in the first interpretation. If this acetaldehyde is also completely adsorbed on the catalyst and subsequently burned to carbon dioxide, when oxygen is passed over the catalyst at a high temperature, the same amount of oxygen would be used up and the same amount of carbon dioxide would be formed as in the former interpretation. Probably both of these hydrogenation-dehydrogenation actions occur. In the experiment cited above, these secondary reactions had taken place to such a small extent (only 18 cc. ethane was formed) that the acetylene or acetaldehyde had been completely adsorbed in a polymerized condition by the catalyst. The formation of free acetaldehyde observed when large quantities of alcohol have been transformed into ethylene, is probably due to the saturation of the catalyst with this acetaldehyde or a polymerization or condensation product of it, so that any further amount formed passes out of the reaction vessel as free acetaldehyde. The experimental data also shows that aluminium oxide catalyses the union of acetylene and water to form acetaldehyde. Similarly the union of ethylene and water to form ethyl alcohol is catalysed. Hence the following scheme shows the possible reactions, all of which are in harmony with the above qualitative and quantitative statements:

(1)

$$\begin{tikzcd} C_2H_4 + C_2H_5OH \arrow[r] \arrow[d, shift left] & C_2H_6 + CH_3CHO \arrow[d, shift left] \\ C_2H_4 + C_2H_4 + H_2O \arrow[r] \arrow[u, shift left] & C_2H_6 + C_2H_2 + H_2O \arrow[u, shift left] \end{tikzcd}$$

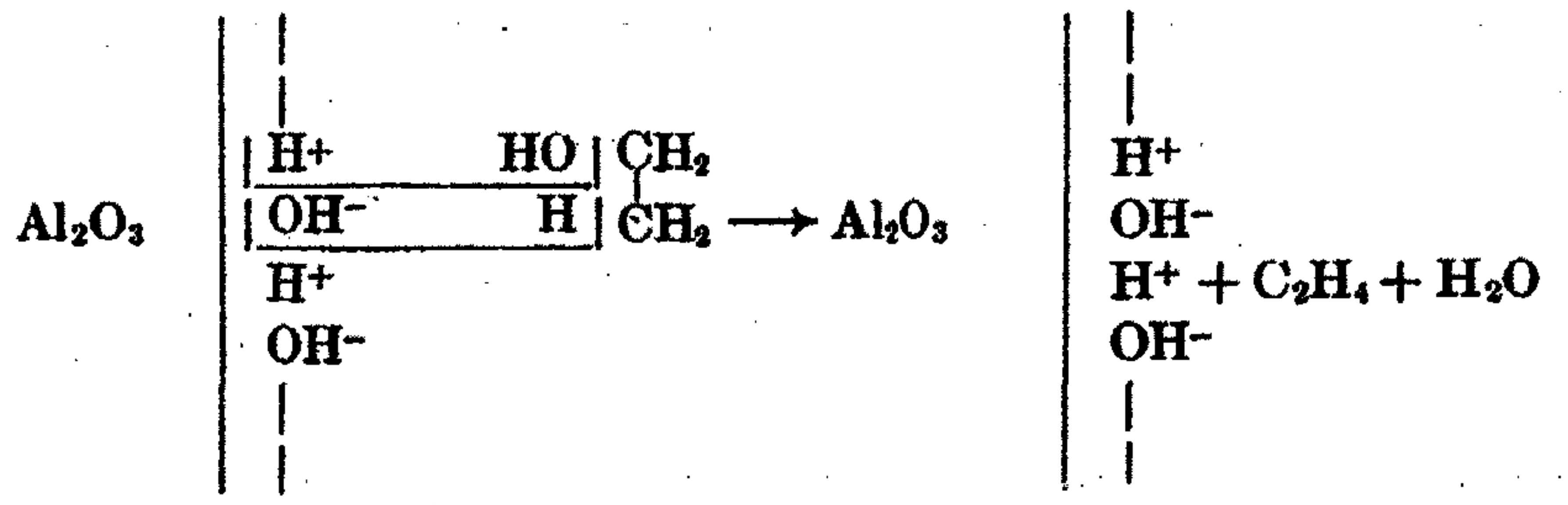
(2) $C_2H_4 \longrightarrow 2C + 2H_2$

The inference seems justified that when ethyl alcohol vapor is passed over aluminium oxide at 350°C., besides the formation of ethylene and ether commonly observed, there is also the formation of ethane, acetaldehyde, acetylene, carbon, and hydrogen, the three former being produced by simultaneous hydrogenation and dehydrogenation and the two latter by the dissociation of ethylene, these two sets of reactions being quite independent.

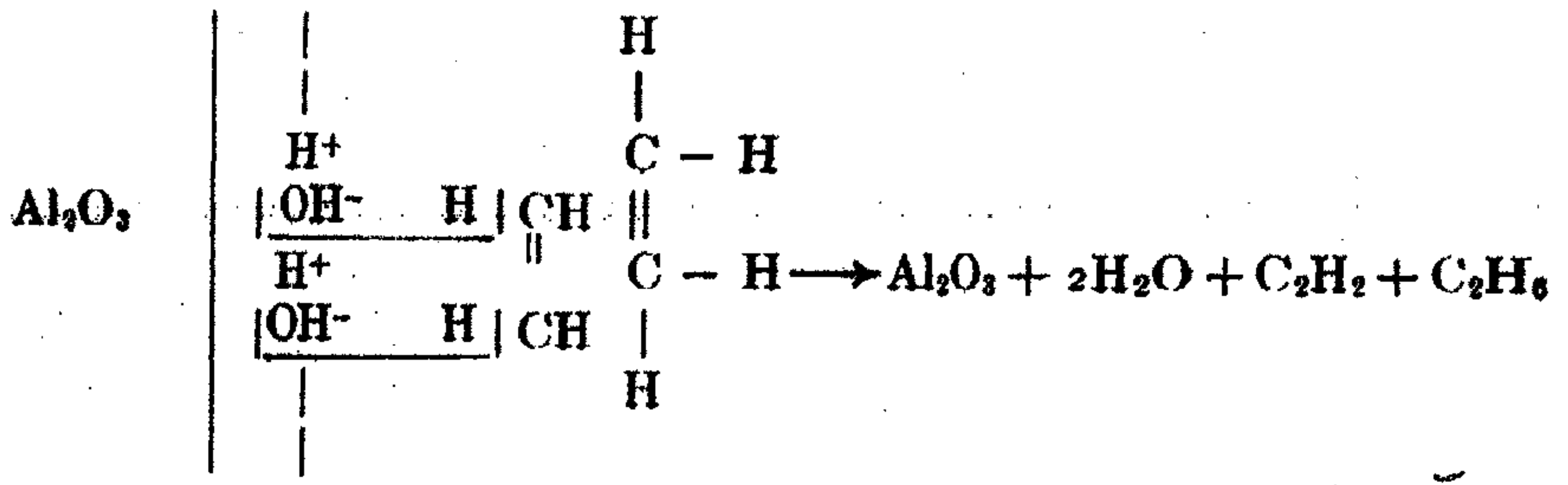
One conclusion of this experiment is that aluminium oxide will not catalyse the union of ethylene and free hydrogen. However, this failure to catalyse the union of ethylene and hydrogen furnishes no argument against the existence of charged hydrogens and hydroxyls in the surface film, for, as we have found, the ethylene is itself altered and adsorbed in this altered condition on the aluminium oxide before the temperature necessary to effect its hydrogenation has been attained. The above quantitative relationships could not hold had any of the ethane had its origin in this reaction. Separate experiments show that ethylene and hydrogen are not catalysed to form ethane. Also since, as pointed out above, aluminium oxide can catalyse the transfer of hydrogen from ethyl alcohol to ethylene it is probable that in the presence of free oxygen, alcohol would pass directly to acetaldehyde, the oxygen acting as hydrogen acceptor in place of ethylene. The experiments performed by Duffill in this laboratory showed that considerable acetaldehyde could be obtained by passing alcohol vapor mixed with air over aluminium oxide at 350°C. in those cases where the apparatus was not destroyed by explosion.

The mechanisms of the various reactions catalysed by aluminium oxide receive a satisfactory interpretation if the catalyst has the constitution advanced in this paper. Thus

(1)



(2)



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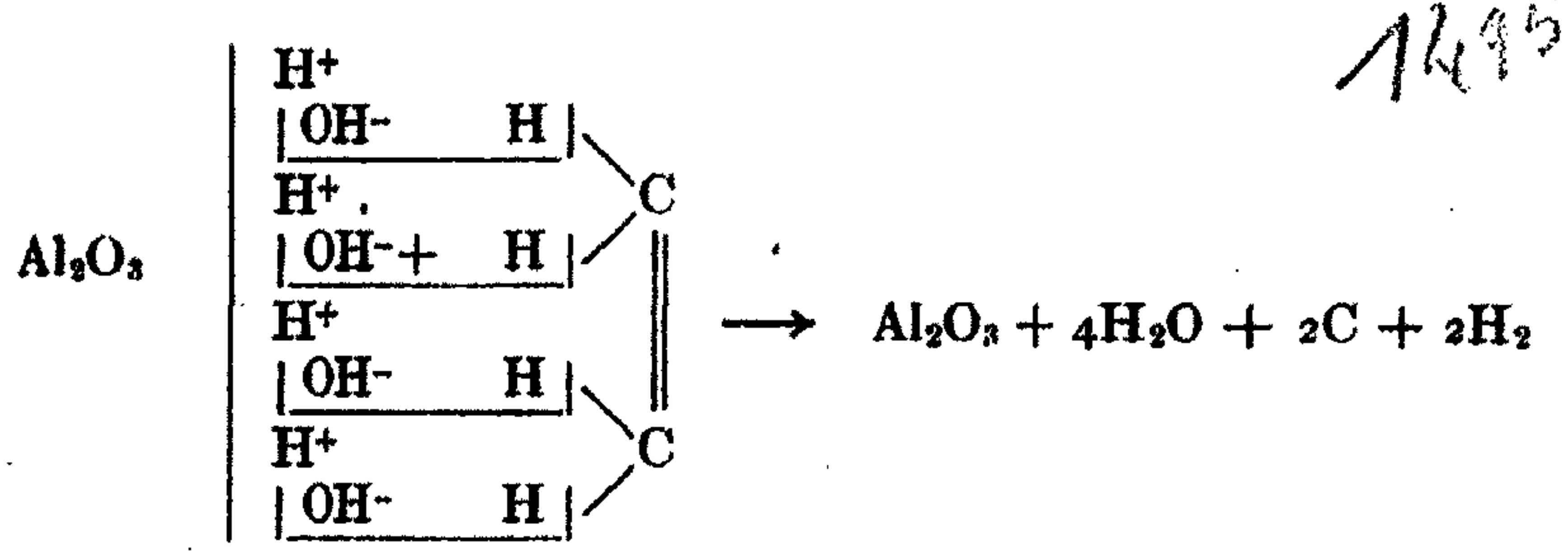
(3)



That is, the initiation of the reactions comes from the charged hydrogens and hydroxyls on the aluminium oxide particles. These react with the hydrogens or hydroxyls, or both, in the compounds brought in contact with the heated surfaces, thus setting up the reactions which always result in the formation of as much water as has been removed from the catalytic surface. The surface film is restored and the cycle continues. Or it may be that the charged hydrogens and hydroxyls are not actually removed from the surface, in all reactions, but remain in place, while exerting attractions upon the oppositely charged hydroxyls and hydrogens in the compounds brought in contact with the surfaces, thereby weakening the attractive forces holding the constituent atoms of these compounds together and thus enabling a readjustment to a more stable condition of equilibrium to be rapidly attained.

From this point of view the initial system (say ethyl alcohol), while having a smaller entropy than the final system into which it is transformed by the catalyst (an equilibrium mixture of ethyl alcohol, ethylene and water), yet cannot alone effect any measurable change at the temperature at which the catalyst can rapidly bring it about (350°C. in this case), owing to the stability of the molecules of the bodies comprising the original system (ethyl alcohol in this case). The catalyst interjects the loosening effect referred to above by means of attractions due to the dissociated water constituting the surface film, and thus enables the system to pass rapidly towards the final equilibrium condition of maximum entropy.

The catalyst from this point of view does not accelerate a reaction already in progress notwithstanding that the final system has a greater entropy than the original system, but actually initiates the change from the one to the other. This does not imply any violation of the second law of thermodynamics, for the transformation from the initial to the final system is not completely reversible. The system cannot return to pure alcohol.

Adsorption on Al_2O_3.

Perhaps the most convincing support for the theory presented in this paper comes from the facts of adsorption of gases and electrolytes on aluminium oxide. It seemed to us highly probable, that the phenomena associated with adsorption, not only of gases, but also of electrolytes from water solutions, are influenced more by these surface water films than by any other factor. The commonly accepted view in the case of water solutions of electrolytes pictures the adsorption of the salt BA as follows:

$$\mathrm{BA + H.OH \longrightarrow B.OH + HA.}$$

where the salt BA is hydrolysed in a reversible reaction to a slight extent, followed by adsorption of either the base B.OH or the acid HA on the adsorbing material. If the specific adsorption is of the base B.OH, then the presence of hydrogen-ion in the solution, moving the above equilibrium to the left, diminishes the amount of adsorption, while the addition of hydroxyl ion produces the reverse effect, and increases the adsorption. Likewise, if the specific adsorption is for the acid HA, then the effect of the addition of hydrogen ion or hydroxyl ion to the solution of BA, is just the reverse. But this says nothing about the mechanism of the actual adsorption of the acid or base on the adsorbing material. The full interpretation of the whole mechanism must, of course, involve a knowledge of (1) the relationship of the electrolyte to the solvent water, and (2) the nature of the adsorption surface. The senior author suggests the hypothesis presented here of the nature of the surface film of aluminium oxide particles, as the second part of this mechanism. Without modifying at all the usually accepted view that the salt BA exists in solution as B^+ ions and A^- ions and undissociated mols BA, could not the mechanism of adsorption of the cation B^+ and the accumulation of H^+ ion in solution be with equal force represented by the scheme:

$$\mathrm{Al_2O_3}\left|\begin{array}{ll} | & \\ | & \\ \mathrm{H^+} & \multirow{2}{*}{$+\,\mathrm{BA}$} \\ \mathrm{OH^-} & \\ \mathrm{H^+} & \multirow{2}{*}{$+\,\mathrm{BA}$} \\ \mathrm{OH^-} & \\ | & \\ | & \end{array}\right. \longrightarrow \quad \mathrm{Al_2O_3}\left|\begin{array}{l} | \\ | \\ \mathrm{B^+} \\ \mathrm{OH^-} \\ \mathrm{B^+} \\ \mathrm{OH^-} \\ | \\ | \end{array}\right. + 2\mathrm{H^+} + 2\mathrm{A^-}$$

However, the particular states of B and A and BA and their relationships to the water intervene, and must play a vital part in the adsorption. The senior author hopes to present experimental evidence in connection with this problem of electrolytes in solution in the near future, which may help in the solution of the first part of the mechanism, mentioned above, of adsorption from solution.

Turning to the adsorption of ethylene on aluminium oxide, it seemed that if this also is dependent on the surface water film, its amount should increase as the extraneous free water covering the active film is removed, but should then gradually decrease as this active film diminishes, until, when the water is entirely gone, no adsorption whatever would occur. The following measurements show that this is precisely what happens. The curve (Fig. 2) makes this quite clear. The maximum adsorption occurs with the water content of about 4%. As the water content either increases or diminishes from this amount, the adsorption diminishes. Below this water content of 4% the amount of the adsorption falls off extremely rapidly. The curve falls at an angle of about 75° with the x axis. After the final heating in the Meker burner for two days the adsorption has fallen almost to zero. The conclusion is unavoidable that the union of ethylene with aluminium oxide is directly connected with this water film. Now it is a well known fact that the catalytic properties of aluminium oxide very markedly diminish on prolonged heating of the oxide at high temperatures. This is, no doubt, due to the partial loss of this active water film. That heating does not completely inhibit this activity is due to the fact, which will be shown presently, that even after heating at 500°C. for twenty hours, followed by heating in a Meker burner for two days, there is still a very small amount of water on the particles. These facts regarding adsorption of ethylene and catalytic activity of aluminium oxide show, not that the catalytic decomposition of ethyl alcohol to ethylene is due to the marked capacity of aluminium oxide to adsorb ethylene, but that both the catalytic properties and the capacity for adsorption are due to the water film on the particles. The remarkable stability of the film indicates that it exists in a very special condition, which we believe is due to the existence of oppositely charged hydrogens and hydroxyls in a state of great tension surrounding the particles of aluminium oxide. When it is found, as already pointed out in this paper, that aluminium oxide, especially when heated to 350°C., so as to leave the water content around 4%, is an active catalyst for reactions involving the addition, simultaneously, of hydrogen and hydroxyl to compounds, and the splitting off of hydrogen and hydroxl from

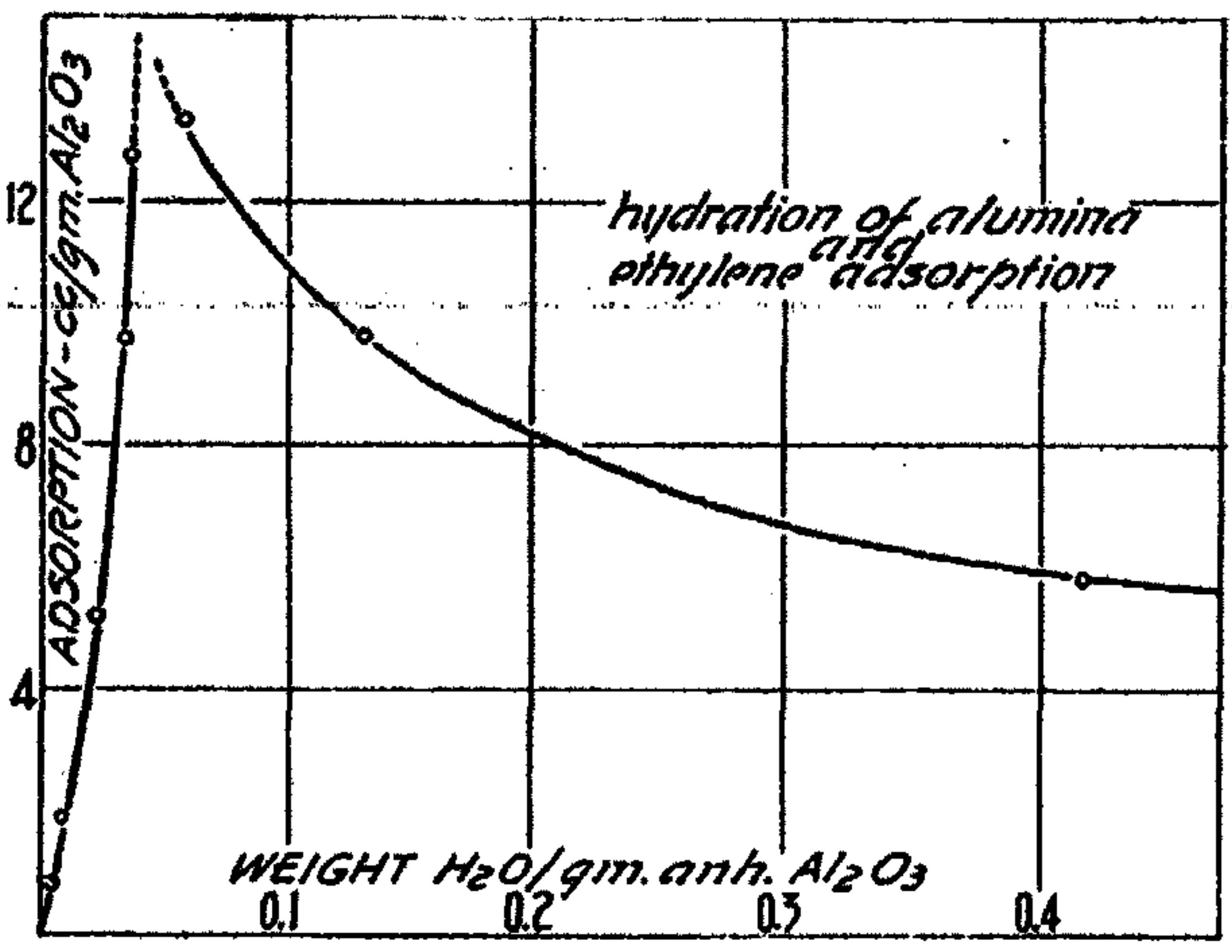


FIG. 2

compounds simultaneously, belief in the validity of the hypothesis is, we believe, very considerably increased.

In view of the great stability of this surface film, it is not surprising that it should exert a great protection for an underlying interior content of oxygen. This oxygen is not available in the case of aluminium oxide. But in the case of partially reduced nickel oxide, iron oxide, platinum black, etc., such oxygen does exist, and the protective power of the surface film has been shown in this laboratory. The senior author hopes to publish shortly experimental data showing similar behaviour by dissociated films of analogous constitution formed by the partial reduction of chlorides, sulphides and nitrides.

Experimental

Materials.

The aluminium oxide used in all the experiments was prepared in the following manner: 400 grams metallic aluminium was dissolved in a solution of 2000 grams sodium hydroxide in 3 litres water. The solution was diluted to 6 litres, heated to boiling and allowed to stand. A precipitate settled out and the clear liquid above was siphoned off. A quantity of nitric acid was added, insufficient, however, to neutralize the sodium hydroxide, the whole heated to boiling, thus precipitating any iron as ferric hydroxide. This was filtered off. Nitric acid was now added in excess so as to redissolve the aluminium hydroxide precipitated at first. Ammonium hydroxide was added slowly with stirring to the hot solution to precipitate the aluminium as hydroxide. This was washed in tall cylinders by decantation for many days until the filtrate gave no reaction for ammonia, filtered on a perforated funnel and dried in an air oven at 110°C. The resulting material was ground up in a mortar to a coarse powder.

The ethylene used was made by the phosphoric acid method of Newth, care being taken to remove ether by condensation and to avoid the collection of air along with the ethylene. Traces of oxygen in the gas used in the experiments, were removed by shaking with alkaline pyrogallol.

The acetylene used was made from commercial calcium carbide.

The nitrogen and oxygen used were from cylinders of the compressed gases. Traces of oxygen were removed from the nitrogen by passage over heated copper.

The hydrogen was electrolytic hydrogen.

The action of the catalyst with hydrogen-oxygen mixtures.

Dry mixtures of hydrogen, oxygen and nitrogen were passed over the aluminium oxide which had previously been heated for twelve hours to 360°C. in an atmosphere of nitrogen. The apparatus was similar to that used in studying the reduction of nickel oxide. The train consisted of two calibrated water-jacketed burettes of about 400 cc. capacity between which was placed a pyrex glass tube three-quarter inches in diameter and twenty inches long containing about 25 grams of the aluminium oxide which could be heated in an electric furnace to various desired temperatures which latter were measured by a standard thermometer inserted alongside the reaction tube in the furnace. Between the reaction tube and each burette were placed two U-tubes containing, in the hydrogen-oxygen experiments, concentrated sulphuric acid on pumice, and in the ethylene and acetylene experiments, fused calcium chloride.

The temperature was gradually raised from room temperature to 365° and the temperature at which the expansion, due to the rise in temperature, was noticeably retarded by the contraction, due to the combination of hydrogen and oxygen, was noted. After the completion of the reduction the total contraction was measured at room temperature and the gas was analysed. It was found that with a gas mixture of the composition 21.0% hydrogen, 30.7% oxygen and 48.3% nitrogen, the reaction set in at 210°C., was proceeding rapidly at 250°C. and soon ran to completion at 365°C. Gas analysis showed that no hydrogen remained; the contraction in volume was approximately that calculated for a combination of all the hydrogen originally present. Also with a gas mixture of the composition 43.0% hydrogen, 15.8% oxygen, 41.2% nitrogen, the reaction set in at about 200°C. When no further contraction was observed at 365°C. the gases showed on analysis that no oxygen remained. The contraction on cooling to the original temperature was approximately that calculated for a combination of all the oxygen originally present.

Thus the combination of hydrogen and oxygen is catalysed by aluminium oxide, the reaction setting in at about 200°C. and proceeding with rapidly increasing velocity as the temperature is raised.

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The action of the catalyst on ethyl alcohol.

It is well known that in the manufacture of ethylene from ethyl alcohol using aluminium oxide heated to 350° as catalyst, the latter becomes dark colored, indicating a desposition of carbon or a tarry material, or both. Also the formation of acetaldehyde and ether in this reaction is well known.

It would seem probable that the carbon, if present, could form by the simultaneous hydrogenation and dehydrogenation of ethylene thus: (1) $3\,C_2H_4 \longrightarrow 2\,C_2H_6 + 2\,C$ or the dissociation of ethylene thus: (2) $C_2H_4 \longrightarrow 2\,C + 2\,H_2$ or (3) the simultaneous hydrogenation and dehydrogenation of ethylene to ethane and acetylene and the dissociation of the acetylene so produced, thus: $C_2H_2 \longrightarrow 2\,C + H_2$. The tarry constituent of the deposit might form by the polymerization of acetylene or acetaldehyde. It thus seemed desirable to carry out an experiment as nearly quantitatively as possible, with a view to determining (1) the volume of hydrogen formed, (2) the volume of ethane formed, (3) the volume of oxygen consumed in burning the deposit completely to carbon dioxide and water, and (4) the volume of carbon dioxide produced in this latter operation. It seemed also very desirable in this experiment to observe a further condition, viz: to run the experiment for only a short time, so that should the tarry part of the deposit be due to the polymerization of acetylene or acetaldehyde, none of the acetylene or acetaldehyde should escape from the tube, but should be all caught by the long layer of aluminium oxide in the polymerized form.

Apparatus used.

About 75 cc. ethyl alcohol was slowly distilled in an atmosphere of nitrogen over the catalyst at 360°C. The issuing gases were passed first through a long water-jacketed condenser into a receiver which in turn was connected with two efficient washers containing a 40% bromine in strong solution of potassium bromide in water, followed by two washers containing potassium hydroxide solution ((1:1), then through a spiral glass condensing tube immersed in alcohol-carbon dioxide snow contained in a Dewar flask, and from this into a gas holder from which portions were taken for analysis.

Analysis of the gas collected showed the presence of hydrogen 27 cc. and ethane 18 cc. at 25°C. and 758 mm. pressure.

A measured volume of oxygen was then passed between the burettes across the heated aluminium oxide. The weight of carbon dioxide formed and the volume of oxygen used were measured with due regard to temperature and pressure. It was found that 71 cc. oxygen calculated to 25°C. and 758 mm. pressure was used up and 61 cc. carbon dioxide calculated to the same temperature and pressure was formed.

The Hydrogenation of Ethylene.

The experiment just described indicated that the combination of ethylene and hydrogen is not catalysed by aluminium oxide. It seemed desirable to verify this by an experiment set up for the purpose. Accordingly carefully purified hydrogen, mixed with ethylene (99.4%) in known proportions, was passed between burettes over aluminium oxide starting at 250°C. and rising in steps to 340°C. The combination, if it occurred, of course would have been indicated by a decrease in volume. Owing to the adsorption of ethylene on aluminium oxide, care was necessary in order not to confuse these two possible causes of any diminution in volume. However, although this adsorption is, as will be shown presently, very considerable at 25°C. and 1 atmosphere pressure (about 11 cc. per gram) it is comparatively small at 253°C. (about 1 cc. per gram). At a partial pressure of one half an atmosphere, which was approximately that used in the experiments, the amount of adsorption is, of course, much smaller (about 5/7 for 25°, of the adsorption at one atmosphere). Hence, using 20 grams aluminium oxide at 253°C. an adsorption of about 12 cc. of ethylene, at 319°C. of about 6 cc., and at 385°C. of about 4 cc., was to be expected. On passing a mixture of 155 cc. ethylene and 162 cc. hydrogen over about 20 grams Al_2O_3 at 253°C. there was in five minutes a diminution in volume of 10 cc., which did not alter on passing the gas mixture back and forth for a further 65 minutes. This diminution was due undoubtedly to adsorption, and if hydrogenation was taking place at all, the rate was negligibly small. Also the aluminium oxide showed none of the discoloration which always occurs, and is easily observable, when ethylene undergoes dissociation in the presence of aluminium oxide. The apparatus was swept out with nitrogen and a mixture of 180 cc. ethylene and 163 cc. hydrogen passed at 319°C. There was a loss in volume of 2 cc. in the first 5 minutes, and no further change in 65 minutes. There was no discoloration of the aluminium oxide. The temperature was now slowly raised to about 380°C., occupying almost 100 minutes. At 380°C. the discoloration of the aluminium oxide and the slow increase in volume showed that ethylene was dissociated. On raising the temperature to 500°C. the volume and discoloration greatly increased. Hence, the first indication of any reaction was discoloration accompanied by increase in volume. Ethylene alone was passed over another sample of aluminium oxide when the same behaviour was found in all particulars, as in the case of the ethylene-hydrogen mixtures. It would seem, then, that if hydrogenation of ethylene to ethane does occur it is a very slow reaction, and is insignificant compared with the reaction involving the dissociation of ethylene. Hence, the conclusion arrived at from the quantitative study of the action of ethyl alcohol and aluminium oxide, that the formation of ethane observed in the alcohol-aluminium oxide reaction does not arise from union of free hydrogen and ethylene, appears to be confirmed.

The action of acetylene and aluminium oxide. 1501

The quantitative experiment of the action of ethyl alcohol and aluminium oxide already described, indicates that acetylene is formed by the reaction $2\ C_2H_4 \longrightarrow C_2H_2 + C_2H_6$. It seemed desirable to determine the action of acetylene alone on aluminium oxide, in order to determine to what extent polymerization takes place and at what temperature it sets in. For the interpretation given of the measurements implies a very rapid polymerization of acetylene at 350°C. and adsorption on the aluminium oxide. About 15 grams aluminium oxide was saturated with acetylene at room temperature. 438 cc. was adsorbed. The tube containing the aluminium oxide was connected at each end with a burette and slowly heated in an electric furnace, the volume being noted. At 100°C. the volume in the burette had increased by 278 cc., at 110°C. by 291 cc., at 120°C. by 296 cc. As the temperature rose above 120°C. the volume slowly diminished. At 135°C. the diminution was much more rapid, the volume in a few hours falling to 78 cc. 300 cc. additional acetylene was added, making the volume 378 cc. In a few hours this had fallen to 246 cc. The aluminium oxide was now deep brown in colour and on extraction with benzene and evaporating the solvent a few drops of an aromatic oil were obtained. Thus, acetylene, even below 150°C. is rapidly polymerized and absorbed by aluminium oxide. The conclusion before drawn, that at 350°C. the relatively small amount of acetylene slowly formed in the experiment (18 cc. in all, along with 18 cc. of ethane) was polymerized and completely adsorbed on the aluminium oxide, seems to be justified.

The Reaction of Ethylene and Steam.

Ethyl alcohol has been made by Wibaut and Dieckmann[1] by passing ethylene and steam over aluminium oxide at 300-400°C. This was repeated at a temperature of 300-350° and alcohol was detected in the reaction product by transformation into, and isolation of, iodoform. The yield is poor under these conditions. However, there is no doubt that aluminium oxide is a catalyst for the reaction $C_2H_4 + H_2O \longrightarrow C_2H_5OH$.

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[1] Chem. Abs. **17**, 3858 (1923).

The Reaction of Acetylene and Water.

Acetylene and steam were passed over aluminium oxide at 160°-170°C. The reaction products were passed through a water condenser and then through a flask immersed in a freezing mixture. The distillate gave a precipitate of silver with ammoniacal silver nitrate solution and also a precipitate with Fehling's solution. The experiment was repeated at 240°-250°C. 3.5 liters acetylene being passed along with steam. The reaction product was distilled. The fraction boiling below 100°C. was collected separately and was found to give a silver mirror and a copious precipitate of silver with ammoniacal silver nitrate, also a copious red precipitate with Fehling's solution. A considerable amount of higher boiling liquid was obtained up to 120°C., leaving a residue which, although giving no reaction with ammoniacal silver nitrate at first, did so on prolonged boiling indicating the probable existence of paraldehyde. Thus aluminium oxide catalyses the union of acetylene and steam to form acetaldehyde.

The Reaction of Aluminium Oxide and Acetaldehyde.

The above experiments showed that acetylene is polymerized and adsorbed in this polymerized condition by aluminium oxide at temperatures above 135°C. It seemed desirable to determine whether the dehydration of acetaldehyde to acetylene would occur at all at temperatures around 135°. Accordingly the vapor of acetaldehyde was passed over aluminium oxide at about 135°C. No acetylene or other gas was observed. However, the catalyst turned a deep brown and an oily liquid was obtained by distilling the reaction product. The experiment was repeated at 300° C. with the same result. The aluminium oxide after the reaction gave an oil on distillation. In view of the behaviour of acetylene alone with aluminium oxide, it is probable that if acetylene had been formed in passing acetaldehyde, it had been polymerized and adsorbed. Also the condensation of acetaldehyde to form crotonic aldehyde and other condensation products might easily happen.

Thus, aluminium oxide can catalyse the following reactions involving simultaneously, hydrogen and hydroxyl:

(1) The dehydration of ethyl alcohol to ethylene.

(2) The combination of ethylene and water to form ethyl alcohol.

(3) The combination of acetylene and water to form acetaldehyde. Also the following reactions accompanying the formation of ethylene from ethyl alcohol are catalysed by aluminium oxide:

(1) The simultaneous dehydrogenation of ethylene to acetylene (which is adsorbed in a polymerized condition on the aluminium oxide) and the hydrogenation of ethylene to ethane.

(2) The dissociation of ethylene to carbon and hydrogen. It has been shown that the combination of free hydrogen and ethylene to form ethane is not catalysed by aluminium oxide, as the dissociation is a very much faster reaction.

The Adsorption of Ethylene and Acetylene on Aluminium Oxide.

On passing these gases separately over aluminium oxide in the course of the experiments just described, the very large power of adsorption of aluminium oxide for these gases, particularly at room temperature, was noticed. It was decided to measure the amount of this adsorption, and, to some extent, its variation with temperature and pressure.

The aluminium oxide used in these determinations was made according to the method described at the beginning of the experimental part of this paper. It was dried in an ordinary air bath at 110°C. for 8 hours and in a glass tube at 360° in a current of nitrogen for 6 hours. 18 grams of this material was used. This was placed in a pyrex tube, which was connected at each end with a U-tube containing calcium chloride, and these U-tubes were each connected to a 400 cc. water jacketed and calibrated gas burette. Various partial pressures of ethylene and nitrogen were used, the composition at equilibrium being determined in each case by gas analysis, using bromine in the gas absorption pipette. Another series of measurements, using acetylene, was also made, using the same procedure. The following table and graph show the results of these measurements.

Ethylene Adsorption at 24°C

Partial Pressure (At.)	Ethylene, Adsorbed cc.	cc. per gram of Aluminium oxide used
0.940	242	13.4
0.750	224	12.3
0.502	180	10.0
0.390	160	8.9
0.214	120	6.7
0.124	83	4.6

Acetylene Adsorption at 25°C

Partial Pressure (At.)	Acetylene Adsorbed cc.	cc. per gram of Aluminium oxide used
0.946	517	28.7
0.331	267	14.8

It is seen that in the case of ethylene the adsorption curve follows the general form of those for carbon monoxide on charcoal and platinum. Also the absolute values are almost as great. Although not sufficient points on the acetylene curve have been determined to definitely fix the whole curve, yet it is seen that the adsorption of acetylene on aluminium oxide at pressures above about 9/10 of an atmosphere is more than double that of ethylene, and amounts at a pressure of .946 atmospheres to 28.7 cc. of acetylene per gram of the aluminium oxide used. This is comparable with the adsorption of carbon monoxide on cocoanut charcoal, which has always been considered very large.

Variation of ethylene adsorption with temperature.

The same apparatus was used as in the latter measurements. The tube was heated in an electric tube furnace and every trace of oxygen was removed from the ethylene by shaking with alkaline pyrogallol. The tube containing the aluminium oxide of the first ethylene adsorptions already recorded was heated in a current of nitrogen to a temperature of 360° for 5 hours. The following are the results obtained:

Temp. °C.	Adsorption of ethylene cc. adsorbed (.580 atmospheres)	cc. adsorbed per g. of oxide used
24	196	10.9
242	21	1.2
378	13	0.7

The adsorption value for 378°C. must necessarily be only approximate, because, as already pointed out, at 350°C. and higher, ethylene undergoes various reactions which could interfere with the accuracy of an adsorption determination. However, as the former reactions occur relatively slowly, while the reading at 378° occupied relatively a short time, it is probably very close to the correct value.

The variation of the adsorption of ethylene with variation in the amount of water in the aluminium oxide.

From the standpoint of the theory presented in this paper the determination of the nature of this variation is of the greatest importance.

A quantity of aluminium oxide, prepared as already described, was placed in a pyrex tube and steam passed over for one hour at 110°C. The sample now weighed 25.7350 g. Nitrogen was passed to expel air and the tube containing the oxide was placed in a train consisting of a water-jacketed and calibrated burette, a U-tube containing calcium chloride, the tube containing the oxide, another U-tube containing calcium chloride and a second burette similar to the first one. The apparatus between the burettes being filled with nitrogen, a measured volume of ethylene was passed back and forth until equilibrium was attained, and the volume of ethylene adsorbed was measured. The gas in the burette was discarded and another 350 cc. ethylene was introduced into the burette and the adsorption again measured. This was continued until no further adsorption was obtained on adding fresh ethylene. The sum of the various adsorptions gave the total volume of ethylene. adsorbed by the aluminium oxide at 24°C., containing an amount of water which later was calculated. This same sample of oxide containing adsorbed ethylene was now heated at a given temperature in a current of nitrogen, the water given off being weighed. The adsorption of ethylene at 24°C. was again measured. A further heating in nitrogen at a still higher temperature was carried out, the water determined and another ethylene adsorption was measured. This procedure was continued until the adsorption of ethylene on aluminium oxide which had been heated at 500° for 70 hours had been measured. The aluminium oxide in this condition was transferred quantitatively to a weighed crucible and the heating continued with a Meker burner for various lengths of time, the water expelled by each heating being weighed and the ethylene adsorption at 24°C. after each heating being determined in the apparatus already described. Weight of aluminium oxide at the completion of the measurements was 18.3100 g. The measurements are recorded in the following table and plotted in curve 3

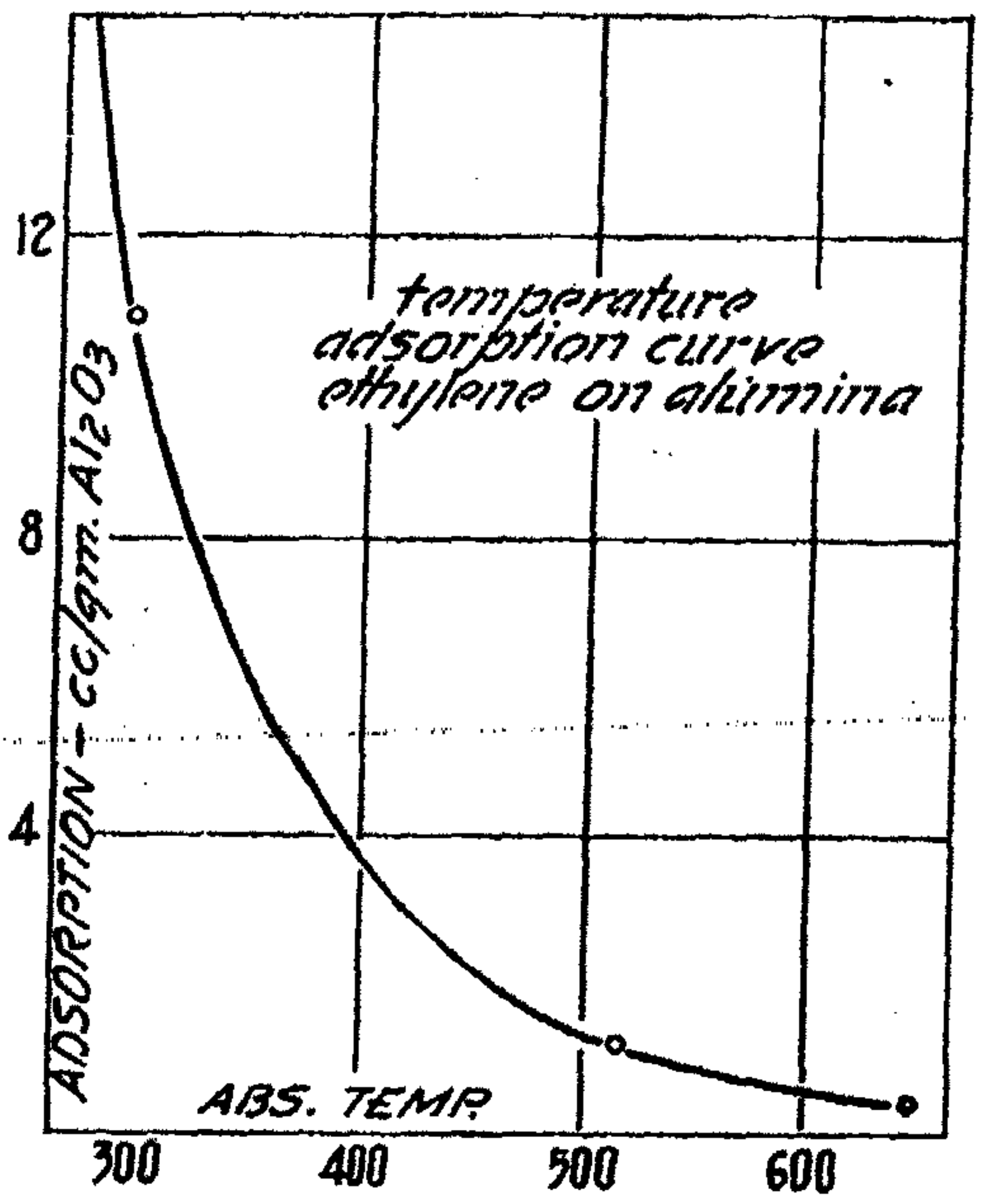

Fig. 3

Ethylene adsorbed cc.	temp. of heating °C.	Length of time of heating hours	Weight of aluminium. oxide sample grams	Water off grams	cc. ethylene per gram aluminium oxide as present at end of series	cc. of ethylene per gram aluminium oxide anhydrous
106			25.7350		5.79	5.81
	300	—		5.0800		
179			20.6550		9.78	9.81
	400	20		1.3750		
242			19.2800		13.22	13.26
	500	20		0.3830		
232			18.8970		12.67	12.72
	500	50		0.0450		
176			18.8520		9.61	9.64
	Meker	4		0.2510		
96			18.6010		5.24	5.26
	Meker	12		0.2030		
35			18.3980		1.91	1.92
	Meker	96		0.0880		
15			18.3100		0.82	0.82
				0.0660		

By extrapolation from the last two adsorptions the water still on the oxide was 0.0660 g. This was calculated from the following equation where x is the water:

$$\frac{\dfrac{x}{18.31 - x}}{\dfrac{x + .0880}{18.31 - x}} = \frac{15}{35}$$

$$x = 0.0660$$

Hence the weight of anhydrous aluminium oxide used in these experiments was 18.2440 g. Thus, the water still present on the oxide after the various heatings was 0.36% of the total weight.

Summary

A mechanism is suggested for the action of aluminium oxide as a catalyst.

A mechanism is suggested for the adsorption of electrolytes from water solutions on aluminium oxide.

The adsorption of ethylene and acetylene on aluminium oxide for several partial pressures has been measured.

The variation of adsorption of ethylene on aluminium oxide with variation of temperature has been determined.

The variation of adsorption of ethylene on aluminium oxide with variation of water content has been determined.

The action of ethyl alcohol and aluminium oxide at 350°C. has been quantitatively studied. Besides the formation of ethylene, commonly observed, the following reactions occur:

$$C_2H_4 \longrightarrow C_2H_6 + C_2H_2 \qquad (1)$$
$$C_2H_4 \longrightarrow 2C + 2H_2 \qquad (2)$$

The acetylene in (1) is polymerized and adsorbed on the aluminium oxide along with the carbon from (2). Ethane is formed solely by reaction (1), none being formed by the addition of free hydrogen to ethylene.

It has been shown that aluminium oxide will catalyse the union of ethylene and water to form ethyl alcohol, also the union of acetylene and water to form acetaldehyde, also the union of hydrogen and oxygen.

The actions of aluminium oxide with ethylene and hydrogen mixtures, with ethylene alone, with acetaldehyde and with acetylene have been studied

THE DETERMINATION OF TRANSITION POINTS IN NON-AQUEOUS SOLUTIONS BY THE ELECTROMOTIVE FORCE METHOD*

BY RALPH B. MASON AND J. H. MATHEWS**

Electrical methods for the determination of transition points are of special value where the material is expensive and hard to obtain, since the transition temperature may be checked and rechecked without the loss of material.

The temperature of transformation of $ZnSO_4 \cdot 7H_2O$ into $ZnSO_4 \cdot 6H_2O$ in the Clark cell has been determined by the E. M. F. method[1]. When a cell of this type is heated, the E. M. F. curve breaks sharply at the temperature where one hydrate changes into the other hydrate. Cells in which both the stable and metastable phases are present have also been studied[2]. In cells of this type the E. M. F. is 0 at the transition temperature.

The conductance method is more limited in its application than the E. M. F. method. Cohen[3] has used this method for several salts in aqueous solution, but found that in most cases the change in conductance was very slight when one phase changed into the other.

The purpose of this paper is to show that the electrical methods can also be used in non-aqueous solutions for the determination of transition temperatures.

Apparatus. The thermostat consisted of two concentric cans, the inner can being insulated from the outer by means of sawdust. The inner can contained nine gallons of light cylinder oil which was kept thoroughly mixed by a rapidly rotating stirrer. The direction of flow for the oil was down the center and up along the sides. For the low temperatures kerosene was used in place of the more viscous cylinder oil.

By a careful adjustment of the heating and cooling elements it was possible to keep the temperature constant to less than .01°. The thermostat thermometer was graduated to tenths and could be read to hundredths. It was always compared with a precision thermometer standardized by the United States Bureau of Standards.

The potentiometer was a Leeds and Northrup type K. The highly sensitive, ballistic type galvanometer was made by the same company and had a sensitivity of .0003 micro-coulombs per mm. or 6.6×10^{-11} amperes per mm. and a resistance of 650 ohms. However, it was used with a scale over two

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*A portion of a thesis submitted by Ralph B. Mason in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

**Contribution from the Laboratory of Physical Chemistry of the University of Wisconsin.

[1] Cohen: Z. physik. Chem. 25, 302 (1898); Callendar and Barnes: Proc. Roy. Soc. 62, 47 (1897); J. Phys. Chem. 4, 1 (1900); Barnes and Cooke: J. Phys. Chem. 6, 172 (1902).

[2] Cohen: Z. physik. Chem. 14, 53 (1894); 30, 601, 623 (1899).

[3] Cohen: Z. physik. Chem. 31, 164 (1899).

meters distant upon which a beam of light was reflected by the mirror of the galvanometer.

The standard cell was a saturated Weston cell and it was always compared with an Eppley unsaturated cell which had been checked by the Standards' Laboratory of the Engineering School, University of Wisconsin.

Two types of cells were used in this research. The first, known as the "Board of Trade" type, was simply a test tube with a platinum wire sealed through the bottom, connecting the inside with a bent glass tube. Electrical connection was made by adding a few cc. of mercury to the glass tube and placing therein a copper wire. The second was the "H" type of cell. It was made entirely of glass and the electrical connections were made to each arm by means of a platinum wire sealed through the glass. A short side tube at the top of each arm could be either opened or closed by turning the glass stopper. Several "H" tubes were constructed which were sealed off after being filled. These were abandoned in favor of the glass stopper type as they required considerable time to make, were harder to fill, and could not be used a second time.

Materials used. The purifications of the salts have been already described in the work on solubility and decomposition potentials (see previous paper).

The pyridine was purified either by the method of Heap, Jones and Speakman[1], or by the method of Mohler[2]. Both methods yield very pure pyridine but the latter is cheaper and easier to carry out while the quality of the pyridine is just as good. The pyridine boiled at 115.3° at 760 mm. Hg. and did not vary more than 0.1°. The pyridine was always dehydrated before using by refluxing with freshly ignited calcium oxide. After this treatment it was distilled directly into the flask containing the dry salt, or directly into the cell.

The nitrogen was freed from oxygen by passing through an alkaline cuprous carbonate solution. It was then dried by bubbling through concentrated sulfuric acid and was finally passed over soda lime and P_2O_5.

The mercury was washed several times through a column containing nitric acid and then distilled in a partial vacuum while a slow stream of air was bubbled through. Only the middle portion of the distillate was used.

The cadmium was distilled in an atmosphere of hydrogen in a pyrex tube. Only the middle fraction of the distillate was used. The cadmium amalgam always contained 12.5 percent Cd by weight.

The zinc was a very pure sample and was used in the form of a ten percent zinc amalgam. This amalgam showed practically no E. M. F. when compared with an amalgam made from zinc furnished by the Bureau of Standards.

The lead was of "C. P" grade and was used in the solid state and in the form of a ten percent amalgam.

The copper was used in the form of a five percent amalgam, which was prepared electrolytically from pure copper sulfate.

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[1] J. Am. Chem. Soc. 43, 1936 (1921).

[2] Ber. 21, 1015 (1888).

Clark Cell

As a preliminary experiment, the temperature coefficient for the Clark cell was determined. The cell was made according to the directions given by Callendar and Barnes. The transition temperature checked very closely with that obtained by Callendar and Barnes (38.75°). The electromotive force was very easy to read and was quite constant. An attempt was next made to measure a transition in pyridine solution.

Cupric Chloride in Pyridine

Some pure mercury was placed in the bottom of one of the "Board of Trade" type of cells and covered with $HgCl_2$ crystals moistened with a small amount of pyridine. The cell was then filled with a paste of cupric chloride in pyridine. The copper electrode consisted of an amalgamated copper wire.

Cu-Hg | $CuCl_2 \cdot 2py$ | Saturated $CuCl_2$ solution | $HgCl_2 \cdot 2py$ | Hg

The cell was placed in the thermostat and the E. M. F. read after the cell had come to the temperature of the bath. The temperature was then raised several degrees and held at that temperature until the E. M. F. did not vary more than .2 or .3 millivolts in fifteen minutes. A sharp break in the temperature E. M. F. curve was found at approximately 55°. From solubility determinations Mathews and Spero[1] found the transition temperature, for the transformation of $CuCl_2 \cdot 2C_5H_5N$ into $2CuCl_2 \cdot 3C_5H_5N$, to be approximately 58°.

TABLE I

Cupric Chloride Cell

Temp.	E. M. F.	Temp.	E. M. F.
35.0	.6143	55.0	.6254
40.0	.6165	56.0	.6265
45.0	.6195	57.0	.6274
50.0	.6227	60.0	.6310
54.0	.6250	65.0	.6350

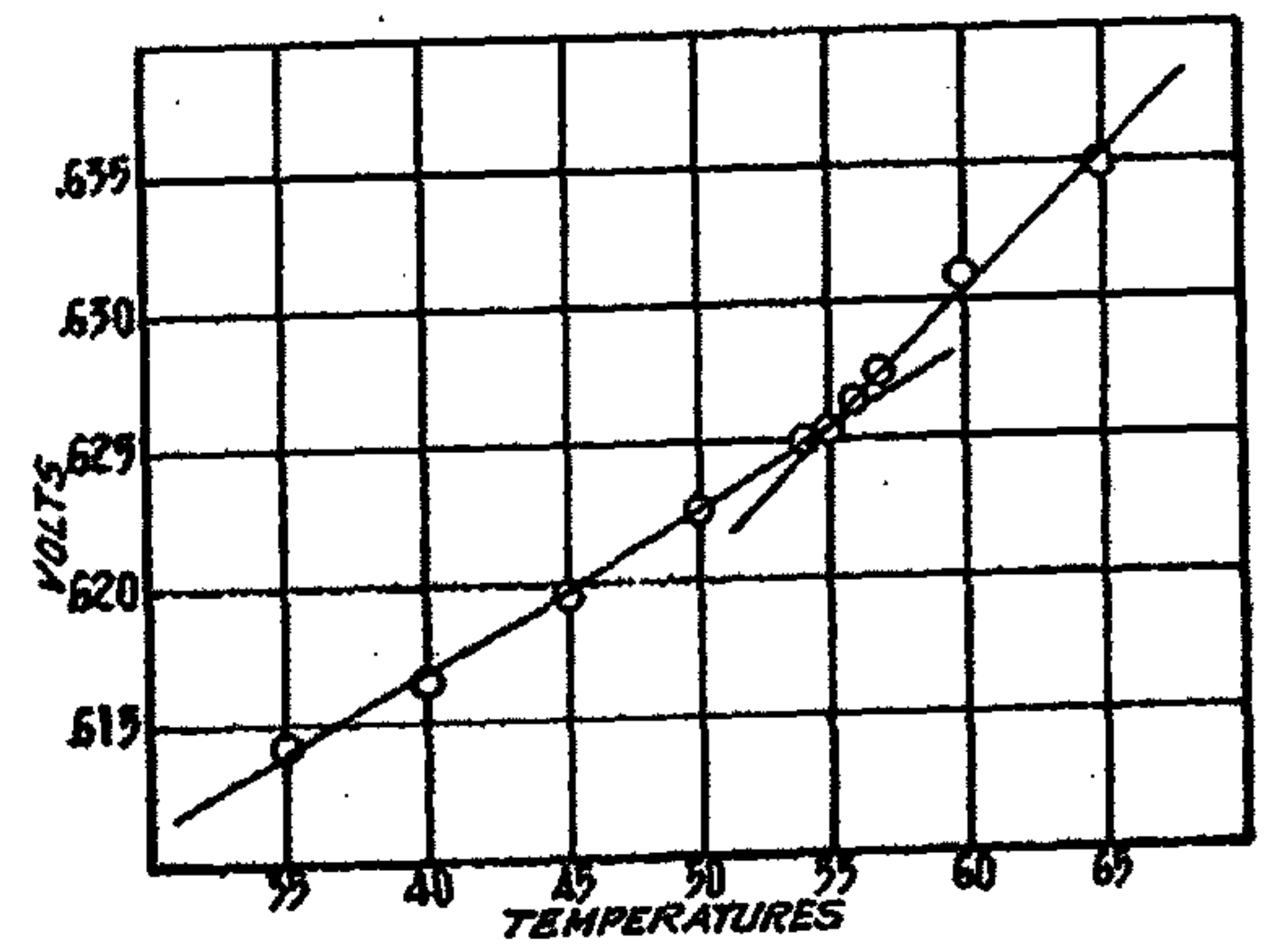

FIG. 1

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[1] J. Phys. Chem. 21, 402 (1917).

Another cell was filled with greater care. The E. M. F. readings were taken only after the cell had remained for a long time at the temperature of the bath. The results are given in Table I and Fig. 1. Again there is a sharp break in the curve at 55°. This lower value for the transition temperature is in accord with the different results obtained for the transition temperatures of the $ZnSO_4.7H_2O$, where the value obtained by the electrical method is lower than that obtained by solubility determinations.

The cupric chloride cell is very unsatisfactory. In the first place, a piece of copper placed in pyridine will soon color the solution green. If left for a long time in pyridine, a copper wire will be entirely disintegrated and a reddish brown colloidal solution will result. The removal of oxygen from the pyridine and the substitution of nitrogen in its place will stop this reaction between copper and pyridine. As a result of these observations, all future experiments were conducted in the absence of air.

Again mercuric chloride is quite soluble in pyridine.[1] This makes it unsuitable to use as a reference electrode, for we do not know what effect this solubility will have upon the transition of cupric chloride.

The most serious objection, however, is the fact that in pyridine solution the following reaction takes place

$$CuCl_2 + Cu \longrightarrow Cu_2Cl_2$$

and the blue solution of cupric chloride changes into the green solution of cuprous chloride. Since cuprous chloride is quite soluble, the excess of cupric chloride disappears and there is only a green solution left.

One of the "H" cells was used in a final experiment. Instead of a mercury reference electrode the $Cd.CdCl_2.2py$ electrode was tried. The scheme for the cell may be written thus:

Cd-Hg | $CdCl_2.2py$ | Saturated $CuCl_2$ solution | $CuCl_2.2py$ | Cu-Hg

The reaction between the copper and cupric chloride still took place. Also, since the cadmium is more active than copper, the amount of insoluble $CdCl_2.2py$ increased very slightly. After long standing the E. M. F. became fairly constant and the temperature coefficient was determined. In the arm of the tube containing the copper, all the cupric chloride had been changed to cuprous, but there was still a large amount of cupric chloride in the other arm of the cell. Again there was a sharp break in the curve at 55°.

Due to the many chemical reactions which took place in the cupric chloride cell, no exact measurements could be made. The cells could not very well be duplicated nor would the E. M. F., at a given temperature, remain constant for a long time. There was however always a sharp break in the curve at 55° and this was due no doubt to the transformation of one phase into the other.

Conductance Measurements

An all-glass conductivity cell was filled with a saturated solution of cupric chloride in pyridine. The cell was placed in the thermostat and cooled a few

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[1] McBride: J. Phys. Chem. 14, 189 (1910).

degrees while being shaken and then was held at constant temperature until there was no change in the resistance. This was repeated for each temperature and the results are given in Table II and Fig. 2. There was a sharp break in the conductance-temperature curve around 56.5° but since the readings were not taken close enough to the transition point, this experiment is to be regarded as a preliminary determination.

Table II

Conductance of a Saturated Solution of Cupric Chloride in Anhydrous Pyridine

Temp.	Resistance in Ohms.	Temp.	Resistance in Ohms
66.8	3184	51.2	3777
60.6	3325	47.4	3879
57.2	3558	43.3	4005

Cadmium Chloride-Zinc Chloride Cell

After examining a large number of metallic chloride electrodes, the cadmium electrode was found to be the most satisfactory. As cadmium is rather high in the electrochemical series, it was rather hard to find another electrode which would act in a suitable manner with the cadmium electrode. Zinc chloride is so hygroscopic that one would hesitate to use it, where it is absolutely necessary to exclude moisture. However, after zinc chloride has reacted with pyridine to form $ZnCl_2 \cdot 2C_5H_5N$, this property of absorbing moisture is gone. Anhydrous zinc chloride and pyridine react with such vigor that the pyridine nearly boils. The heat of reaction between zinc chloride and pyridine is probably greater than the heat of reaction between zinc chloride and water.

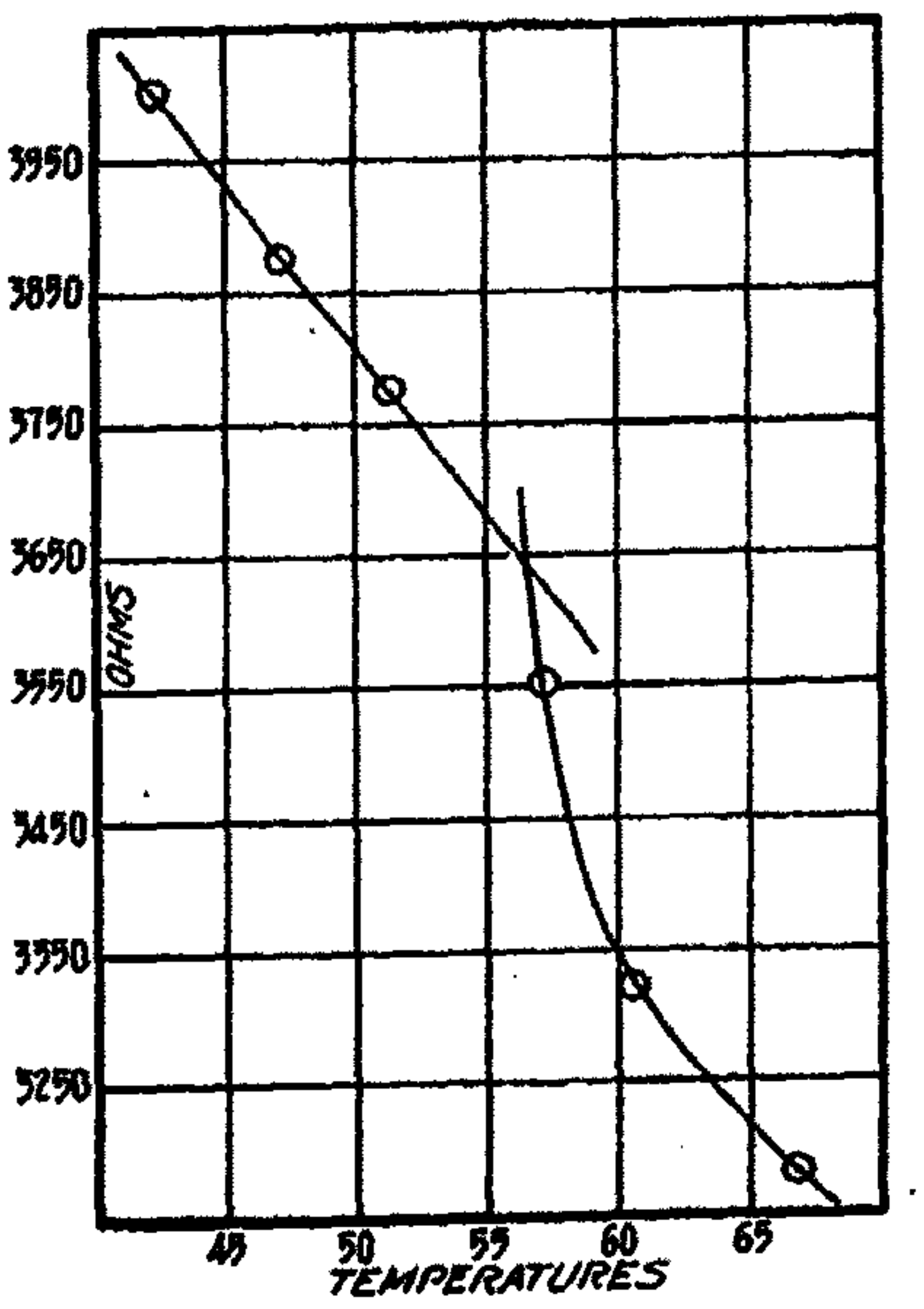

Fig. 2

Several cells containing zinc chloride and cadmium chloride in pyridine were prepared. Of all the cells tried, these cells acted the best, as to reproducibility, stability, and ease with which the E. M. F. readings could be made.

While filling these cells, extreme care was exercised to avoid entrance of moisture and oxygen. The cadmium amalgam was added while a stream of nitrogen was flowing through the cell. Next was added the cadmium chloride, either anhydrous or in the form of $CdCl_2.2C_5H_5N$. The cell was then evacuated and filled with nitrogen. After this a few cc. of pyridine were added in order to make a paste of $CdCl_2.2C_5H_5N$ over the cadmium electrode. The cell was again evacuated and filled with nitrogen and allowed to stand for a day.

The ten percent zinc amalgam was added in a manner similar to the cadmium amalgam.

The pyridine was distilled directly into a flask containing the $ZnCl_2.2C_5H_5N$ and this mixture was forced into the cell. The cell was then evacuated and filled with nitrogen several times. The closely-fitting ground-glass stoppers were then sealed in order to make sure that they would not become loose. The scheme for the cell may be represented thus:

Cd-Hg | $CdCl_2$.2py | Saturated $ZnCl_2$ solution | $ZnCl_2$.2py | Zn-Hg

The cadmium is positive and the zinc negative.

TABLE III

Cadmium Chloride—Zinc Chloride Cells

Temp.	E. M. F. 1.	2.	3.	4.	5.
50				.30990	.31015
45				.31032	.31068
				.31010	.31012
40	.3133	.3163		.31065	.31078
				.31090	.31095
35	.3142	.3170		.31068	.31078
				.31116	.31052
30	.3127	.3175	.3035	.31100	.31065
				.31068	.31107

In each case the cells were placed in the thermostat and an attempt was made to measure the temperature coefficient. The results obtained are shown in Table III. The cells are not so reproducible as the standard cells in aqueous solution. Oxygen and especially moisture must be kept out of the cells. Cells 4 and 5 behaved the best and were the ones where the greatest care had been exercised in filling. The two values given for cells 4 and 5 represent two distinct determinations. The cells were left for many hours in the thermostat before equilibrium was reached. The temperature coefficient was apparently small, while in non-aqueous cells it is usually large. In these particular cells an increase in temperature increased the solubility of the zinc chloride but decreased the solubility of the cadmium chloride. These changes in solubility balanced each other and the resulting temperature coefficient was small.

On several occasions one of the cells became unsteady. It was found that by heating to 60° or 70° and cooling again the cell would settle down. The instability of these cells is no doubt due to the different allotropic forms of cadmium in the amalgam. Getman[1] and Cohen[2] have both emphasized this fact in the case of the Weston cell.

From the solubility determinations it was found that at about 9° there is a transition of $CdCl_2.6C_5H_5N$ into $CdCl_2.2C_5H_5N$. An attempt was made to find this transition temperature by the E. M. F. method. One of the cells was placed in the ice box over night and then was placed in the small oil thermostat and allowed to warm up gradually. The voltages were read at intervals and the temperatures noted. Around 9° there was a very sharp break in the curve. The experiment was repeated by gradually cooling the cell and reading the E. M. F. at different temperatures. A sharp break in the curve was found around 9°. As a final experiment, cells numbered 4 and 5 were placed in the ice box for two days. They were then placed in the thermostat and allowed to come to temperature. They were warmed one degree at a time and allowed to stand until the E. M. F. was constant to 0.1 millivolt in fifteen minutes. The results are given in Table IV and Fig. 3. The voltages of the two cells are not the same, yet the transition temperature checks very well. It is between 9.3° and 9.4° and compared favorably with the value obtained by the solubility method. It is therefore possible to use the E. M. F. method for the determination of transition points in pyridine solution as well as in aqueous solution. This

TABLE IV

Transition Cells of Cadmium Chloride

Cell Number 4.		Cell Number 5.	
Temp.	E. M. F.	Temp.	E. M. F.
6	.3022	6	.2907
7	.3038	7	.2924
8	.3051	8	.2938
9	.3057	9	.2944
10	.3061	10	.2956
11	.3073	11	.2969
12	.3082	12	.2985
13	.3092	13	.2999

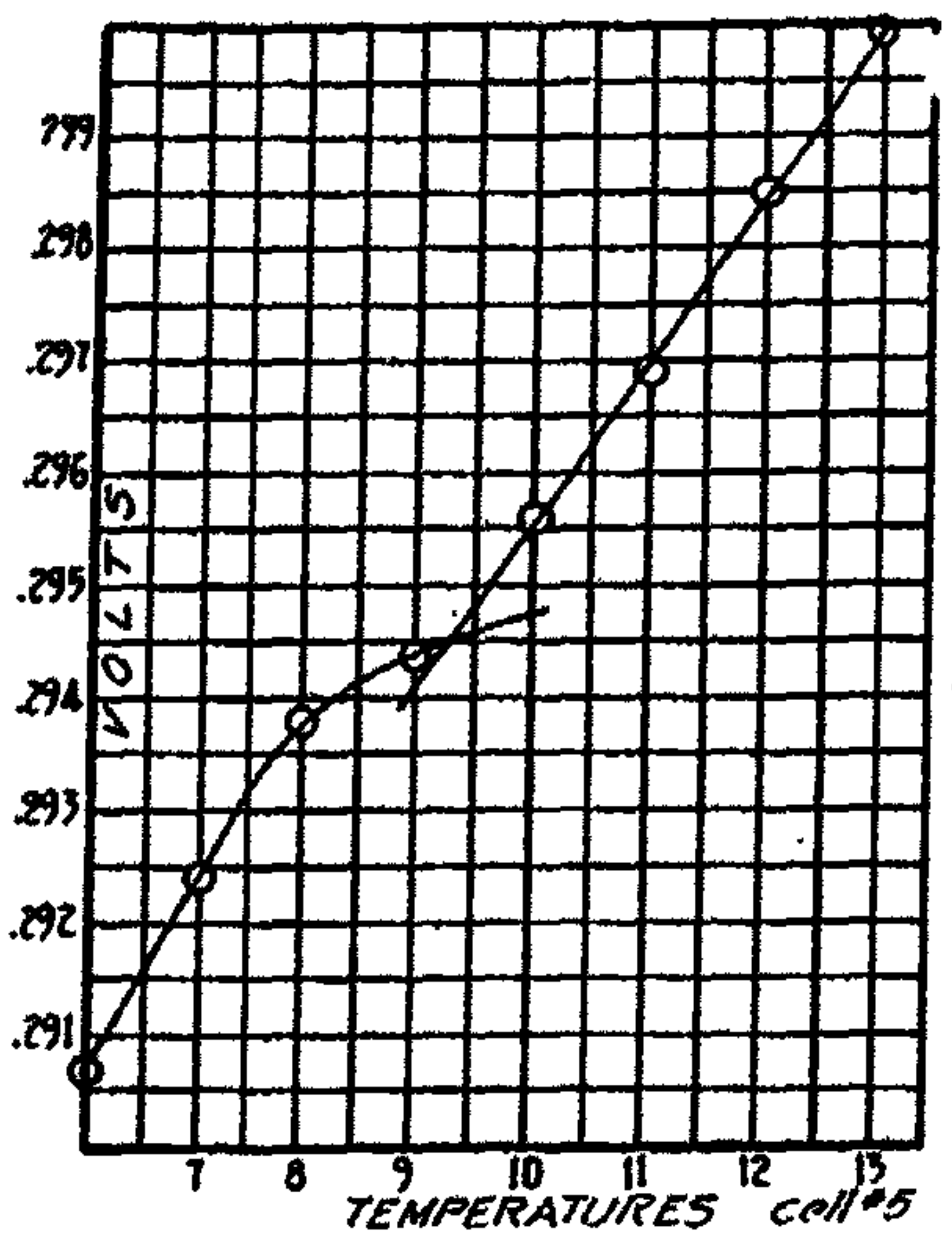

FIG. 3

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[1] J. Am. Chem. Soc., 39, 1806 (1917).

[2] J. Am. Chem. Soc., 40, 1149 (1918).

is a new transition temperature and it has been determined by a method never before applied to pyridine solutions.

Cadmium Chloride—Mercuric Chloride Cells

The heat of reaction between mercuric chloride and pyridine has been determined by Mathews, Krause and Bohnson[1]. Knowing this value, it should be possible to determine the heat of reaction between cadmium chloride and pyridine with the following cell:

Hg | $HgCl_2$.2py | Saturated $HgCl_2$ solution | $CdCl_2$.2py | Cd—Hg

Several cells of this type were constructed and the values obtained are given in Table V. The cells were not constant and no satisfactory temperature coefficient was obtained. The cadmium is more active than the mercury and the amount of $CdCl_2.2C_5H_5N$ gradually increases. Hence this method is not applicable to the determination of the heat of reaction between cadmium chloride and pyridine.

TABLE V

Cadmium Chloride—Mercuric Chloride Cells

Temp.	E. M. F.		
	1.	2.	3.
30	.8632	.8776	.7991
	.8692	.8797	.8393
40	.8851	.9132	.8564
	.8667	.8993	.8649

Cadmium Chloride—Lead Chloride Cell

This cell was filled in the same manner as the zinc chloride cell. In the first cell ten percent lead amalgam was used. The cell can be represented by the following scheme:

Cd-Hg | Cd Cl_2.2py | Saturated $PbCl_2$ solution | $PbCl_2$.2py | Hg-Pb

TABLE VI

Lead Chloride Cell

Temp.	E. M. F.	Temp.	E. M. F
25.0	.1330	60.5	.0206*
28.2	.1277	65.7	.0257*
30.3	.1238	70.2	.0309*
34.0	.1093	75.3	.0446*
39.3	.0829	80.9	.0649*
45.1	.0427	85.3	.0870*
50.5	.0105	90.2	.1071*
56.1	.0132*		

*Sign changed.

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[1] J. Am. Chem. Soc., 39, 398 (1917).

The cell was allowed to stand over night and on the following morning it was placed in the thermostat. The cadmium is positive and the lead negative, just opposite to the positions in aqueous solution. The cell was heated gradually and the voltages were read for the different temperatures. The results are given in Table VI and Fig. 4. It will be noticed that the position of the lead and cadmium is reversed around 51° where the voltage becomes zero. There is also a sharp break in the curve around 53°. When the cell was cooled the lead remained positive and did not change back again to its original negative value. The experiment was repeated using a massive lead electrode instead of the amalgam. The reversal took place again but not at exactly the same temperature, since the cell was not heated as slowly as before. This reversal takes place either when the electrode is massive lead or lead amalgam, a fact which indicates that the phenomenon is not due alone to the amalgam.

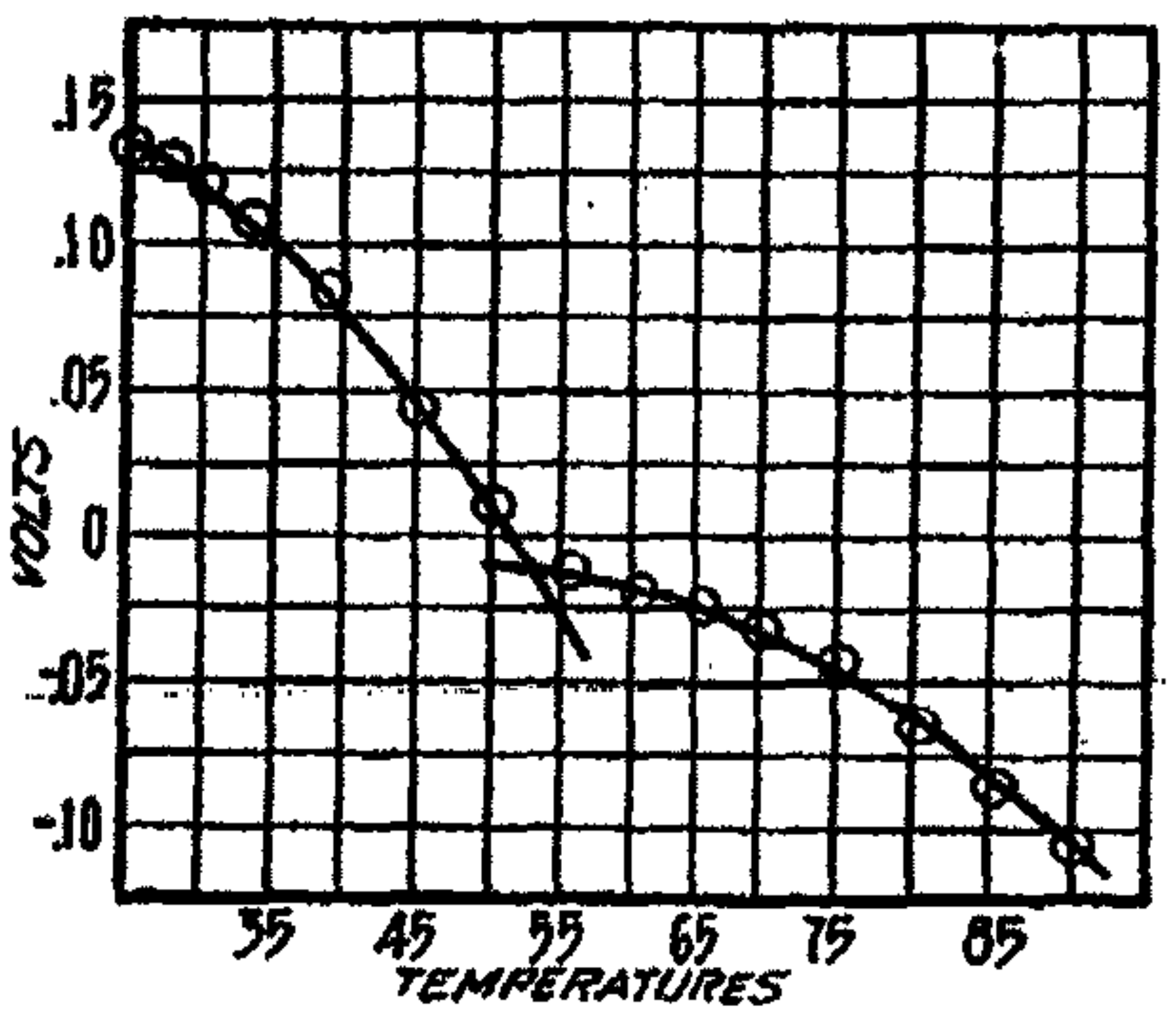

FIG. 4

Thinking that there might be a metastable phase of the $PbCl_2$ and pyridine complex present, some $PbCl_2.2C_5H_5N$ crystals were added to the cell but the reversal would not take place even after standing a few days.

Another cell containing the massive electrode was constructed and allowed to stand for several weeks. The lead always remained negative to the cadmium. Still another cell was constructed, but in this case the $PbCl_2$ was heated with the pyridine at 80° for several hours before adding to the cell. In this cell the Pb was positive and remained so for several weeks at room temperature. This last experiment showed that there was a reaction which took place between the lead chloride and pyridine which was not reversible, at least for several weeks, and which accounted for the most peculiar behavior of this cell upon heating. From solubility determinations, Heise[1] concluded that there is only one compound of $PbCl_2$ and pyridine ($PbCl_2.2C_5H_5N$) in equilibrium with the solution from—20° to 102°. A close examination of this solubility curve indicates that there is a slight break at 52° and further work will be conducted to investigate this apparent transition point.

Summary

1. The electromotive force method has been used for the determination of transition points in anhydrous pyridine solutions.

2. There is a sharp break in the temperature-electromotive force curve at 55° for the half cell Cu-Hg. $CuCl_2$.2py when connected to either the half cell $HgCl_2$.2py. Hg or $CdCl_2$.2py.Cd-Hg. This break is evidently due to

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[1] J. Phys. Chem. 16, 373 (1912).

the transition of $CuCl_2.2py$ into 3 $CuCl_2.2py$. Due to several secondary chemical reactions, the E. M. F. of the $CuCl_2$ cell gradually changes. The temperature-conductance curve shows a break at approximately 56°.

3. The Cd-Hg | $CdCl_2$. 2py | sat. solution of $ZnCl_2$ | $ZnCl_2$. 2py | Zn-Hg cells were the most satisfactory of all the cells tried when considered from the standpoint of conductance, stability and reproducibility. The temperature-electromotive force curve breaks sharply at 9.3°, the temperature at which the compounds $CdCl_2.6py$ and $CdCl_2.2py$ are in equilibrium. This value checks very well with the temperature as obtained by the solubility method (9°).

4. The cadmium and zinc amalgams change polarity when the following cell is heated

Pb-Hg | $PbCl_2$. 2py | Sat. solution of $PbCl_2$ | $CdCl_2.2py$ | Cd-Hg.

This reversal is apparently an irreversible change although there is some indication of a transition point at 53°.

Madison, Wisconsin
May 1925.

A METHOD OF MEASURING THE RELATIVE SURFACE CHARGES ON ELECTROLYTES

BY ALLEN GARRISON

From the fact that bubbles of air when suspended in an electrolyte move under the influence of an electric field, it is known that the film forming the interface between the air and the electrolyte contains an electric charge, an excess of either positive or negative electricity depending on the nature of the electrolyte. From the direction of the cataphoresis of the bubble the sign of the charge can be determined, but due to the many disturbing factors the relative magnitude of the electric charge can not be accurately estimated. In fact the sign of the charge is sometimes doubtful.

Experiments have also been performed in which air bubbles were driven through the liquid by the force of gravity and the sign of the charge estimated from the difference in potential set up along their path. (1) This is similar in principle to the cataphoresis method and in spite of certain advantages it has not yet yielded quantitative results.

In the experiments to be described the method of measuring the surface charge was independent of the cataphoresis method and has been found to be capable of giving a quantitative measure of the relative surface charge to within .01 of a volt.

The Experimental Method

If an electric condenser is constructed of two metallic plates separated by a dielectric such as air, it is possible to determine when the surfaces of the plates have the same potential. This can be done by moving one of the plates nearer the other thus increasing the capacity of the condenser. It the surface of the plate moved is positive relative to the surface of the stationary plate a positive charge will tend to flow off of the stationary plate and may be detected by insulating the plate from its surroundings and connecting it by a wire to an electrometer. If no charge flows off the stationary plate when the capacity of the condenser is changed, there is no electric field between the plates and their surfaces have the same potential. This principle has been used to measure the potentials of the surfaces of a number of electrolytes relative to the surface of water.

The apparatus employed is illustrated in Figure 1. The electric condenser consisted of the electrolyte A and the horizontal metal plate F. The electrolyte was contained in a round glass vessel 10 cm. in dimeter and 2.5 cm. deep. The vessel was supported on and insulated from the base D by sulphur plugs 2 cm. in height. The base D was equipped with leveling screws so that the surface of the electrolyte in A could be made flush with the rim of the vessel. This surface formed one plate of the electric condenser.

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[1] Billitzer: Z. Elektrochem. 8, 638; Ann. Physik, (4) 2, 902 (1903), Kleeman: J. Phys. Chem. 29, 508 (1925).

The electrolyte was connected through the glass tube B to a 0.1 N calomel electrode C. The tip of the calomel electrode contained a salt bridge of saturated potassium chloride which eliminated the electrolytic potential difference to a magnitude which was less than the experimental error. Thus the inside of the electrolyte at A may be taken as the same potential as the electrolyte in C which is maintained at a very constant potential relative to the mercury. The mercury of the calomel electrode was connected by a copper wire to the quadrant electrometer E and could be connected to a ground wire through the key K. The calomel electrode was supported and insulated from the table by the sulphur blocks S.

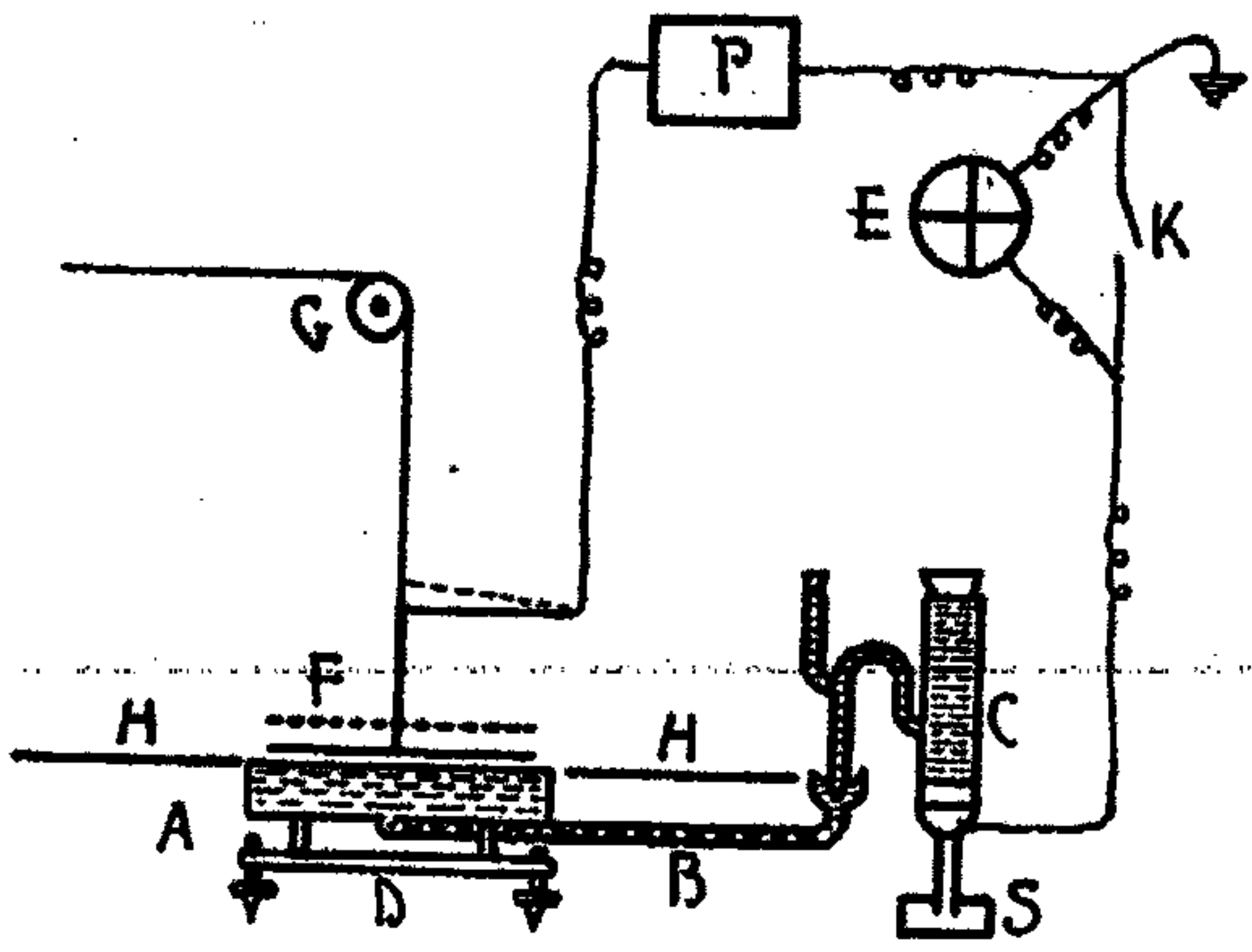

Fig. 1

The metallic plate F formed the reference plate of the condenser and could be raised to the position indicated by the dotted line by drawing the cord which passed over the pulley G. The plate was connected to the ground wire through the potentiometer P which was of standard make and requires no description. By setting the potentiometer the potential of the plate could be set at any desired value relative to the mercury of the calomel electrode.

The vessel containing the electrolyte was surrounded by a circular ring made of sheet copper H, H. This was separated from the vessel A by a 2 mm air space and was connected to the ground wire. It thus acted as a guard ring.

The table top was covered with a sheet of tin foil also connected with the ground wire. This prevented the induction of any charge by the sudden change in potential of the table top or supports.

In performing the experiment the electrometer was used as a null instrument. The electrolyte whose surface charge was sought was placed in A and connected to earth through the key K. The key was then opened and the plate F moved thus changing the capacity of the condenser. If a charge was induced in the electrometer the potential of the plate was changed by adjusting the potentiometer. Thus the plate was made more negative if a positive charge was induced and more positive if a negative charge was induced. The experiment was then repeated until no charge was induced when the capacity of the condenser was changed. The reading of the potentiometer would then give the potential difference in volts between the electrolyte surface and the reference plate if they had both been earthed.

If now a second electrolyte is placed in A its inside potential will be the same as the electrolyte in C and will thus be the same as the inside potential of the first electrolyte. When there exists a surface charge on the first electrolyte having a different magnitude from the surface charge on the second electrolyte, the plate F must be given a different potential by the potentiometer in order to get its potential to the same value as electrolyte number two. Therefore the difference between the readings of the potentiometer for the two electrolytes is the difference in their surface charge. In this way a number of electrolytes have been compared with pure water taken as a standard.

Since the metallic plate is used as a reference it is necessary that the potential of its surface shall remain constant during the experiments. The plate was first constructed of copper but it was found that the oxidation of the surface of the copper in air rapidly changed its contact potential. To avoid this the copper plate was covered with a sheet of palladium foil. The resistance of palladium to chemical action made it a very satisfactory standard. Its polished surface would retain approximately the same contact potential for several days.

The Experimental Results

It was found that the surface charge on water is an exceedingly variable quantity. Distilled water taken from the same container varied several hundredths of a volt the same day and even more on different days. Thus seven determinations with distilled water on different days gave the following values: +.005, +.035, +.060, +.040, +.080, +.010 and +.505 with an average of +.040 volts. The experimental error in making the measurements was less than .005 of a volt.

The larger part of the variation occurred on the surface of the water and not on the surface of the palladium for a salt solution taken from the same bottle on successive days shows far less variation than distilled water. For example a 0.1 N KCl solution measured +.110, +.120, +.130, +.130, and +.125 volts the readings being taken on five succeeding days.

When the copper plate was used in the place of palladium the variations were larger and in a direction to indicate that the surface of the copper was becoming positive. With the freshly polished copper plate the 0.1 N KCl had a potential of −.030 and on succeeding days −.035, −.055, and −.090 volts.

The Influence of Various Substances on the Surface Charge of Water. In order to compare the effects of various salts on the surface charge of water a number of 0.1 molar solutions were measured. Table I gives the results of the measurements.

The first column gives the substance in solution and the second column the potential to which the palladium plate must be raised in order to be at the same potential as the electrolyte surface. The average value for pure water (+.040 volts) was subtracted from these measurements to give the voltages relative to the water surface in column three.

It was found that the surface charge was shifted appreciably by even the smallest traces of substances of oily nature. A sample of pure water measuring +.045 volts was changed to +.110 by touching with a glass rod on which there was a trace of oil of cloves and in another experiment pure water

TABLE I

The Surface Charge on Various Electrolytes.

Salt .1 Molar	Potentiometer Voltage	Volts Relative to Pure H_2O
KCl	+.110	+.070
KBr	+.085	+.045
KI	−.015	−.055
KSCN	+.080	+.040
K_2SO_4	+.050	+.010
K_3FeCN_6	+.100	+.060
K_4FeCN_6	−.030	−.070
KCl	+.110	+.070
NaCl	+.120	+.080
$CaCl_2$	+.135	+.095
$BaCl_2$	+.160	+.120
$CuCl_2$	−.025	−.065
$AlCl_3$	+.215	+.175
$FeCl_3$	+.130	+.090
HNO_3	+.250	+.210
HCl	+.210	+.170
.1% Picric Acid	+.100	+.060
.1% Benzoic Acid	+.120	+.080

measuring +.010 was changed to +.115 by contact with the tip of the finger. This explains in a large measure the fact that it is difficult to get consistent results with water.

The Variation of the Surface Charge with the Salt Concentration. Table 2 gives the results of the measurement of several salts and acids at different concentrations.

TABLE II

Surface Charge and Concentration.

Normality	HNO_3	HCl	KI	$Cu(NO_3)_2$	$CuAc_2$	KSCN	K_4FeCN_6
3.000		.030				.020	
2.000	.270	.100					
1.000	.265	.185	.125	.190	.230	.070	
.500	.260	.230	.075	.120	.040	.090	
.250	.250	.230	.020	.110	−.030	.080	−.040
.125	.250	.210	−.010	.090	−.020	.080	−.040
.0625	.240	.190	−.040	.080	−.020	.085	−.020
.0312	.215	.175	−.030	.060	−.015	.070	+.010
.0156	.200	.130	−.025	.050	−.010	.060	+.020
.0078	.180						
.0039	.160						

The most concentrated solution was placed in the apparatus first and for each successive measurement a measured fraction of the solution was removed and replaced by distilled water taken each time from the same container. In the case of HNO_3 it was found that the exposure of the palladium plate to the vapors of the acid altered its potential relative to .1 N KCl solution. A correction was made for this change so that the results compared with the other solutions.

The results in Table II are presented in the form of graph in Figure 2. The concentration is expressed on the X-axis and the charge in volts relative to water on the Y-axis. The curves are numbered in the order in which they appear in Table 2, thus, HNO_3 is I, HCl is II, KI is III, etc.

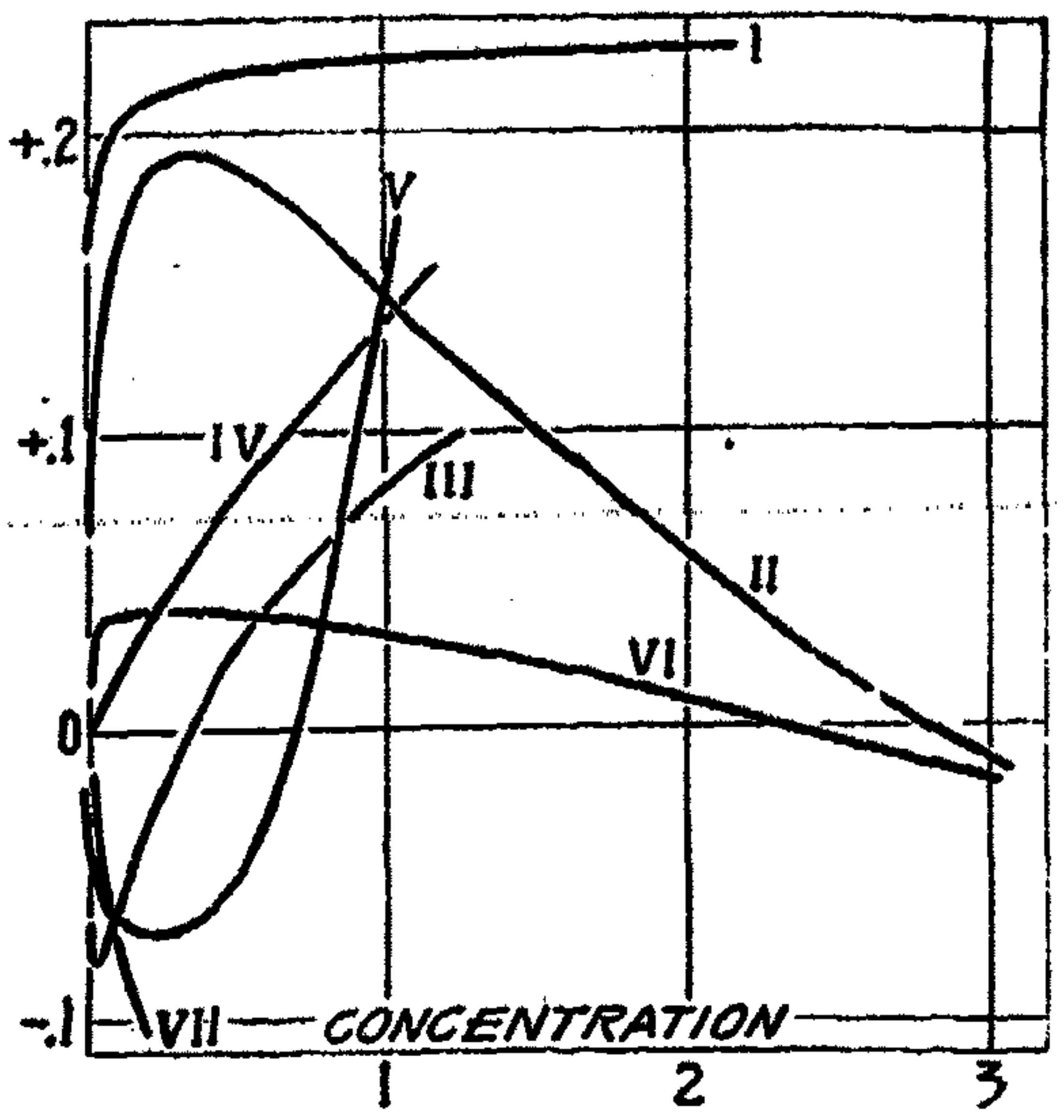

FIG. 2

Discussion of Results

From Figure 2 it is at once apparent that the largest effects on the surface charge are produced by the first traces of the substance added and that the subsequent additions produce relatively little change. In most cases the effect appears to approach a maximum at a small concentration and on further addition of solute the charge is reduced and sometimes reversed in sign.

This is closely analogous to the phenomenon of adsorption. In fact, exactly this type of curve has been obtained for the relation between the concentration and the charge on several colloidal suspensions.[1]

The arrangement of ions in Table I was intended to test as far as possible the "valence rule" for the surface charge. While the lowest potential was obtained with the tetra-valent ferro-cyanide ion and the highest with the

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[1] Svedberg: A. C. S. Monograph, "Colloid Chemistry", page 193 (1924).

tri-valent aluminum ion, with the exception of the hydrogen ion, the rule is not rigorous. The mono-valent iodine ion gives a lower potential than the di-valent sulphate ion, and $FeCl_3$ drops below $BaCl_2$. It is worthy of note that the order of the concentration of the halide ions in the surface is the same as the order of adsorbibilities.

The hydrogen ion is noted for its power of precipitating colloidal suspensions and may be seen to have the largest influence on the surface charge of water. It is therefore possible that the high charge on aluminium chloride is due to the hydrogen ion of hydrolysis rather than the trivalent aluminum ion.

The experimental method has the advantage over the other methods depending on the cataphoresis phenomenon in that the measurments are capable of greater speed and accuracy. The observation of the motion of air bubbles is a tedious proceedure. The calculations of charge also depend on certain quantities which are difficult to measure such as size of bubbles and thickness of films.

The method of Billitzer and Kleeman has the advantage that the bubbles are formed under the surface of the liquid and thus eliminates the error which may be introduced by traces of oily substances which may be floating on the surface in the film. On the other hand the method is not capable of giving quantitative results comparable with the contact potential method.

The chief disadvantage of the contact potential method is that the results are relative only. They do not give any idea about the isoelectric point. The results have been expressed relative to water but from cataphoresis phenomenon there is evidence that the hydroxide ion in the pure water is concentrated in the surface and the isoelectric point would thus lie somewhere above the line in Figure 2. If this exact potential in volts were known from cataphoresis data the exact potentials could be determined for any surfaces by the contact potential method.

Summary

An experimental method has been described by which the relative surface charge on an electrolyte may be measured to .005 of a volt.

The surface charge on a number of electrolytes has been measured.

The first traces of a substance added to water have the largest effect on its surface charge while subsequent additions as a general rule have a small effect often decreasing the charge and sometimes reversing the sign.

The general relations between concentration and surface charge are similar to the relations between concentration and adsorption.

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THE STRUCTURE OF GELATIN GELS[1]

BY ELMER O. KRAEMER[2]

Ever since the work of Graham, the behavior and properties of protein sols and gels have been of great interest to colloid investigators, especially to those concerned with biological problems. Due to the frequent occurrence of gel-like bodies in living organisms, the formation and behavior of gels are particularly important; and gelatin systems have often been taken as prototypes of such bodies. It seems, however, that during the attempts of the past few years to coordinate a few of the properties of protein systems[3] on the basis of considerations which are formally identical with those underlying Donnan's treatment of membrane equilibrium, there has been a tendency to overlook or neglect the special problems which the gels present. Since the Donnan equilibrium considerations really direct the attention upon the behavior of *electrolytes* (in the sense of the ordinary acids, bases and salts) in the presence of proteins, they have not shed light upon important colloid questions more closely identified with the protein itself, such as the mechanism and necessary conditions for gel formation by these "solid aggregates", the structure and characteristic properties of gels, and the changes in state which the gels and "solid aggregates" undergo.

If one considers the matter in a general way, it is perfectly clear that in the great majority of cases, gel formation is the result of an incomplete or unsuccessful attempt at precipitation of a solid phase from a liquid system. Thus metathetical reactions, which are expected to yield solid insoluble products, may result in gel formation; or a change in solvent may cause a solute to precipitate out in the form of a gel; or a gel may be formed by the coagulation of a sol[4]. Furthermore, it is certain that the rigidity and elasticity of these gels are due to the presence in them of a highly dispersed solid or semi-solid phase, the elements of which are bound together in some way so as to confer upon the system as a whole, the rigidity and elasticity which the dispersed solid framework possesses. As is well known, the structure is in many cases actually demonstrable with the ultramicroscope. The heterogeneity in structure is also attested to by the pronounced Tyndall effect to be observed

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[1] Presented at the Third National Colloid Symposium in Minneapolis, June 17-19, (1925).

[2] Fellow of the National Research Council.

[3] See for instance J. Loeb: "Proteins and the Theory of Colloidal Behavior", (1924): p. 22, "the influence of electrolytes on the osmotic pressure of protein solutions, on the viscosity of certain *but not all* protein solutions, on the s[illegible]ls . . . and on membrane potentials." p. 31: . . . "The reason that osmotic p[illegible]sity of protein solutions, and the swelling of protein gels are all influenced in a [illegible] by electrolytes is that all three properties are in the last analysis functions of [illegible] the same property, namely, osmotic pressure" (*of the electrolytes in the protein solution*) . . ."we are dealing with the influence of the electrolytes on the swelling of *solid aggregates of protein*, and this swelling is due to the osmotic pressure" (*of the electrolytes*) "inside the aggregates". (italics by E. O. K.).

[4] Gels of manganese arsenate, dibenzoylcystine and ferric oxide are examples of these cases respectively. For a discussion of these and other examples, see the chapter on "Jellies and Gelatinous Precipitates" by Harry B. Weiser in Bogue's "Colloidal Behavior" (1924).

in gels, and by the use of gels as ultrafilters. The formation of such a gel must be considered as a colloidal process involving a change in the mutual relationship between the particles of a *colloidal* solution. In other words, *gel formation is a process possible only in dispersed systems;* a sol must immediately precede the gel state, although the sol state may be a temporary and short-lived one between "true" solutions and a gel, as in the formation of a gel by double decomposition between two appropriate salt solutions. This picture of gel formation and structure is essentially the original micellar theory of Nägeli, and is the only one which has been found to be consistent with the general behavior of gels.

Gelatin gels, however, appear to present a more complicated question; their structure may be entirely invisible under the ultramicroscope, and their light-scattering capacity may be surprisingly low. But this probably is merely a demonstration of the small size and low index of refraction of the structural elements in the gelatin gels; such characteristics are in this case to be expected. Otherwise, there seems to be no sufficient reason for not supposing that the mechanism of formation and the structure of gelatin gels are in general like those of other gels, and that the capacity to form gels is dependent upon the presence of discrete solid or semi-solid units which for some unknown reason become knit together upon gelation to form a solid reënforcing structure giving rigidity and elasticity to the entire system.

This then raises the interesting question as to the microstructure of gelatin gels and the order of magnitude of the discontinuities within them. The optical properties and the general behavior of the gels indicate a rather fine-grained structure. But the high vapor pressure of the water over a weak gelatin gel, and the very slight increase in resistance which such a gel offers to the motion of ions and molecules diffusing through it, demonstrate that, on a *molecular scale, such gels do not possess the high rigidity which they display in bulk.* This was already appreciated by Sutherland[1]: "It has been argued that because an electrolyte dissolved in a stiff jelly has nearly the same conductivity as a pure aqueous solution of the same strength, viscosity can be of little importance; but it is obvious that the correct inference is that in the jelly, the water is so immersed in the gelatin that it exhibits great viscosity and quasi-solidity as regards *bulk* movements, while to ions moving through its meshes quite freely, the confined water exhibits almost only the viscosity of ordinary water". Likewise, studies of diffusion in gelatin gels led Bechhold and Ziegler[2] to the conclusion that "it is highly probable that the diffusion of electrolytes in gelatin does *not* take place through a *homogeneous, continuous* gel, but through the water filling the pores between the walls of gelatin" (italics are by B. and Z.). Entirely similar data and conclusions followed from the work of Öholm[3] on diffusion in gelatin gels. These observations are very significant and can not be overemphasized in connection with the question of

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[1] Phil. Mag., (6) 3, 165 (1902).

[2] Ann. Physik, (4) 20, 900 (1906).

[3] Meddel. Vetenskapsakad. Nobelinst., 2, No. 30 (1913).

gel structure. Unfortunately, a careful attempt has not yet been made to give a detailed and quantitative interpretation of diffusion data in terms of a heterogeneous gel structure and the possible dimensions of the pores.

An approximate estimation of the order of magnitude of the spaces between the elements of the gel structure may be obtained in another way. Although it has not been possible to demonstrate the existence of a chemical entity or molecular species of definite composition which may be called "gelatin"[1], the views of those who speak of gelatin molecules may be developed in this connection in order to estimate the discontinuities or gel spaces. Cohn[2] has given 123,600 as the probable minimum molecular weight of gelatin. Since the partial specific volume[3] of gelatin in aqueous sol is 0.6894, a single such gelatin molecule must occupy a volume of ca. 140 cubic millimicrons into which *water molecules do not penetrate*. Or, to avoid considerations of an hypothetical molecule, the particle volume may be calculated from the average particle weight given by osmotic pressure measurements (96,000)[4] to be ca. 109 cubic millimicrons. In either case, the sol unit, considered as a compact impenetrable cube[5] must measure about 5 millimicrons on a side, a magnitude considerably greater than what is usually assumed to be the range of atomic and molecular forces.

If, like most other gels, a gelatin gel be supposed to consist of threads or short chains of these "molecules" or sol units loosely knit together in three dimensions, an average value of the interval between two threads may be shown to be $19\sqrt{\frac{1}{\text{percent conc.}}}$ times the thickness of the threads. This

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[1] See Knaggs and Schryver: Biochem. J., 18, 1095 (1924); Rakusin: Chem. Ztg., 48, 249 (1924).

[2] J. Biol. Chem., 63, xv (1924).

[3] Wintgen: Kolloidchem. Beihefte, 7, 260 (1915). The use of the partial specific volume in this way is justified by the fact that, unlike "true" aqueous solutions of crystalloids, the partial specific volume of gelatin is *constant* over an extremely wide range of concentrations (in fact, over the complete range studied). This constancy of partial specific volume is characteristic of many colloidal systems.

[4] C. R. Smith: J. Am. Chem. Soc., 43, 1350 (1921). His value was obtained with deashed gelatin at 35°C, i.e. in the finely dispersed, non-gelling condition. The pressures were proportional to the concentrations.

[5] It seems necessary to assume the ultimate sol units which make up the aggregates to be compact rather than loose and porous for two reasons. In the first place, the application of Einstein's equation ($D = \frac{RT}{N\,6\pi\eta r}$) to the diffusion coefficients of proteins gives values for the size of the diffusing unit which are of the same order of magnitude as those calculated above upon the assumption of complete compactness. (See Bechhold: "Kolloide in Biologie und Medizin", p. 53 (1920). Although Einstein's equation has not been found to give a completely adequate description of diffusion, a considerable body of data indicates its general consistency and usefulness, particularly for particles and large molecules; these data may be found in the papers of Thovert: Compt. rend., 135, 579 (1902); 137, 1249 (1903); 138, 481 (1904); 150, 270 (1910); Svedberg: "Die Existenz der Moleküle", 78 (1912); Öholm: Meddel. Vetenskapsakad. Nobelinst., 2, Nos. 22, 23, 26 and 30 (1912); Herzog and co-workers: Z. Elektrochem., 13, 533 (1907); 17, 679 (1911); Z. physik. Chem., 87, 449 (1914); Cohen and Bruins: Z. physik Chem., 103, 404 (1923); 109, 397, 422 (1924); 114, 441 (1925); and many others.

In the second place, the considerable light-scattering capacity of a gelatin system, even at temperatures above 50°, forces one to the conclusion that the sol units can not be so loose and permeable as to produce a system with the homogeneity of a "true" solution of small molecules.

would mean that in a 0.5 percent gelatin gel, which can easily be shown to possess a bulk elasticity, the average interval between such threads would be 27 times the thickness of the threads, i.e. about 100 millimicrons. The threads may not and probably do not consist of rows of single compact "molecules" or sol units. However, aggregation of the units to form thicker threads can only result in an increase in the size of the spaces. With such a loose structure, the water phase in the interstices would be expected to have the properties of water in mass, as the facts demand. Now of course, this is admittedly a rough calculation. But the considerations underlying it force one to admit that the structure of dilute gelatin gels must be considerably looser and less homogeneous than ordinarily assumed by those who picture a gelatin gel to be essentially as homogeneous as a "true" solution.

Attempts to study directly the micro-structure of weak gelatin gels have been very few. Bachmann's[1] ultramicroscopic observations of gelatin gel formation are perhaps not so significant because it is possible to prepare gelatin gels which show no structure in the ultramicroscope. The studies of Freundlich and Seifriz[2] are of considerable interest however. They investigated the micro-rigidity and elasticity of weak gels by observing the behavior of small nickel particles (7-18 microns in diameter) in a magnetic field. It was found that, on a micro-scale, the rigidity and elasticity of gelatin gels are far from uniform; within distances of a few hundredths millimeter, relatively great and sudden differences in elasticity exist. The distances involved in these studies were greater than 20 microns.

In order to decrease the scale of the observations still further, Svedberg[3] suggested at the First Colloid Symposium that a study of the Brownian motion of very small particles imbedded in weak gels might throw light upon the structure of the gel. This suggestion was considered in greater detail at the Second Symposium[4] in connection with a discussion of the use of the cinematograph in colloid research.

The Brownian motion of a particle immersed in a viscous liquid is described by the two equations

$$(1)\quad W_x dx = \frac{1}{\sqrt{2\pi\,\overline{\Delta_x^2}}}\, e^{\frac{-x^2}{2\overline{\Delta_x^2}}}\, dx$$

$$(2)\quad \overline{\Delta_x^2} = \frac{RT}{N}\,\frac{t}{3\pi\eta r}$$

where $W_x dx$ is the probability for the occurrence of a displacement of magnitude x along the x-axis in the time interval t, and $\overline{\Delta_x^2}$ is the mean square of all such displacements for a particle of radius r moving in a medium with

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[1] Z. anorg. Chem., **73**, 125 (1911).

[2] Z. physik. Chem., **104**, 233 (1923).

[3] "Colloid Symposium Monograph", **1**, 93 (1923).

[4] Kraemer: Colloid Symposium Monograph, **2**, 57 (1924).

the viscosity η. The equations are valid only for a medium with the internal structure of a liquid or "true" solution; such a medium will be called "homogeneous". Changes in the character of the medium would be reflected by changes in the character of the Brownian motion of suspended particles.

Mercury particles were prepared by electrical pulverization[1] and roughly fractionated by fractional sedimentation. Particles about 200 to 250 millimicrons in radius were mixed with dilute gelatin systems before gelation. Cinematographic records of the Brownian motion of these particles were made with the apparatus described at the last Symposium. The magnitudes of the displacements were measured by projection on a ruled screen.

In gels of 0.5 percent and over, the Brownian motion was practically prevented. With slight warming, the gel structure gradually broke down, allowing the Brownian motion to reappear. During the breakdown of the gel, the non-uniform character of the gel became clearly evident. Brownian motion appeared at scattered isolated spots. These broken regions spread, forming here and there invisible channels, the presence of which was indicated by the motion of the mercury particles. In weaker gels—about 0.3 percent in concentration—a measurable Brownian motion persisted. The distribution of the displacement magnitudes was normal, i.e. in agreement with the equation 1. From this behavior, it appears that the structure of such weak gelatin gels is still considerably finer than the indicating mercury particles and their displacements; the system behaved as a "homogeneous" liquid. The resistance to the motion, however, was quite considerable. Solving equation 2 for the effective viscosity of the system gave values many times (20-30x) greater than the viscosity of water, but varying from particle to particle.

It thus seems that even this technique is not able to detect the heterogeneities of these gels. On the other hand, this fact lends no support for the view that the structure is molecular in magnitude. For there is a considerable unexplored range between the scale of the Brownian motion experiments, the mean displacements of which varied between 1 and 2 microns, and molecular magnitudes. It is hoped that this region may be successfully explored by a study of the diffusion of molecules into or through gels.

University of Wisconsin.

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[1] Kraemer and Svedberg: J. Am. Chem. Soc., 46, 1980 (1924).

AN EBULLITION DEVICE FOR LOW TEMPERATURE AND VACUUM DISTILLATION

13-10

BY A. F. O. GERMANN AND D. M. BIROSEL

In their experimental study of the separation by fractional distillation of the rare gases of the atmosphere, Ramsay and Travers attempted to isolate neon and helium from nitrogen by the fractional distillation of the more volatile portions of liquid air. Travers says in connection with this experiment that the "result was disappointing, for on removing the nitrogen from the gas the inactive residue was found to consist of normal argon only. It appeared that the evaporation of the liquid in the bulb had taken place at the surface only, and that there had been no fractionation. This is probably connected with the fact that liquid nitrogen shows a remarkable tendency to become superheated, and can only be made to boil steadily by passing a current of gas through it."[1] As a result of this experience, a method was developed in which the liquid gas solution could be stirred continuously by means of a current of air bubbled up through the solution. Ramsay and Travers say about the importance of this innovation:—"It is absolutely necessary to blow air through the contents of the liquefying bulb, while evaporation is proceeding; if this is not done, evaporation takes place chiefly from the surface, and the gas collected in the gasholder will contain very little neon; it was only after several unsuccessful trials that we discovered the cause of our failure to obtain gas rich in neon. Moreover, liquid nitrogen is very apt to become superheated, and to boil from the surface."[2]

The phenomenon of superheating (with consequent bumping) and boiling from the surface is well known in the case of ordinary liquids, and various methods are used to overcome it—such, for example, as the use of boiling stone and ebullition tubes, all involving the bubbling of air through the heated liquid. In the case of liquefied gases, however, application of similar methods, except as carried out by Ramsay and Travers, has apparently not been used because the process of condensing the gas in the distilling bulb involves evacuation of the apparatus, with consequent elimination of the air filling the capillary spaces, and because methods depending on the introduction of air into the liquefied gas are worse than useless, as dissolved air is precisely one of the impurities to be removed by fractional distillation. Agitation of the liquefied gas seems to be the only other method at present generally available—for example, the use of a magnetic stirrer—but apparently such methods have not been used in connection with the fractional distillation of liquefied gases, probably because of the trouble involved in their operation.

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[1] "Experimental Study of Gases", p. 212 (1901).

[2] Phil. Trans., 197A, 58 (1901).

In the purification of technical phosgene by fractional distillation, one of us has applied a modification of the ordinary ebullition tube to obtain effervescent distilling without the use of any foreign gas[1]. The device, illustrated in Figure 1A, may be used in any distillation, but is particularly designed for the needs of vacuum distillation. The essential feature of the new tube is the closed tube D, drawn out to a capillary at C, and sealed into the neck of the distilling bulb. When used with liquefied gases, a constant stream of gas bubbles issues from the lower end of the capillary, and, rising through the liquid, produces uniform boiling. When used with ordinary liquids, the capillary tube, containing air, functions in the usual way; but if the distillation be interrupted, liquid will fill tube D; after bringing the liquid back to the boiling point, all that is necessary is to heat the tip of tube D with the free flame until enough vapor is produced to drive the liquid out; ebullition then begins, and continues as long as the process is not interrupted. The apparatus functions in the same way for the distillation of liquids in a vacuum; it is only essential to bring the liquid to be distilled to the boiling point before vaporizing the contents of tube D.

To prove the value of the device, a series of parallel fractional distillations was made with the new (Fig. 1A) and the old type (Fig. 1B) of distilling bulb, with tubes having identical dimensions, and under as nearly similar conditions as possible.

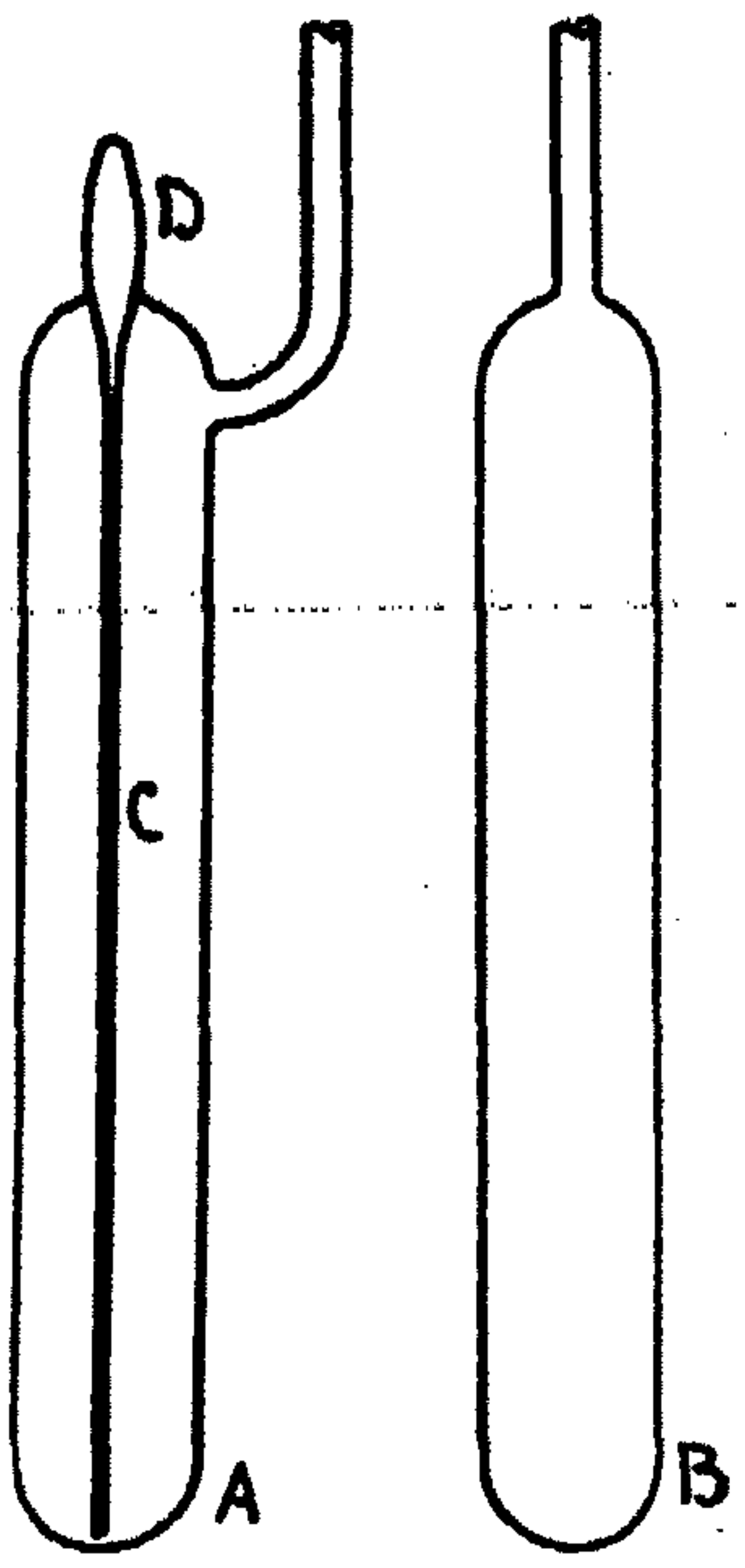

FIG. 1

Procedure. Technical phosgene contains impurities more volatile than phosgene, and as the purification of phosgene requires a great many fractional distillations by the usual method, it seemed worth while to use this as the basis of a comparative study in one set of measurements, and a solution of sulfur dioxide (B. P. −8°) in pure phosgene (B. P. +8°) as the basis of another.

An all-glass apparatus, comprising distilling tubes, safety tubes, pressure manometer, separate vacuum connections for each portion of the apparatus, phosgene and sulfur dioxide supply tubes, and waste gas outlets, was constructed on the same general plan as has been described and figured in previous papers[2]. The progress of the distillation was followed by interrupting the process after the distillation of aliquot portions of liquid (determined with the aid of centimeter calibrations on the receiver) the distilling bulb was then surrounded with an ice bath, and the vapor tension of the liquid remaining was read on the pressure manometer after attainment of pressure and temper-

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[1] J. Phys. Chem., 29, 353 (1925).

[2] See, for example, J. Phys. Chem., 28, 965 (1924).

ature equilibrium; in some of the runs, the total weight of the distillate was determined by removing the receiver and weighing. The receiver was a weighing tube for liquefied gases like that used by Germann and McIntyre in their study of the vapor tension of phosgene solutions.[1] The vapor tensions were plotted against the fraction of the total weight that had been distilled off, and the efficiency of the distillations by the two methods determined by the purity of the residue in the receiver for any point on the curve, as judged by the deviation of its vapor tension from that of pure phosgene at 0°, 555 mm. The volatile impurities in technical phosgene are largely hydrogen chloride and carbon dioxide, both gases much more volatile than phosgene, the vapor tension of hydrogen chloride at 0° being 25.4 atmospheres[2], and that of carbon dioxide at 0°, 34.3 atmospheres[3]; these gases might be expected to be relatively easily removed by fractional distillation. To compare the performance of the new tube with the old with a solution containing a quantity of an impurity having a vapor tension only slightly higher than that of phosgene, a little sulfur dioxide was dissolved in purified phosgene, and the solution was fractionated in the same way. The vapor tension of liquid sulfur dioxide at 0° is 1164 mm.[4], or approximately double that of phosgene.

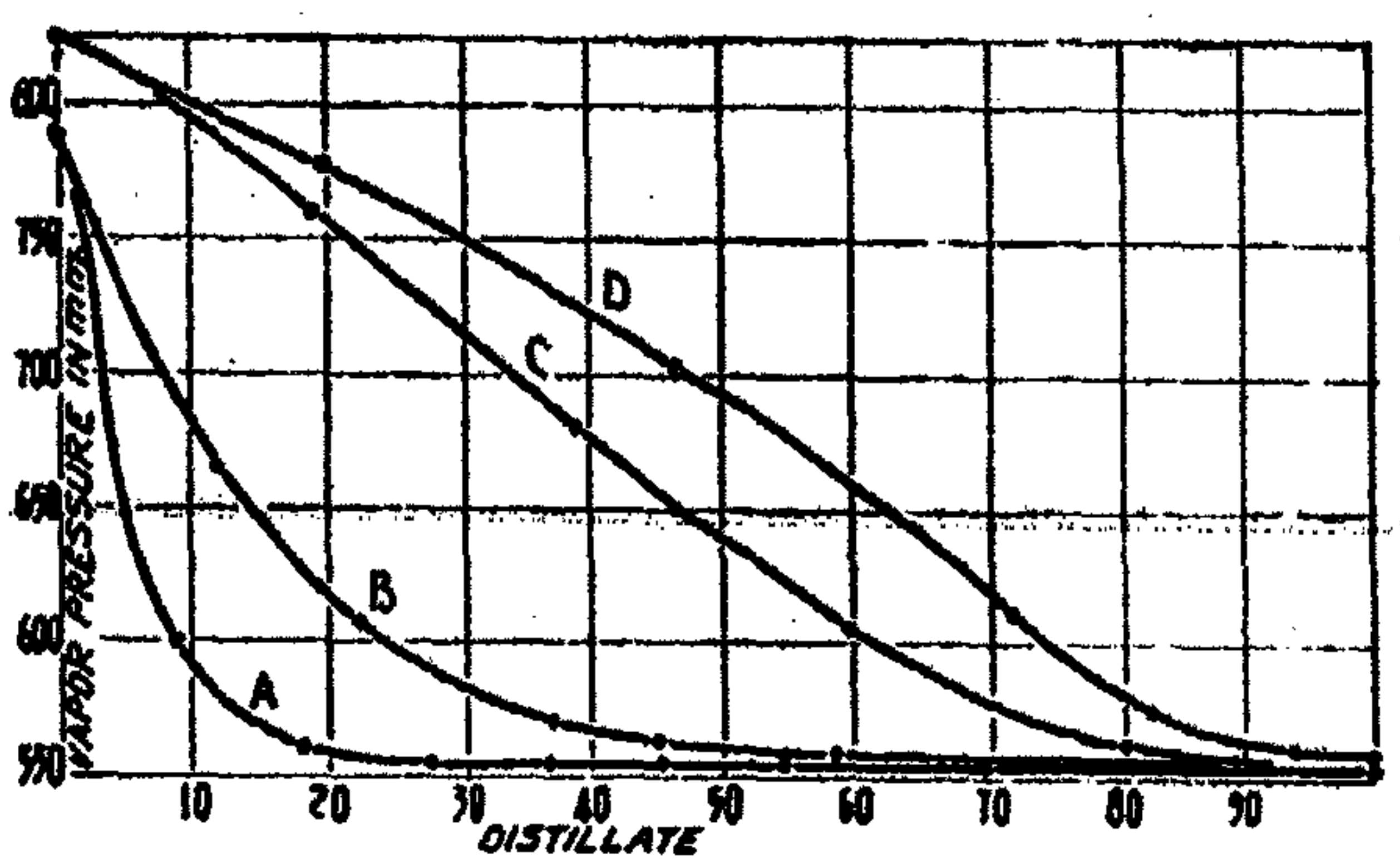

FIG. 2

Technical Phosgene.
A. Bubble distillation
B. Surface distillation
Phosgene – SO_2.
C. Bubble distillation.
D. Surface distillation.

The curves shown in Figure 2 are typical of all the results obtained. Curve B represents the distillation of technical phosgene in a simple distilling tube, and shows that after the distillation of 60% of the sample, the remaining 40% had a vapor tension of 557 mm. Curve A represents the distillation of the same sample in the new type of distilling bulb, and shows the same vapor

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[1] J. Phys. Chem., 29, 102 (1925).

[2] Cardoso and Germann: J. Chim. phys., 11, 632 (1913).

[3] Kuenen and Robson: Phil. Mag., (6) 3, 149 (1902).

[4] Mund: Bull. Acad. Sci. roy. Belg., (5) 5, 529 (1919).

tension, 557 mm., for 80% of residue, with a loss of only 20% of the sample. Curves D and C show similar results for the solution of sulfur dioxide. It is quite evident then, where a series of fractional distillations is carried out, that the vacuum ebullition tube is quite as efficient in the fractional distillation of liquefied gases as is the use of an inert gas as described by Ramsay and Travers, and makes it possible to secure all the advantages of air ebullition devices for all types of distillation.

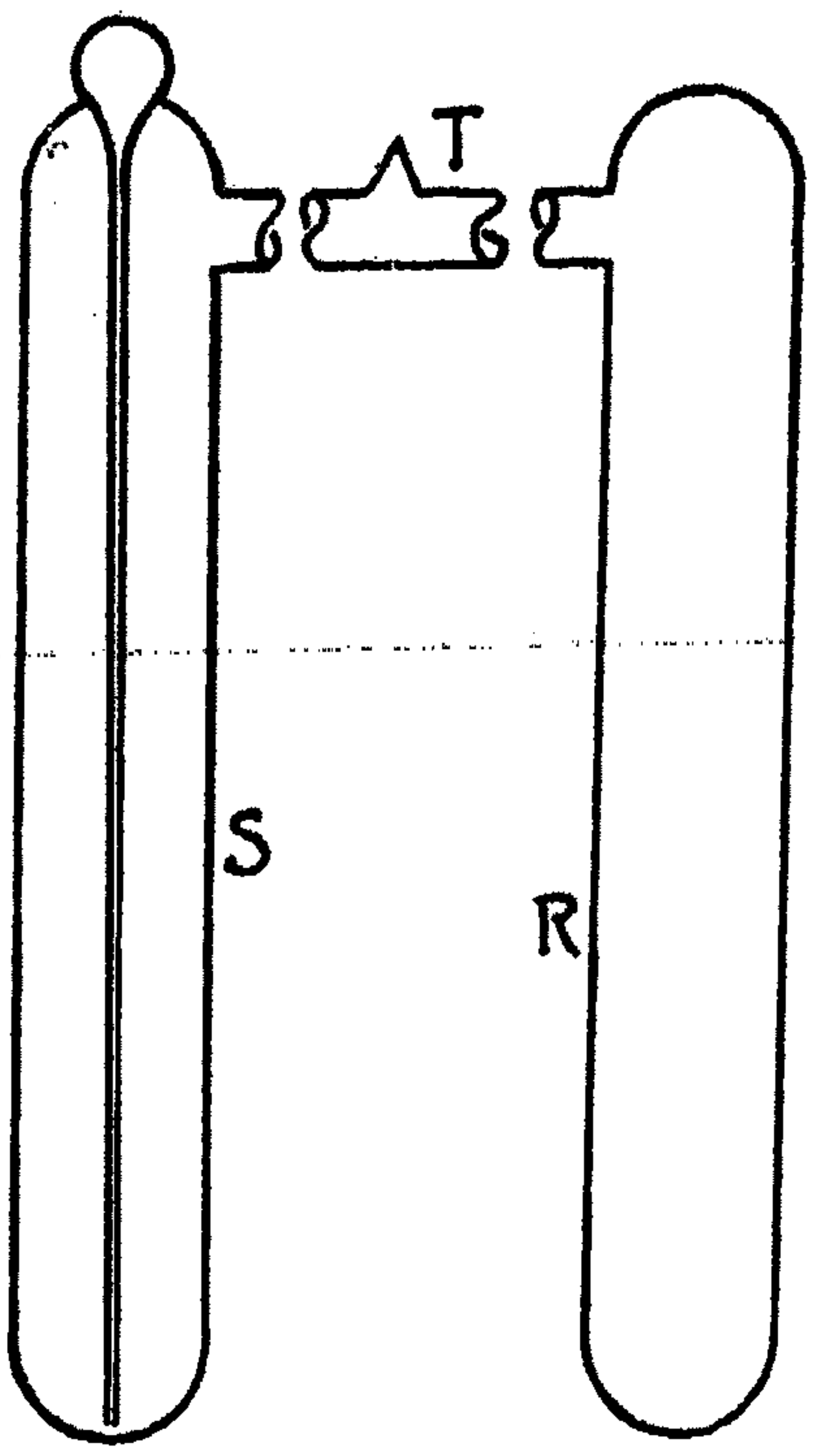

Fig. 3

Explanation of the Ebullition Phenomenon

In the ordinary distilling tube, where evaporation takes place entirely at the surface, the lower portions of the liquid will be at a higher temperature than the surface layer, where the heat received by conduction and radiation from the environment is used up as latent heat of evaporation. This accounts for the phenomenon of bumping, due to the sudden production of a free surface in the superheated lower part of the liquid, and the conversion of a large amount of liquid into vapor at the free surface thus formed. In the ebullition type of distilling bulb, a free surface is maintained near the bottom of the liquid, at or near the end of the capillary tube, and the higher vapor tension of the liquid beneath the surface, caused by the tendency of the liquid to superheat, results in evaporation at this nearest free surface, increasing the volume of the vapor in the capillary tube to overflowing, with consequent uniform boiling. With liquefied gases the maintenance of a free surface in the capillary below the surface of the liquid results at first from the fact that the pressure over the surface is diminished by cooling the receiver, thus expanding the vapor in the capillary tube, and forcing the liquid out; later, i.e. after the establishment of approximate pressure equilibrium, the capillary tube above the liquid surface is warmer than that below the surface, so that even though the liquid were to rise in the capillary to some point above the surface of the bulk of the liquid, by virtue of its surface tension, the higher temperature would cause evaporation, driving the liquid down again.

Fig. 3 represents a form of demonstration apparatus, a simple distilling tube R joined to an ebullition type tube S; the apparatus contains a volatile liquid, such as ether, all air is pumped out, and the apparatus is sealed off at T. Either tube may serve as receiver, while the other acts as distilling tube; the receiver is placed in an ice bath, and either surface or bubble distillation demonstrated.

The phosgene for this investigation was supplied by Edgewood Arsenal.

Summary

A simple ebullition device has been described which functions positively for all classes of distillation.

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ON THE THEORY OF PEPTISATION

BY K. C. SEN

Several papers have been published which intend to give an outline of the general theory of peptisation of a substance. In general it is assumed that adsorption of the peptising agent precedes the formation of a colloidal solution. If we have a precipitated substance, then in order to peptise it, it is necessary that the cohesive force which exists between the individual particles of the agglomerated substance for one another should be made less. Thus according to Bancroft[1], "peptisation consists in the disintegration of particles so that they form a colloidal solution. We get a permanent colloidal solution[2] whenever the particles are small enough to be kept in suspension by the Brownian movements and *in some way* are prevented from coalescing. Freundlich[3] has postulated that all adsorption is accompanied by a lowering of the surface tension of the adsorbing phase. The theoretical deduction is unsound because the Gibbs theorem applies explicitly to true solutions and not to suspensions. On the other hand, Freundlich's assumption seems to be true experimentally in all cases which have been studied from this point of view. If we accept Freundlich's generalization as true empirically, a theory of peptisation follows at once. Any substance which is adsorbed by a second will lower the surface tension of the second substance and will therefore tend to disintegrate it, in other words, to peptise it. If every adsorbed substance tends to peptise the adsorbing substance, we may expect to get peptisation by a solvent; peptisation by a dissolved non-electrolyte; peptisation by an ion; peptisation by a salt; peptisation by a colloid".

There is no doubt that Bancroft's conclusions are perfectly general if we assume that adsorption always lowers the surface tension between the adsorbing substance and the medium. The less the interfacial tension, the easier it should be to disintegrate the substance in the particular medium. Hence normally there should be some connection between peptisation and the amount of adsorption, though Bancroft considers it to be not necessary. "Since the adsorption depends on the surface and since peptisation involves breaking down the cohesion of particles, there is no necessary connection between the amount of adsorption and the ease of peptisation". This reasoning may well apply in the case of porous substances such as charcoal, but it is difficult to follow in the case of, say, precipitated hydroxides like iron hydroxides or albuminium hydroxide. Thus in these cases it is no doubt true that "the colloidal mass which has only just agglomerated, can often be peptised without difficulty. If the coalescing surfaces are allowed to set or if the substance is heated so that sintering takes place, peptisation becomes extremely difficult",

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[1] J. Phys. Chem. **20**, 85 (1916).

[2] J. Phys. Chem. **18**, 552 (1914).

[3] "Kapillarchemie" 52, 154 (1909); Patrick: Z. physik. Chem. **86**, 545 (1914).

but along with this fact it should be observed that the amount of adsorption of the peptising substance is also diminished. This will be illustrated with an example from the results obtained with hydrated ferric oxide and arsenious acid.

TABLE I

Nature of the hydroxide	Amount of adsorption	Remarks
Freshly precipitated dark brown	80%	Peptisation extremely easy
Same sample after four months under water	40%	With low concentration of the acid, there is no peptisation
Air dried Sample	10%	Can be slightly peptised with high concentrations of the acid

It will be observed that with the change in the physical nature of the substance, peptisation becomes difficult and along with this, the amount of adsorption also decreases. It is well known that increasing the concentration of the solute means an increased adsorption by the adsorbent. It is therefore expected that with higher concentrations of the arsenious acid, more of the hydroxide would be peptised. This view is confirmed by the results given in Table II.

TABLE II

Adsorbent—freshly precipitated ferric hydroxide. wt. = 0.2645 gr.

Conc. of As_2O_3 in grms. per 100 cc.	amount of adsorption in grams	Remarks
0.09468	0.07448	No colloid
0.12624	0.08748	No colloid
0.15780	0.09228	Supernatant solution slightly turbid
0.18936	0.09846	Supernatant solution very turbid.

These results therefore show that there is some connection between the amount of adsorption and ease of peptisation. It is also well known that with the addition of greater and greater amounts of the peptising agents the colloid reaches a maximum point in stability, after which the stability actually diminishes in some cases[1]. Hence peptisation of a substance with increase in the addition of the peptising agent would also reach a limit in cases where

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[1] Sen: J. Phys. Chem. **28**, 1029 (1924); Sen and Mehrotra: Z. anorg. Chem. **142**, 345 (1925).

there is no soluble salt formation at higher concentrations of the peptising agent. This effect is due to the ion charged oppositely to the stabilising ion. This phenomenon has also been realised in the peptisation of ferric hydroxide by arsenious acid. Hence when ion peptisation is taking place, the amount of the substance which can be peptised is limited owing to the presence of oppositely charged ions in the solution, and to the possibility of the formation of a soluble salt. Thus in the peptisation of alumina by acetic acid, Bentley and Rose[1] state that, "equal portions of a specimen of the hydrated oxide containing about four molecules of water, were treated with equal volumes of acetic acid varying by tens from 99.8 percent acid down to 40 percent and by ones down to one percent. It was found that above 40 percent acid scarcely any hydrosol was formed, since hydrochloric acid did not produce coagulation. Normal aluminium acetate was the product formed. From 40 percent down, the amount of hydrosol steadily increased as did the ease with which the material dissolved until a 4 percent acid was reached. Below 4 percent the material dissolved only partly, the remainder swelling up to an almost transparent mass, which after prolonged treatment, formed an opalescent and most easily coagulated solution. For practical purposes, we consider about 8 percent the most favorable strength". It will appear therefore that when the same substance is used for peptisation, favourable conditions are a high degree of adsorption and a suitable concentration of the peptising agent. When however different substances are used with the same peptising agents, a marked specificity is observed. Table III the results obtained experimentally on the peptisation of different hydroxides by various acids and some salts are summarised.

TABLE III

Peptising agent	Substance		
	$Fe(OH)_3$	$Al(OH)_3$	$Cr(OH)_3$
Hydrochloric acid	++	++	+
Acetic acid	+	++	−
Propionic acid	+	++	−
Butyric acid	+	++	−
Benzoic acid	−	++	−
Amido benzoic acids	−	+	−
Citric acid	−	−	−
Tartaric acid	−	−	−
Oxalic acid	−	−	−
Sulphuric acid	−	−	−
Arsenious acid	++	+	−
Sodium arsenite	+	−	−
Sodium phosphate	+	−	−
Sodium citrate	+	−	−

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[1] J. Am. Chem. Soc. 35, 1490 (1913).

In Table III + + means very readily peptisable; + means that the peptisation takes place only with high concentrations of the peptising agent whereas – means that no peptisation takes place under ordinary conditions[1]. The hydroxides used were all freshly prepared and from the results given in another paper it will be found that all these acids are greatly adsorbed by the hydroxides. The main point which has come out from these peptisation experiments is that though adsorption always precedes colloid formation, the peptising powers of different acids are not necessarily proportional to the amounts of their adsorption as measured by the decrease in the hydrogen ion concentration of the solutions. Also the same acids behave differently in the case of different hydroxides. Thus chromium hydroxide could not be peptised by the majority of the acids used though this hydroxide has the greatest adsorbing power. Aluminium hydroxide could not be well peptised by arsenious acid, though ferric hydroxide is peptised very readily by arsenious acid. From equivalent concentrations, acids like oxalic, sulphuric, etc. are more adsorbed than acetic, benzoic or hydrochloric acids, but hydrochloric or acetic acid peptises the hydroxides of iron and aluminium while the former acids can hardly peptise them. On the other hand, benzoic acid does not peptise ferric hydroxide, but not only benzoic acid, but other derived benzoic acids such as oxybenzoic acid, o-m-p amido benzoic acids etc. can peptise aluminium hydroxide very readily. In the case of monovalent acids, the rule is approximately followed—namely, the greater the adsorption the greater is the peptising power. The exceptional behaviour of the dibasic and tribasic acids is due to the presence of divalent and trivalent negative ions which prevent the formation of a positively charged colloid.

There are other differences manifested when salts are used. Thus sodium arsenite, sodium phosphate or sodium citrate can stabilise a suspension of ferric hydroxide with a negative charge; but they have no action on either aluminium hydroxide or chromium hydroxide, though chromium hydroxide adsorbs sodium arsenite to a much greater extent than ferric hydroxide does. It appears therefore that we have to recognise some selective tendency in colloid formation. Simply amount of adsorption is not a measure of the peptising power of an electrolyte, and the nature of the adsorbing surface is also important.

The general conclusions of Bancroft have already been given. It will be noted that according to the theory, peptisation may be brought about by any substance which is adsorbed by an adsorbing substance. Thus the peptising power of water on glass at higher temperature, that of a mixture of alcohol and water on zein etc. may be cited as instances of peptisation by the medium. Cases of ion peptisation and peptisation by means of a colloid are well known. Sugar and several such non-electrolytes prevent the precipitation of ferric hydroxide in solution, and Bancroft considers it to be a case of peptisation by non-electrolyte. Though no case of peptisation by a dissolved undissociated

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[1] Compare however Sen and Dhar: Kolloid-Z. 33, 193 (1923); J. Phys. Chem. 27, 376 (1923).

salt has been studied, he considers that such cases will undoubtedly be found. In this paper I shall only deal with the peptisation of substances by ions, by colloids and by non-electrolytes. Since the experiments have been mainly done in aqueous solutions, I shall limit the study to colloids which are dispersed in water, and as such the cases of organic liquids will not be considered.

In the first page I have italicised a few words from the quotation taken from Bancroft's paper. Since by peptisation we mean that a stable colloidal solution is obtained, it is obvious that disintegration of a precipitate must be followed by the stabilisation of the particles against gravitational force and the surface forces on the particles. This stabilisation after disintegration is at least as important as the process of disintegration itself, and no study of peptisation is complete without a concomitant study of the stability relations of the peptised substance. A scrutiny of the sources of stability of these peptised substances reveal certain interesting facts which seem to the author to change some of our conceptions about the phenomenon of peptisation by different substances.

It is well known that the existence of a Brownian movement alone does not make a colloid stable and a suitable surface film[1] is necessary to prevent the coalescence of the particles. In the case of *pure hydrosols, this film is* almost entirely of electrical origin. This fact has been recognised by almost all the colloid chemists. Thus Hatschek[2] observes: "It follows from Perrin's investigation that particles in Brownian movement—like molecules of a gas or a dissolved substance—tend to fill the space in which they are contained according to definite laws. The movement must therefore be considered as one of the factors which keep a sol stable, but is not by itself, sufficient to account for its stability, as particles showing moderate Brownian movement may still settle with comparative rapidity. The stability is intimately connected with the electric charge, to which reference has already been made. It may be said generally that any substance in contact with water and many other liquids, assumes an electrical charge, the origin of which is not definitely explained. Most substances become negatively charged in contact with water. The charge can be varied and even reversed by the additon of electrolytes and may become zero at suitable concentrations. In this condition, as shown by Burton and by Hardy, sols are particularly unstable, and tend to precipitate.

"It need be hardly mentioned that the electric charge is not confined to submicroscopic particles, but is found equally on the particles of a coarse suspension. It has also been known for a considerable time that the speed of settling in many suspensions —which settle in any event—can be increased by the addition of electrolytes. The greater sensitiveness of the highly dispersed systems must be ascribed to the very much greater charge due to the enormous increase in surface. At the same time, while the existence and the stabilis-

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[1] Bancroft: J. Phys. Chem. 18, 552 (1914).

[2] "An Introduction to the Study of the Physics and Chemistry of Colloids", pp. 27-29 (1913).

ing influence of the charge is fully established[1], it must be said that the origin of the charge and the mechanism of its action is still rather obscure".

It is thus evident that the existence of electric charge which, among others, is the source of stability of a colloidal solution and is equally important as the Brownian movement of the particles must be accounted for in any theory of peptisation. Since electrical charge is necessary for the stabilisation of the sol, it is evident that the peptisation is not complete where simply the disintegrating effect of the peptising substance has taken place. To make the disintegrated particles stable as a suspension in the medium, the particles must get the necessary amount of surface charge. Two processes are therefore involved in the phenomenon as pictured above: (1) The decrease in the interfacial tension between the particles and the medium owing to an adsorption of the peptising substance by the adsorbing mass whereby the cohesive force between the individual particles are diminished and (2) the formation of an electrical film on the surface of the particles which counteracts the effect of surface attractions of small particles to form big ones. Since it is now generally assumed that the charge on colloidal particles and surfaces is due to a preferential adsorption of some ions from the medium, it is easy to account for the electric charge on the particles once they have been disintegrated through the adsorption of the peptising substance.

If these considerations are applied to the case of peptisation of a precipitate by ions, the phenomenon becomes simple and the two processes become actually identical. If every adsorbed substance lowers the surface tension of the adsorbing substance, then when ions are adsorbed preferentially, both the disintegration of the mass and the electrification of the surface of the particles become probable. The same reasoning would apply in the case of peptisation by colloids.

In the case of peptisation by non-electrolytes and by undissociated neutral salts the explanation is however difficult and we have to assume that disintegration and electrification of the surfaces are two distinct and separate processes. Since non-electrolytes would disintegrate the precipitate and preferential adsorption of ions from the medium would stabilise the suspension, it is difficult to say which is really the peptising agent. We may however assume in the first instance that only ions are effective in peptisation. By peptisation is meant the final stage at which a precipitate or a precipitating substance is obtained as a stable colloidal solution. Assuming this as a working hypothesis, I shall deal with the effect of solvent, of non-electrolytes, of ions and salts on the stabilisation of a colloid.

Cases of ion peptisation are well known in the literature. When one ion of an electrolyte is adsorbed more than the other, it will tend to peptise the adsorbing material and to give rise to a colloidal solution containing positively or negatively charged particles according to the ion adsorbed preferentially.

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[1] It is obvious however that there may be non-electrical suspensions, e.g. Wo. Pauli's electrolyte-free albumin, where the stability is probably due to the high solvation of the micellae. The conditions of stability of these suspensions are rather obscure, and in the article only those colloids which are usually electrically charged have been considered.

Since usually the higher the valence of an ion, the greater is its tendency to become adsorbed, it follows that higher valent ions will have a greater peptising power than ions of lower valence. There are however exceptions to this, namely in some cases, monovalent ions are more adsorbed than higher valent ions.

Since hydroxides of metals are known to be good adsorbents of acids and alkalis, it is expected that ionic peptisation would be easy in these cases. Several instances of peptisation of metallic hydroxides by acids are already known in the literature. A Müller[1] has prepared colloidal solutions of aluminium, iron, cobalt, thorium and yttrium oxides by peptisation with dilute hydrochloric acid. Bentley and Rose[2] peptised alumina with acetic acid. In this paper I have shown that both ferric and aluminium hydroxides can be peptised by suitable acids, and the nature of the charge on the particles depends on the nature of the ion adsorbed preferentially[3].

Among peptisation by means of salts, Müller's[4] experiments on the stabilisation of thorium hydroxide by thorium nitrate and zirconium hydroxide in zirconium nitrate solution may be mentioned. Szilard[5] peptised a number of rare earth hydroxides by means of the chlorides or nitrates of the same metals. Both chromic chloride and ferric chloride appear to dissolve a certain quantity of the respective hydroxides, and we know that these apparently clear solutions contain peptised hydroxides. In a previous paper[6] it has been assumed that the free acid is the real peptising agent, but it appears that it is almost impossible to decide experimentally whether the metal ions are also active or not[7]. It is probable that both the hydrogen ion and the metal ion are simultaneously adsorbed by the hydroxide in some cases.

In the case of peptisation by acids, it is usually considered that the hydrogen ion is the peptising agent. There is no reason therefore why in the peptisation of hydroxides by alkalies, hydroxyl ions would not be considered to be the peptising agents. Both chromic oxide[8] and copper oxide[9] are peptised by caustic alkali. Hantzsch[10] considers that beryllium oxide is peptised by caustic potash and apparently so is cobalt oxide.[11] An alkaline solution of zinc hydroxide may be colloidal,[12] partly colloidal[13] or may be a definite zincate.[14]

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[1] Svedberg: "Die Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe", 400 (1909).

[2] J. Am. Chem. Soc. 35, 1490 (1913).

[3] Sen and Dhar: Kolloid-Z. 33, 193 (1923); J. Phys. Chem. 27, 376 (1923).

[4] Ber. 39, 2857 (1906); Z. anorg. Chem. 52, 316 (1907).

[5] J. Chim. Phys. 5, 488, 636 (1907).

[6] Kolloid-Z. (1925).

[7] Compare Weiser: J. Phys. Chem. 24, 310 (1920).

[8] Nagel: J. Phys. Chem. 19, 331, 569 (1915): Fischer and Herz: Z. anorg. Chem. 31, 352 (1902).

[9] Loew: Z. anal. Chem. 8, 463 (1870); Fischer: Z. anorg. Chem. 40, 39 (1904).

[10] Z. anorg. Chem. 30, 289 (1902).

[11] Tubandt: Z. anorg. Chem. 45, 368 (1905).

[12] Hantzsch: Z. anorg. Chem. 30, 289 (1902).

[13] Fischer and Herz: Z. anorg. Chem. 31, 352 (1902).

[14] Klein: Z. anorg. Chem. 74, 157 (1912).

Bancroft[1] considers that freshly precipitated zinc hydroxide is peptised by alkali; but the solution is very unstable, the zinc hydroxide often coagulating inside of half an hour. The relatively small amount of zinc remaining in solution is present chiefly or entirely as sodium zincate. Freshly precipitated alumina may be partly peptised[2] but the alkaline solutions contain some sodium aluminate[3].

Alkaline copper hydroxide solutions present some peculiar features. That these solutions are more or less unstable is evident from the fact that light of suitable wave-length will decompose Fehling's solution[4] with the precipitation of cuprous oxide. When an ammoniacal solution of copper sulphate is exposed to strong sun-light, decomposition also takes place. Much more interesting is the fact that all alkaline solutions of copper hydroxide are blue in colour. Reference to this behaviour has already been drawn in a previous paper[5]. It is generally believed that alkaline solutions of tartrates dissolve cupric hydroxide forming a complex negative ion and the colour of these solutions is blue[6]. The same sort of blue colour is obtained when cupric hydroxide is dissolved in ammonia, or caustic soda, as also in the case of peptisation of cupric hydroxide by means of alkali in presence of glycerol or sugars. It is very difficult to explain the production of the same colour on the view of complex formation, as the same colour is developed by so many different reagents. Since, however, the production of this blue colour is dependent upon an excess of hydroxyl ions, it appears probable that the colour is due to the negatively charged colloidal copper hydroxide. As a matter of fact, Grimaux[7] thought long ago that in ammoniacal copper oxide solutions part of the copper oxide is colloidal and part dissolved.

The peptisation of metallic sulphides by means of hydrogen sulphide is an instance where the negative ion is more adsorbed than the easily adsorbable hydrogen ion, thus giving a negative charge to the particles. Thus colloidal copper sulphide[8], cadmium sulphide[9], zinc sulphide[10] etc. can be easily prepared by suspending the freshly precipitated and well washed sulphides in water and passing a current of sulphuretted hydrogen through them. The excess of hydrogen sulphide may then be removed by a current of hydrogen, but it is not possible to free the colloids from adsorbed hydrogen sulphide[11].

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[1] J. Phys. Chem. 20, 99 (1916).

[2] Mahin, Ingraham and Stewart: J. Am. Chem. Soc. 35, 30 (1913).

[3] Herz: Z. anorg. Chem. 25, 155 (1900); Hantzsch: 30, 289 (1902); Rubenbauer: 30, 331 (1902); Fischer and Herz: 31, 355 (1902); Slade: J. Chem. Soc. 93, 421 (1908); Z. anorg. Chem. 77, 457 (1912); Trans. Faraday Soc. 10, 150 (1914); Blum: J. Am. Chem. Soc. 35, 1499 (1913).

[4] Bennett: J. Phys. Chem. 16, 782 (1912); Leighton: 17, 205 (1913); Byk: Z. physik Chem. 49, 659, 679 (1904).

[5] Dhar and Sen: loc. cit.

[6] Masson and Steele: J. Chem. Soc. 75, 725 (1897).

[7] Compt. rend. 98, 1434.

[8] Spring: Ber. 16, 1142 (1883).

[9] Prost: J. Chem. Soc., 54, 653 (1888).

[10] Winssinger: Bull. (3) 49, 452 (1888).

[11] Linder and Picton: J. Chem. Soc. 61, 116 (1892).

Since from an acid solution either the positive or the negative ion may be adsorbed preferentially at certain concentrations of the acid, it is evident that in studying adsorption we must take note of the simultaneous adsorption of both the ions from solution. The preferential adsorption of one ion stabilises the colloid, but with the increase in the concentration of the added electrolyte, the stability usually reaches a maximum owing to the increased adsorption of the other ion of the added electrolyte. With the further addition of the electrolyte the colloid will coagulate, and at the coagulation point the stabilising ions adsorbed by the colloid are just neutralised by the adsorption of the oppositely charged ions of the coagulating electrolyte. This being the usual conception of the coagulation process, it is evident that the adsorbed salt does not function as a peptising agent. Hence it becomes difficult to follow Bancroft's views as to the importance of the adsorbed salt in the phenomenon of peptisation. As the facts however have an important bearing on the theory, I will quote from Bancroft's paper to some extent.

"The possibility of peptisation by an adsorbed salt seems to have been pretty generally overlooked in the books on colloid chemistry, presumably because an increase in the concentration of a peptising salt is apt to cause coagulation. Theoretically the matter is quite simple. We start with an ion peptisation because one ion is adsorbed more than the other. With increasing salt concentration we reach the point where the adsorption of the first ion varies but slightly with the concentration. The adsorption of the second ion continues to increase relatively to the first ion until we get what has been called neutralisation of the adsorbed ion[1], and consequently coagulation. At the same time the adsorbed salt is tending to peptise the substance; but if its peptising action is relatively small, there may be quite a large range of concentrations over which the ion peptisation has ceased to be effective and the salt peptisation has not begun to be effective. With still greater salt concentration, we should expect to get salt peptisation; but a number of disturbing factors may come in. The salt may not be sufficiently soluble at the temperature of the experiment or it may react with the substance to be peptised. If we increase the hydrochloric acid concentration with the oxides of aluminium, iron, cobalt, etc., we finally get the chlorides of these metals in true solution. If we increase the caustic soda concentration with silicic acid, we consider that we get sodium silicate in true solution. If we increase the potassium bromide concentration with silver bromide we say that we get a complex salt in true solution. It may be that we are wrong in this and that we are getting peptisation in some of these cases. For years we thought that the so-called basic chlorides were definite compounds forming true solutions, whereas now we know that many of them are not. With silver iodide and a concentrated silver nitrate solution[2] we apparently get a definite compound, $2AgNO_3 . AgI$; with silver bromide also a definite compound $AgNO_3 . AgBr$; but it is not

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[1] Bancroft: J. Phys. Chem. 19, 363 (1915).

[2] Risse: Ann. 111, 39 (1859).

probable that there is any such compound as $18AgNO_3 . AgCl$, so it may be that here we have a case of peptisation by an undissociated electrolyte.

"It is possible that von Weimarn's peptisation of cellulose[1] by salt solutions may come under this head. Three grams of cellulose were heated with about 100 cc concentrated salt solution and were thereby peptised, the mixture usually cooling to a jelly. With NaI, CaI_2, SrI_2, $CaBr_2$, $Ca(SCN)_2$ and $Ba(SCN)_2$ peptisation took place at atmospheric pressure. With NaCl a temperature of 170° and a pressure of 8 atm. were necessary, and incipient decomposition seemed to take place. Deming[2] peptised cellulose with salts dissolved in acid solutions. In all these cases of possible peptisation by undissociated salts, there may be an ion peptisation and a water peptisation superposed which, of course, complicates matters considerably. Oxides of mercury or less noble metals are adsorbed by mercury. I do not know any conditions under which they will peptise mercury unassisted, though it is very possible that this might take place at higher temperatures. If we disintegrate the mercury mechanically, it is possible to obtain a colloidal solution and here we unquestionably have an undissociated salt".

This would be undoubtedly true if we can prove it, but unfortunately no case exists in which peptisation by undissociated salt has been obtained. The assumption that an undissociated salt may disintegrate a substance follows from the theory of Freundlich, but the adsorption of undissociated salt cannot stabilise a suspension because it does not confer any electrical charge nor will it usually form a suitable surface film on the particles. As such, theoretically no case would be found where a precipitate has been peptised by the adsorption of undissociated salt. When metals are disintegrated by means of high tension electric current, we ought to get a colloidal solution very easily. As a matter of fact, a number of precautions are due to be taken otherwise the particles would soon settle. A trace of alkali in the medium facilitates the formation of stable colloidal solutions of copper, etc. Beans and Eastlack[3] conclude that the stability of the colloidal solutions of gold is due to the adsorption of OH′ ions from water.

It is certainly true that with the increase in the concentration of the peptising agent, say hydrochloric acid in the case of alumina, we get a true salt in solution; that is chemical action takes place. Silicic acid can be peptised both by hydrogen as well as by hydroxyl ions. When caustic soda is added in excess, there is every probability of the formation of sodium silicate. There is nothing abnormal in these phenomena. The difficulty of explaining these lies in the way in which we have sharply differentiated the phenomenon adsorption from chemical reactions. In another paper I have shown of that there is practically no difference in the mechanism of selective adsorption and chemical reaction. When dilute hydrochloric acid acts on alumina, considerable adsorption of the acid takes place. With increasing concentration of the acid, the adsorption also increases, but after

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[1] Kolloid-Z. 11, 41 (1912).

[2] J. Am. Chem. Soc. 33, 1515 (1911).

[3] J. Am. Chem. Soc. 37, 2667 (1915).

some time we get aluminium chloride in solution. Since adsorption gradually merges into a definite chemical change, we may consider that adsorption is preliminary to chemical reaction. If this is conceded, and there are numerous experiments to support it, there is no difficulty in understanding why in some cases we get true salt formation and not peptisation with the increased concentration of the electrolyte. Since peptisation is an intermediate condition between a precipitate and molecular solution, we can get all three states according to the amount and nature of adsorption. Thus if we have a positively charged silicic acid sol, we can coagulate it by the addition of alkali due to the adsorption of OH′ ions. On increasing the concentration of alkali, the silicic acid will be peptised and in this condition it will be associated with a varying quantity of alkali. On further increasing the concentration of the alkali, we get a molecular solution of sodium silicate. The third stage may or may not be obtained according to the nature of the final product of the chemical change. If the final product is soluble in water, we may get it in true solution.

Lottermoser[1] showed that a stable colloid solution of silver halides can be only obtained when either silver nitrate or the halide of potassium is in excess in the solution. The nature of the charge was different and it indicated that the stabilisation was due to the preferential adsorption of either silver or the halide ions. If we increase the amount of one reagent, we may get or may not get a definite salt formation and this does not affect the theory in any way. For the explanation of the peptisation, the sufficient condition would be to have the necessary amount of adsorption for the disintegration and the stabilisation of the particles. The stabilisation is naturally due to the adsorption of ions and as such there can be nothing gained by postulating that undissociated salts have any effect on these systems. Simple ion adsorption would explain the stability of these suspensions.

From this point of view I would consider the peptisation of cellulose by salt solutions as cases of ion peptisation. Since cellulose appears to be a good adsorbing agent[2], it is probable that preferential adsorption of some ions takes place when it is heated with salt solutions. This ion peptisation would be marked in an acid or alkaline solution. This was found by Deming[3] who observed that working in an acid solution facilitated peptisation. It is of course not possible to say whether any preferential adsorption takes place from the medium when only salts are used. The H˙ or OH′ ions of water may have something to do with it. When glass is peptised by water at high temperature, we have undoubtedly a case of ion peptisation since the resulting sol is electrically charged. Gelatine can be liquefied by the addition of potassium iodide. Here the peptisation is due to the adsorption of iodide ions.

The peptisation by means of another colloid admits of the same explanation as in the case of ion peptisation. Since a colloid is usually charged, it can

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[1] J. prakt. Chem. (2) 68, 341 (1903); 72, 39 (1905); 73, 374 (1906); Z. physik Chem. 62, 371 (1908).

[2] Leighton: J. Phys. Chem. 20, 188 (1916).

[3] J. Am. Chem. Soc. 33, 1515 (1911).

stabilise a suspension of another substance provided it is adsorbed in suitable amounts, though in many cases the stabilisation seems to be due to ion peptisation. Thus hydrous chromium oxide is an alkali-soluble colloid[1]. Hydrous chromium oxide adsorbs the hydrous oxides of iron, nickel, cobalt, manganese, and copper; and hence peptises them to a certain extent. When chromium salt is present in large excess relatively to the iron salt, no iron oxide is precipitated; when the iron salt is present in excess, the chromium oxide remains in the water phase, the latter becoming colourless. The usual explanation is that colloidal chromium hydroxide adsorbs the iron hydroxide, and the resulting complex is stable or unstable according to whether the chromium salt concentration is very high or not. There is no objection to this, but it complicates matters because chromium hydroxide is itself stabilised by a third substance, namely hydroxyl ions. One wonders why the same substance, namely the hydroxyl ions, is not given the credit of peptising the small quantity of ferric hydroxide. That alkali does not peptise pure ferric hydroxide easily is no difficulty. I have found experimentally that chromium hydroxide adsorbs more alkali than hydrous ferric oxide. We can therefore suppose that the ease of peptisation with hydrous chromic oxide is due to the fact that greater amounts of hydroxyl ions are adsorbed by it, and hence though no peptisation occurs with hydrous ferric oxide under the same conditions, the latter can be peptised if hydroxyl ion adsorption can be increased. When alkali is added to a mixture of iron and chromium salt, both the hydroxides will tend to precipitate, and in doing so, will adsorb each other. The resulting complex will have different adsorption value from that of the individual substances. If the iron salt is much less, then the complex will have an adsorption value almost equal to that of the pure chromium hydroxide of same weight, and so the amount of adsorption of hydroxyl ions by the complex will mean an adsorption far in excess to that which could be adsorbed by the ferric hydroxide if it was present alone. The alkali will therefore peptise both the hydroxides. In case the iron is in excess, the resulting complex adsorbs as if the whole substance is pure iron oxide, and hence alkali does not stabilise the precipitates. As a matter of fact, the amount of ferric hydroxide which can be kept in suspension by colloidal chromium hydroxide is relatively very small. It is also reported that colloidal copper oxide peptised by ammonia causes the peptisation of hydrous chromic oxide by ammonia[2]. A similar explanation will apply to this case also.

The peptisation of substances by means of the so-called water-soluble colloids may be explained in the same way. It is probable that these colloids are really cases of ion peptisation and not water peptisation. There is no question about casein, which is insoluble in water and is only peptised by hydrogen and hydroxyl ions. Bancroft[3] prefers to consider albumin as a case of ion peptisation. There is no reason therefore why gelatine or tannin should not be considered also as cases of ion peptisation, the only assumption being that the

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[1] Nagel: J. Phys. Chem. 19, 331, 569 (1915).

[2] Prud'homme: J. Chem. Soc. 25, 672 (1872).

[3] J. Phys. Chem. 19, 349 (1915).

range of instability is very small. That gelatine is functioning as an ion-peptised colloid at least when it stabilises other suspensions seems to be probable from some results of Loeb[1], who found that at the isoelectric point of gelatine, it will not stabilise a suspension of collodion particles, but will do so only in presence of salts. When positively charged gelatine is mixed with negative tannin, precipitation is more marked, and here we are considering the effect of the mutual adsorption of two ion-peptised colloids. When ammoniacal gelatine is added to a ferric hydroxide colloid, precipitation occurs, whereas there is no precipitation if the gelatine and ferric hydroxide sols are mixed before the ammonia is added. The explanation is not difficult. Ammoniacal gelatine is negatively charged and hence by the addition of this negative colloid to the positive ferric hydroxide sol, we get charge neutralisation due to the mutual adsorption of the two sols. When however simply gelatine is added to the ferric chloride solution, in presence of acid, it becomes positively charged. By the addition of small quantity of ammonia a positively charged colloid complex of ferric hydroxide and gelatine is formed and when excess of ammonia is added, the charge on the colloid is reversed. The whole phenomenon seems nothing but a case of charge reversal of colloidal ferric hydroxide. An exactly analogous case will be given. When alkali is added to a mixture of ferric chloride and glycerol or sugar, no peptisation is obtained. If a mixture of sugar and alkali is however added to a ferric chloride solution immediate precipitation of the hydroxide takes place. We know definitely that in presence of glycerol or sugar, hydrous ferric oxide can remain peptised either as a positively charged or a negatively charged colloid, depending upon the concentration of the added alkali. The only difference between the two cases is that in one we have sugar which is a non-electrolyte, and in the other gelatine which is either an uncharged substance or an ion peptised colloid. It is also well known that gelatine behaves as a positively charged colloid in acid solution and as a negatively charged one in presence of hydroxyl ions. Thus Billitzer[2] finds that gelatine precipitates such negative colloids as antimony sulphide and arsenic sulphide in acid or neutral solution, but does not precipitate positively charged sols such as hydrous ferric oxide. Positively charged sols are only precipitated when an alkaline gelatine is added. Bismark brown, which is a positive colloid, is precipitated by alkaline gelatine solution while eosine is precipitated by an acidified gelatine solution. When gelatine is mixed with the so-called soluble silicic acid, Graham[3] finds that "silicate of gelatin falls as a flaky, white and opaque substance, when the solution of silicic acid is added gradually to a solution of gelatine in excess. The precipitate is insoluble in water and is not decomposed by washing". This is apparently a coagulation of two oppositely charged colloids.

When gelatine solution is poured on a freshly precipitated silver bromide, the latter is peptised[4]. The effect is more marked in presence of a slight

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[1] J. Gen. Physiol. 5, 479-504 (1923).

[2] Z. physik. Chem. 51, 145 (1905).

[3] J. Chem. Soc. 15, 246 (1862).

[4] Eder's Handbuch der Photographie, 31, 28 (1902); Lüppo-Cramer: Phot. Correspondenz, 44, 578 (1907).

excess of potassium bromide or silver nitrate. Freshly precipitated red silver chromate can be dispersed by gelatine into a yellow sol. In all these cases it is probable that the peptisation is due to the water-soluble colloid, but ion peptisation is also possible. It would be interesting to investigate whether isoelectric gelatine can emulsify pure silver bromide.

The nature of peptisation of certain hydroxides in presence of some non-electrolytes is interesting when we consider that these peptised solutions are only stable in presence of an excess of acid or alkali. Thus ferric hydroxide is stable both in acid and alkaline medium whereas copper hydroxide can only be peptised when the solution is alkaline. When alkali is added gradually to a mixture of ferric chloride and sugar, there is no formation of a precipitate but at the same time no test of free alkali is obtainable in the solution. What happens is that at first a positively charged colloid is formed. Owing to the presence of undecomposed ferric chloride, the stability is quite high, but with the gradual addition of alkali, the charge diminishes and the colloid ultimately coagulates. If the hydroxyl ion concentration is still more increased, the coagulum dissolves, forming a negatively charged sol. This coagulation and stabilisation into either positively charged or negatively charged sol can be brought about as many times as desired by simply adding suitable quantities of either acid or alkali. Since this is so, the question arises, what is the function of sugar or glycerol in this case of peptisation? That the non-electrolyte has some action is evident from the fact that we do not usually get a negatively charged ferric hydroxide with caustic soda unless precautions are observed[1]. On the other hand, sugar does not stabilise the colloid in the absence of an excess of H' or OH' ions.

I consider that this simple experiment shows definitely that non-electrolytes like sugar or glycerol do not peptise a precipitate. Their disintegrating action, if any, is small. But the mechanism of their action lies in the fact that when they are present in the solution, they are adsorbed by the precipiting particles and thus prevent the growth of crystals[2]. In other words, due to this surface film, coalescence is to a certain extent prevented and the precipitating substance is at this moment stabilised by the preferential adsorption of some ions present in the solution. It is also probable that the presence of these non-electrolytes increases the amount of ion adsorption. If no ion is preferentially adsorbed, the precipitate settles down because the surface film of the non-electrolyte is not sufficient to counteract the effect of the surface forces in the absence of electrical films over the particles. Thus the non-electrolytes help the ion peptisation of the substance indirectly. This explanation of the protective action of the non-electrolytes seems likely from the fact that their adsorption is usually small, and in presence of electrolytes the stabilised colloid shows changes in its migration velocity under an electrical field almost proportional to the concentration of the added electrolyte.

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[1] Powis: J. Chem. Soc. 107, 818 (1915).

[2] Bancroft: "Applied Colloid Chemistry", 165 (1921).

When we powder a substance, we call it disintegration. When dilute hydrochloric acid acts on alumina, we say that the alumina is disintegrated and stabilised into a colloid solution. This is peptisation. When gelatine acts on silver bromide we are getting peptisation. When non-electrolytes are present in the solution before precipitation, they prevent the growth of crystals. In presence of gelatine, the crystals of barium sulphate are very small. Here we have got some protective action, but no peptisation. There may not be any real difference between disintegration and protective action because both are due to the adsorption of the disintegrating or the protective substance. But these disintegrated or protected substances must be stabilised by the preferential adsorption of some ions, which make the colloid stable. Here we actually get peptisation. This is true at least in the case of suspension colloids stable in aqueous solution, and may also be true in the case of pure emulsions. From this point of view I think that the terms protective action, disintegration, and peptisation should be carefully defined.

The general results of this paper are:

1. In the peptisation of a substance, a high degree of adsorption and a suitable concentration of the electrolyte is necessary.

2. When the same electrolyte and the same peptisable substance are used, peptisation depends upon the amount of adsorption to a certain extent.

3. The agglomeration of a precipitate decreases its power of adsorption and consequently its peptisability.

4. When different peptisable substances are used, peptisation is specific and depends both upon the nature of the adsorbent and also on the nature of the peptising agent.

5. With different acids and the same adsorbent, there may not be any connection between the amount of adsorption and the ease of peptisation. Peptisation is markedly retarded by the presence of bivalent or trivalent negative ions, though these acids are usually the highest adsorbed. With monovalent acids, the rule is approximately followed—namely the greater the adsorption the greater is the peptising power.

6. It has been shown that almost all the known cases of colloid formation in aqueous solution can be explained as cases of ion peptisation or peptisation by means of an ion-peptised colloid. It is extremely doubtful whether non-electrolytes can peptise a substance. It has been shown that peptisation by an undissociated salt is not probable.

7. The stability of hydrosols is dependent on the formation of a suitable surface film and in the majority of cases it is electrical in origin. Hence in any theory of peptisation, the existence of these films must be explained.

8. The peptisation of some substances in organic solvents, such as pyroxylin in amyl acetate or ether-alcohol mixture, or the peptisation of vulcanised rubber has not been discussed because the conditions of stability in these cases are obscure.

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THE ELECTROLYSIS OF ACID SOLUTIONS OF COPPER SULPHATE

BY L. V. REDMAN

The electrolysis of copper sulphate solutions has been the subject of much research; in 1800 Cruikshank[1] shewed that copper could be separated from its solutions by means of the electric current, in 1834 Faraday[2] determined its electrochemical equivalent to be 31.6, in 1867 Regnault[3] shewed that in solutions of cuprous chloride the equivalent was double that value, and in 1897 Förster and Seidel[4] established the existence of cuprous salt in solutions of cupric sulphate. As a result of these investigations, the quantitative relations between the amount of copper deposited and the current seemed to be fairly well established, when, in the Spring of 1901, Jos. Siegrist[5] published the results of his researches "on the velocity of the electrolytic deposition of copper in the presence of sulphuric acid".

This author's very numerous and careful experiments shew that although the amount of copper deposited per coulomb from concentrated solutions is about that calculated from Faraday's law, yet, when the ratio of concentration to current-density falls below a certain critical value,[6] the rate of deposition is almost independent of the current and is roughly proportional to the concentration of the copper sulphate in the solution.

These results he explained by assuming that the reduction of copper sulphate by the cathode, like that by chemical reducing agents, is a process requiring time; and that the rate of this reaction, like that of many others, is dependent on the concentration of the solution; in support of this explanation he cites the work of Haber[7] on the electrolytic reduction of nitrobenzene. Under given conditions of concentration, temperature, etc., then, the amount of copper that could be reduced in a given time would be limited; and if the current called for more, the deficit would have to be made up in some other way—by liberation of hydrogen, for instance. In experiments carried out well below the critical concentration-density ratio, Siegrist found that the rate of deposition of copper is proportional to the concentration of copper in the solution; in the language of chemical kinetics, the electrolytic reduction of copper is a reaction "of the first order".

The researches of Noyes and Whitney[8] and of Brunner[9] on the rate of solution of solids, and those of Salomon[10], Nernst and Merriam[11], and others

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[1] Nicholson's Journal, 4, 187 (1800).

[2] "Experimental Researches", VII Series, Sec. 846 (1834).

[3] Ann. Chim. Phys. (4) 11 137 (1867).

[4] Z. Elektrochem. 3 479 (1897).

[5] Z. anorg. Chem. 26 273 (1901).

[6] I use the term "limiting current" to indicate the greatest current that under the conditions of the experiment liberates copper only.

[7] Z. physik. Chem. 32 193 (1900).

[8] Z. physik. Chem. 23 689 (1897).

[9] Z. physik. Chem. 47 56 (1904).

[10] Z. physik. Chem. 24 54 (1897).

[11] Z. physik. Chem. 53 235 (1905).

on the "residual current" suggest a wholly different explanation. These authors worked with cylinders of various solids rotating in a solution, or with flat plates and a mechanical stirrer; and their experiments justify the assumption that a thin film of liquid adheres to the surface of the solid, and that the constituents of the solution can reach the surface of the solid only by diffusion through the film. From this it follows that the concentration of copper sulphate at the surface of the cathode in Siegrist's experiments must have been lower than it was in the rest of the solution, and that the amount of copper that could be deposited electrolytically in a given time would be limited by the amount that could reach the cathode by diffusion. This view explains at once the great influence of stirring on the quantity of copper deposited; it also accounts for Siegrist's observation that his "rate" is a linear function of the temperature and not an exponential function like the rates of most chemical reactions. It is, moreover, in agreement with the generally accepted theory of decomposition-voltages, according to which the concentration of the copper sulphate must fall almost to zero before the liberation of hydrogen is possible; and with the outcome of experiments by Sand[1] undertaken to test this very point.

In the autumn of 1907, while Professors T. R. Rosebrugh and W. Lash Miller were developing the mathematical theory of the changes of concentration at the electrode brought about by diffusion and by chemical reaction[2], I began the work described below (as a student in the electrochemical laboratory of the University of Toronto) with solutions of copper sulphate in maximum-conducting sulphuric acid, to see in how far the conclusions of the theory were borne out by the experiment. After preliminary verification of Siegrist's results—which shewed, incidentally, that the "limiting-current" could be determined much more easily by the use of a voltmeter than by Siegrist's method of weighing—my attention was directed to measurements with interrupted current, because for this case the kinetic theory and the diffusion theory make contradictory predictions. The balance of probabilities was, no doubt, strongly in favour of the latter theory; but an *experimentum crucis* seemed necessary, as the linear temperature coefficient, and the influence of stirring on the kinetic "constant", both of which are hard to explain on the kinetic view, were well known to Siegrist; and that he did not regard the results of Sand to be fatal to his theory is proved by the following quotation from his paper: "Wie die Verhältnisse im Inneren des elektrolytischen Troges gestalten interessiert uns hier nicht; besonders da im vorliegenden Falle das Kupfer nicht durch Ionenwanderung, sondern durch heftiges mechanisches Rühren der Elektrode zugeführt wurde. (Während der Korrektur dieser Arbeit erschient die Arbeit von H. J. S. Sand, welche sich speziell mit dieser Frage beschäftigt.)"

If the liberation of hydrogen first occurs when the rate of deposition of copper called for by Faraday's law exceeds the maximum rate at which copper

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[1] Phil. Mag. (6) 1 45 (1901); Z. physik. Chem. 35 641 (1900).

[2] J. Phys. Chem. 14 816-884 (1910); referred to as "R & M".

can be chemically reduced from a given solution, then periodic interruptions of the current will be without effect and a current which when uninterrupted will liberate hydrogen, will also liberate it if periodically interrupted. If on the other hand the liberation of hydrogen is due to the exhaustion of copper salt in the solution at the cathode, then during the interruption the supply of salt will be replenished, and if the interruptions are frequent enough and of sufficient duration, nothing but copper may be deposited by a current which if uninterrupted would bring about liberation of hydrogen.

As cathode I used a platinum cylinder 2.3 cm. in diameter and 0.97 cm. high, rotating 1630 times per minute on a vertical axis between horizontal plates of ebonite in 1.25 litres of a solution containing 1.0 or 2.0 g. of crystallized copper sulphate $CuSO_4.5H_2O$ per litre of maximum-conducting sulphuric acid (7.6 normal acid). The anode was a concentric copper cylinder, and the temperature 19°C. With this arrangement the minimum current that would liberate hydrogen was determined for different numbers of interruptions of the current per second, a sudden rise in the voltage over the cell being taken as evidence of liberation of hydrogen. The interruptor was constructed of one hundred plates of copper insulated by mica, like the commutator of a dynamo, and could interrupt the current from 0.5 to 3000 times per second; owing to the thickness of the insulation, the duration of each interruption was trifle longer than that of each beat of current.

Current and voltage were determined by Weston instruments; the inertia of their moving parts was so great that, unless the number of interruptions fell below twelve per second, the needles were stationary enough to permit of accurate readings; calibration shewed that these readings represented 47% of the current and voltage respectively during the intervals when the current was flowing. When the interruptions were fewer than twelve per second, however, the oscillations of the voltmeter needle were too great and the voltmeter was replaced by two copper points dipping in maximum-conducting sulphuric acid in a small Erlenmeyer flask, the idea being that when the voltage rose high enough to liberate hydrogen in the cell, hydrogen would be liberated also at the point connected to the cathode. The wall of the flask acted as a lens and enabled the gas to be easily detected, and the device worked well in practice; but on trying it out with known constant currents it was found that a considerable empirical correction had to be applied, thus the results with fewer than twelve interruptions per second are less reliable than the others.

TABLE I

1.0 g. per l.

Int. per sec.	0	0.6	1.1	2.0	3.2	4.5	5.7	6.5	9.0	126	212	2500	3000
Amp. per cm².	0.0044	52	56	70	82	84	86	86	92	98	98	98	0.0098

2.0 g. per l.

Int. per sec.	0	1.5	2.8	4.2	7.0	12.0	126	212	2500	3000
Amp. per cm².	0.0088	132	164	176	178	180	178	178	178	0.0178

The results, given in Table I, shew that the limiting current rises continuously with the number of interruptions per second, and that when the interruptions are frequent enough the limiting current is about double that with uninterrupted current. This result not only directly contradicts the predictions of Siegrist's theory, but it is in quantitative accord with the predictions of the diffusion theory; for equations 33 and 24 of the paper by Rosebrugh and Lash Miller lead to the conclusion that "the stationary state reached by electrolysis with a rapidly interrupted, alternated, or varied two-beat current is practically the same as would be reached by electrolysis with a constant current of the same number of coulombs, reckoned algebraically".[1]

Siegrist's theory being thus eliminated, I endeavoured to determine point by point the voltage-time curve during the first second or so of an electrolysis, with the help of a mechanical device which connected anode and cathode for exactly one-hundredth of a second to the terminals of a previously calibrated ballistic galvanometer, and which could be arranged so that this connection was made at any desired interval after closing the current through the cell. Some of the curves constructed in this way agree fairly well with those obtained with the apparatus described further on; but the work was extremely tedious, for it was found necessary to clean and polish the cathode before each measurement, as the rough deposit formed at the end of each electrolysis affected the voltage of the succeeding experiment.

Recourse was therefore had to the oscillograph, and after some preliminary work with an instrument kindly loaned by the Department of Electrical Engineering, a two-element Siemens-Halske instrument was purchased for this work. Each element had an undamped frequency of 2900 per second, its resistance was 2.5 ohms, and a current of 4 milamperes through the element gave a deflection of 45 millimetres on the photographic paper.

In order that the 4 or 5 milamperes taken by the oscillograph might be negligible in comparison with the current passing through the cell, the (rotating) cathode was constructed of a solid copper cylinder 4.6 cm. in diameter and 6.4 cm. high, the ends covered with an insulating gum; contact was made through a mercury cup on the top of the shaft; the anode was a concentric copper cylinder of 9.5 cm. diameter and the same height as the cathode, while two horizontal ebonite plates, the upper one perforated to admit the cathode shaft, ensured a uniform electrolytic field.

One of the oscillograph elements, with a suitable resistance (about 280 ohms) in series, served to measure the potential difference across the cell, the second element was connected in series with a resistance of 90 ohms and the secondary of a small induction coil (7.7 ohms) through the primary of which a constant current of 1.2 amperes was maintained by a storage battery. A tuning fork (middle C, 128 cycles per second) vibrating just above the core of the coil, induced a sinusoidal current in the secondary, which was recorded on the photographic paper of the oscillograph. This sinusoidal current

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[1] *loc. cit.* page 840.

was short-circuited once per revolution of the cathode shaft, so that the speed of revolution of the shaft was also recorded on the photographic paper.

The electrolysis circuit is shewn in Fig. 1. *S* is a heavy copper bar which in its normal position short-circuited the cell and the oscillograph circuits and thus enabled the current to be adjusted by means of the lamp rheostat *R* and the ammeter *A*; when the bar was pulled back by an electromagnet the current flowed through the cell. The potential difference set up over the 0.01 ohm sent a trifling current through the second element (*II*) of the oscillograph, in parallel with the sinusoidal current from the coil; this displaced the time-wave on the photographic paper, and identified the moment when the electrolysis current was thrown on.

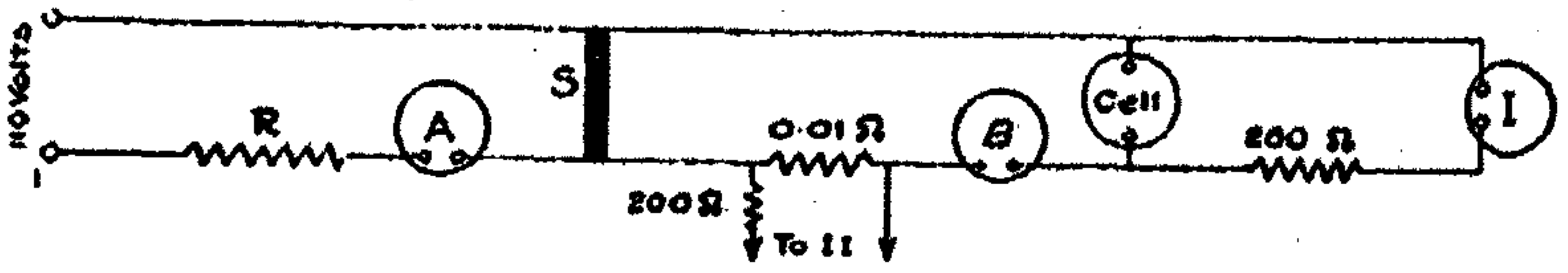

FIG. 1

To get a good record it was necessary that the electrolysis should begin immediately after the photographic shutter of the oscillograph had opened; this result was secured by tapping the circuit that leads to the "opening-magnet" of the oscillograph, and sending part of the current through a relay which operated the magnet that drew back the short-circuiting bar.

To secure a time-voltage curve with this apparatus the following operations were necessary:—The cathode was cleaned and polished,[1] the electrolyte analyzed and poured into the cell, the cathode set revolving at the desired speed (estimated by means of an electrical speed-counter attached to the cathode shaft), the current adjusted, the tuning-fork set in vibration by a blow from a rubber hammer, the key of the oscillograph pressed and the photograph taken, the current read on ammeter *B*, and the short-circuiting bar restored to its normal position. All the data needed, except the composition of the electrolyte, its temperature, and the current used, were recorded on the photographic paper.

Fig. 2 shews one of the records so obtained; the electrolyte contained 1.0 g. of copper per litre, its temperature was 17.7°C, the current was 1.09 amperes, the cathode revolved once in 0.133 seconds (17.0 waves). The horizontal line at *A* is the zero-voltage line, the line *BCD* gives the potential difference over the cell, while the horizontal at *E* (the "voltage calibration line") corresponds to a voltage of 0.528 volts over the cell. If it be assumed that hyd-

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[1] This is very necessary; if three or four oscillograms be taken in close succession on the same paper, without changing the electrolyte or varying the current, the time required to liberate hydrogen in the last may be noticeably greater than in the first. This is due to the dark powdery deposit formed during the final moments of each electrolysis (while hydrogen is being evolved) which in effect decreases the thickness of the diffusion film. If a prolonged electrolysis be carried out with a constant current somewhat greater than the limiting current, hydrogen is at first evolved and a dark deposit formed, but later on the evolution of hydrogen ceases and the deposit turns red.

rogen was first liberated when *BCD* ceased to become steeper (at the point of inflexion, marked with an arrow), the concentration of copper fell from 1.0 g. per litre to zero in 0.211 seconds. The limiting current $-I'$ under the conditions of this experiment was 0.403 amperes, thus the ratio $I' : I = 0.37$, which is less than 0.5, and the "parabolic approximation" can be used to determine the diffusion constant k, without knowledge of the thickness of the diffusion film. From the equation (R. & M. Eq. 22b)

$$96500\,Ak(z-z_0) = -1.129\sqrt{kt}$$

setting A (area of cathode) $= 92.5$, $z = 0$, $z_0 = 1.0/31800$, $t = 0.211$, $I = -1.09$ (the negative sign because the electrode is cathode) there follows $k = 4.1\times10^{-6}$.

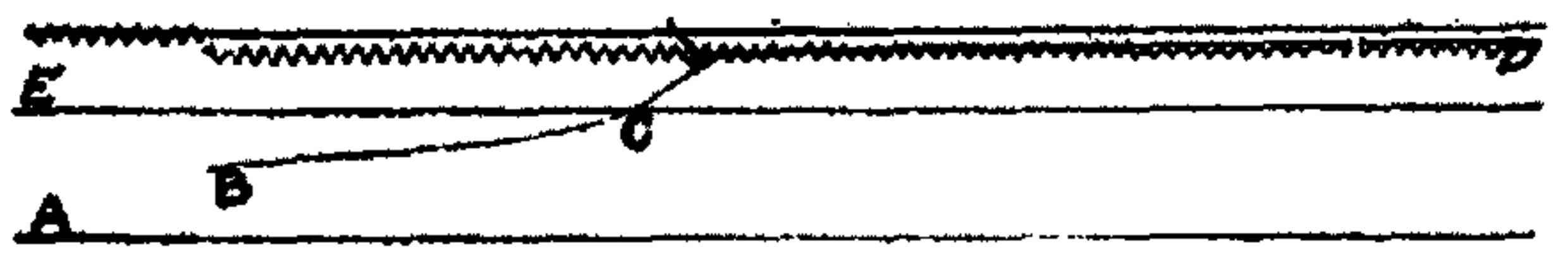

Fig. 2.

I made some fifty or sixty determinations of this type, with solutions containing from one to six grams of copper per litre, currents from 0.9 to 6.2 amperes, and cathode speed from 0.03 to 0.15 sec. per revolution. The values of k varied from 3.5×10^{-6} to 5.5×10^{-6} at 18°C, the higher values being obtained with the most dilute solutions. While at first inclined to ascribe this regularity to change of k with the concentration of copper in the electrolyte, ultimately I found a source of error in my apparatus which made this conclusion unreliable, viz: the solution of the copper electrodes in the strongly acid electrolyte which was unprotected from the air. The values of z_0 used in the calculations, being based on analyses made before the electrolyses, were, therefore, too low by a variable amount which depended on the interval between filling the cell and taking the photograph, and the error so introduced (which results in too high values of k) must obviously be greater the smaller the original concentration of the solution. By the time that blank experiments had established the magnitude of this error, it was too late to rebuild the apparatus; critical examination of the note book gave $10^6k = 4.0 \pm 0.5$ as an approximate value for the diffusion constant at 18°C.

A sharper check on the predictions of the diffusion theory was gained from time-voltage curves obtained with periodically interrupted currents. The interrupter used in my previous work could not handle the comparatively heavy currents needed by the large cathode without sparking, and was replaced by a sliding contact made and broken by a reciprocating piston.

Fig. 3 shews one of the records; the current was 2.86 amperes, the electrolyte contained 2.0 g. copper per litre, and its temperature was 18°C. Hydrogen was first liberated 0.359 seconds after the current first flowed through the cell (the point is marked with an arrow in the figure); assuming the value

$k = 4.0 \times 10^{-6}$, equation (R & M. 29 *d*) predicts 0.377 seconds. I made about a dozen such records, under different conditions of current and concentration, towards the end of my work, and in every case the hydrogen was first liberated in the "beat" of current predicted by the mathematical theory; owing to the uncertainty as to the diffusion constant closer agreement could not be expected.

Overvoltage

While the lapse of time before the first liberation of hydrogen could be predicted fairly well, the potential difference over the electrodes was very different from that calculated from the concentrations given by the diffusion theory if it be assumed that the cell is reversible, and that the "concentration E. M. F." can be calculated from the logarithm of the concentration ratio by the ordinary formula. While I was making my first measurements with the oscillograph, LeBlanc's paper "On the E. M. F. of Polarization" appeared[1], in which he pointed out that the potential difference at the moment of throwing on the current in acid solutions of copper sulphate is much greater than corresponds to the product of current into the resistance of the cell. LeBlanc calls the difference "overvoltage"; I prefer to call it "initial overvoltage", because not only is the height *AB* (Fig. 2) too great, but the line *BC* rises much more than can be accounted for by the fall in copper concentration as calculated from the mathematical theory. In addition, then, to the "initial overvoltage" noticed by LeBlanc, Reichinstein, and others, there is a further overvoltage which builds up during electrolysis before the liberation of hydrogen; this second sort of overvoltage was not noticed by LeBlanc, for it could not be recognized without knowledge of the concentrations at the electrode furnished by the "mathematical theory", and although the equations for calculating these concentrations were published fifteen years ago, I have seen no reference to it until Professor Lash Miller summarized the results of Mr. A. R. Gordon's work at the Centenary of the Franklin Institute[2].

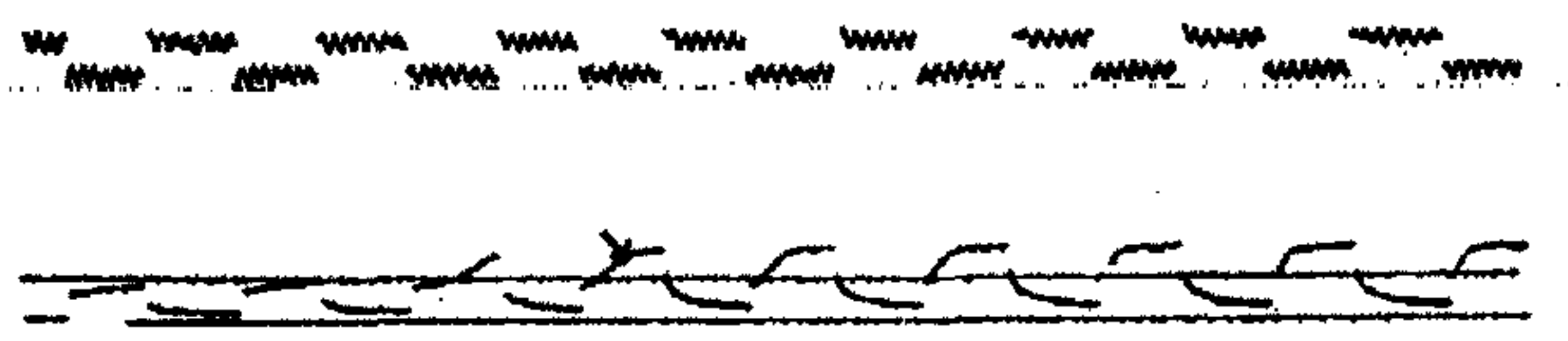

FIG. 3

Summary

I think it may fairly be said that the experiments recorded in this paper dispose of Siegrist's "kinetic theory", and shew that the assumptions made

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[1] Abh. deutsch. Bunsen-Ges., Nr 3 (1910).

[2] Franklin Inst. Centenary Publication.

by the "mathematical theory" are fairly applicable to the case of acid solutions of copper sulphate. At the time the work was done more could not be claimed; for it was uncertain whether the lack of sharper agreement between equations and experiments was due to experimental errors, or to an error in the assumption made by the theory, that the diffusion constant is strictly independent of the concentration. This matter has since been thoroughly investigated by Mr. J. T. Burt-Gerrans and Mr. A. R. Gordon in the Toronto laboratory; before publishing their own results they wish to see in print an account of the preliminary studies on which their work was based, and it is at their request and that of Professor Lash Miller that this abridgment of an old thesis and laboratory report is brought to light.

University of Toronto
July, 1925

VISCOSITY OF COLLOIDS IN PRESENCE OF ELECTROLYTES

BY N. R. DHAR

In two previous papers[1], we have discussed the important question whether sols are more or less hydrated than the freshly coagulated masses of the same substances. I have advanced the view that the phenomenon rests on the charge on the colloid. "Now if we can obtain a sol which is not charged at all or is only very feebly charged, the particles of this sol on keeping will gradually lose its reactivity by dehydration. On the other hand if the colloidal particles are charged, and which is usually the case, the charged particles because of their charge are not as much hydrated as the freshly coagulated sol, the colloidal particles because of their charge and probably because of their micellar nature have a tendency to contract or shrink and during this shrinking process the absorbed water may be squeezed out just as water can be squeezed out of a sponge.

"We know that if we add potassium iodide to a gelatine jelly, the jelly melts into a liquid. We can explain this phenomenon in the following way. The particles of jelly have a chemical attraction for the iodide ions and they adsorb these ions with the formation of a negatively charged sol. Now these charged particles of micellar nature tend to shrink and squeeze out the adsorbed water; consequently the jelly containing potassium iodide passes into the liquid condition, and forms a negatively charged colloid. If a bivalent salt like $CaCl_2$ or $SrCl_2$ is added to this liquid, the whole thing sets into a jelly again, because the negatively charged particle of the jelly adsorb the bivalent Ca-ions and become neutral and as soon as they become neutral they adsorb again the water molecules which they have squeezed out because of their previous charge. Consequently, I am of the opinion that sols carrying a charge are less hydrated than the freshly coagulated mass of the same substance.

"In this connection it is interesting to observe that in a foregoing paper[2] I have shown that ions occupy less space than molecules. Moreover, it has been observed that elements with low ionisation potentials have large atomic volumes e.g. metallic caesium has an ionisation potentials smaller and atomic volume greater then that of lithium.

"Lillie[3] has shown that cilia of the larva of a ring worm Arenico-Arenicola are liquefied by a solution containing sodium ion; the addition of a small amount of a bivalent cation stops the process. We can explain the above facts and also the biological salt antagonism in the following way. Cells in the larva of the ring worm (or any other animal matter) are of an albuminous nature and, like albumin, are either weakly negative or weakly positive or neutral. We can assume that the cells are either neutral or carry a very small

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[1] Sen, Ganguly and Dhar: J. Phys. Chem. 28, 313 (1924); Dhar: Z. Elektrochem. 31, 261 (1925).

[2] Dhar: Z. Elektrochem. 19, 748 (1913).

[3] Am. J. Physiol. 10, 433 (1904).

negative charge. In presence of NaCl the cells would adsorb chlorine ion due to chemical affinity becoming negatively charged, and would probably squeeze out the adsorbed water, and consequently the larva would pass into the liquid state. Now the addition of a little bivalent Ca-ion would neutralize the negative charge and the particles of larva would readsorb the water they had previously squeezed out, because of its charge and micellar nature and thus re-establish the original condition of the larva.

"There is a chemical analogy for this phenomenon of the change of mobility due to the adsorption of an ion. When NaOH is gradually added to a fairly concentrated solution of $CuSO_4$, $Cu(OH_2)$, which is first formed, must be positively charged due to the adsorption of positive ions and the mixture is very mobile. If the addition of alkali is continued, a certain stage appears when the mobility of the system decreases considerably and a viscous bulky precipitate of $Cu(OH)_2$ is obtained. At this stage the whole of the copper is precipitated and the hydroxide is practically neutral. If more alkali is added, the mixture becomes again mobile and becomes negatively charged due to the adsorption of hydroxide ions; the precipitate becomes less bulky. It is apparent therefore that the charged hydroxide of copper squeezes out some water of hydration, which it can take up again on charge neutralization. This phenomenon seems to be general in the precipitation of many substances".

From the above quotation it will be seen that I have made the following assumptions:—

1. Other things being identical, the uncharged substance is more hydrated than the sol.

2. The greater the hydration of a substance, the greater is its viscosity.

3. When a sol adsorbs an ion carrying the same charge as the sol because of chemical affinity, the charge on the sol is increased and consequently according to our view the viscosity of the sol should decrease.

I shall show in the subsequent pages that these assumptions are corroborated by the experimental results of various workers on the viscosity of colloids in presence of electrolytes.

In a series of papers[1] published from these laboratories we have proved qualitatively and quantitatively that many sols like As_2S_3, Sb_2S_3, mastic, prussian blue etc., are capable of adsorbing ions carrying the same charge as the sol and are stabilized by this adsorption of ions carrying the same charge as the sol. We are trying to prove experimentally that when small quantities of electrolytes insufficient to coagulate the sols are added to them, these sols adsorb ions carrying the same charge as the sol and the viscosity is slightly decreased. On the other hand, sols like $Fe(OH)_3$, $Cr(OH)_3$, etc., which adsorb ions of the same charge as the sol to a very slight extent, should show much less decrease of viscosity on the addition of small quantities of electrolytes than when small quantities of electrolytes insufficient for coagulation are added to sols of As_2S_3, Sb_2S_3 etc. Moreover, we have proved that when ferric hydr-

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[1] Sen and Dhar: Kolloid-Z. 34, 262, (1924); Ghosh and Dhar: 36, 129, (1925); J. Phys. Chem. 29, 659 (1925).

oxide is coagulated by ferric chloride, aluminium nitrate etc., the sol adsorbs ferric ion, Al-ion etc. Consequently we venture to suggest that when small quantities of ferric chloride or aluminium nitrate are added to a sol of ferric hydroxide, there will be more marked decrease of viscosity that when KCl, $KBrO_3$ etc., are added to the sol. I am of the opinion that those sols, which behave abnormally towards dilution, towards a mixture of electrolytes of different valencies, and show positive acclimatization, should also show more appreciable decrease of viscosity when small quantities of the precipitating electrolyte are added to them, than those sols which are normal towards dilution, towards a mixture of electrolytes and show the phenomenon of negative acclimatization. All these phenomena mainly depend, as we have already proved, on the amount of adsorption of ions carrying the same charge as the sol. It must be emphasised that the change in the viscosity of a sol on the addition of an electrolyte will certainly depend on the ratio of the adsorption of the positive and negative ions. If the sol adsorbs more of the ion carrying the opposite charge than the ion carrying the same charge, the charge on the sol is decreased and more of hydration will take place and the viscosity would be increased. On the other hand, when a sol is capable of adsorbing more of the ion carrying the same charge than the ion carrying the opposite charge, the viscosity should decrease. We have made the tacit assumption that the degree of dispersion remains the same in all cases.

These conclusions are corroborated by the following experimental results.

Albanese[1] has observed that the viscosity of an aqueous solution of gum arabic is lowered to the extent of 30 percent by the addition of small quantities of electrolytes but not by other substances.

It seems that gum arabic is capable of adsorbing ions carrying the same charge as the sol. Woudstra[2] has shown that the viscosity of ferric hydroxide or chromic hydroxide sol slightly decreases on the addition of small quantities of electrolytes; when greater quantities of electrolytes are added the viscosity goes on increasing. Moreover, he has shown that the viscosity of colloidal silver is lowered appreciably by the addition of electrolytes. From an experimental work which is in progress in these laboratories we find that silver sol can adsorb ions carrying the same charge as the sol and is abnormal towards dilution and towards a mixture of electrolytes and would show the phenomenon of positive acclimatization; consequently our conclusion that this sol should show appreciable decrease of viscosity on the addition of small quantities of electrolytes is corroborated by the experimental work of Woudstra.

Farrow[3] has shown that the viscosity of sodium palmitate solution decreases on the addition of small quantities of NaOH, NaCl and KCl; if the amount of the electrolytes is increased the viscosity after passing through a minimum goes on increasing.

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[1] Arch. Exp. Path. Pharm. Suppl. 1908, 16

[2] Kolloid-Z. 3, 199 (1908); Z. physik. Chem. 63, 619 (1908).

[3] J. Chem. Soc., 101, 347 (1912).

These results are very likely due to the adsorption of ions carrying the same charge as the sol of sodium palmitate. If we assume that the colloidal particles existing in sodium palmitate are negatively charged, we can expect that these negatively charged particles will adsorb OH′ or Cl′-ions because of the chemical affinity of the particles of palmitate for OH′ or Cl′ ions, when small quantities of an alkali or a chloride is added to the solution of the palmitate; and hence the charge is increased and the viscosity decreases. Now, if more of the electrolyte is added, the oppositely charged ion is adsorbed in greater quantities and the charge on the colloidal matter is neutralized and hence the viscosity and hydration go on increasing. In this connection, it will be interesting to observe that Salmon[1] has shown that NaCl is appreciably adsorbed by soap, also it is well known that free alkalies are adsorbed by soaps, Egnér[2] has shown that cations flocculate suspensions of china clay and infusorial earth and increase the viscosity, but anions act in the opposite way. The magnitude of the flocculating power generally follows the valency rule, but hydroxide ions often act irregularly in this case, as well as in the cases of many other sols. The properties of these suspensions are very similar to those of colloids and apparently these suspensions are negatively charged.

Some very interesting results have been obtained by Fernau and Pauli[3] along these lines. They have found that on the addition of a quantity of an electrolyte which is not sufficient to produce coagulation, in the case of the sol of cerium hydroxide, there is an immediate drop in the viscosity of the sol. I am of the opinion that this is due to an increase in the charge of the sol by the adsorption of the ion carrying the same charge as the sol.

The above authors have also proved that the sol of ceric hydroxide becomes less viscous on "ageing". In a previous paper I have emphasised that ageing is essentially connected with dehydration specially of hydrophobe colloids; hence an "aged" sol of cerium hydroxide loses its water and becomes less viscous. I have already suggested that this phenomenon of decrease of viscosity and of dehydration on ageing are of common occurrence.

Büchner[4] has shown with sols of molybdenum-blue and $Fe(OH)_3$ that the density of the suspended particles is much smaller than that of the substances in the free condition. This is interpreted in favour of the view that the colloidal particles contain water; the proportion of water which thus becomes associated with the colloid is greater for $Fe(OH)_3$ than for molyledenum-blue.

Odén[5] concluded from theoretical considerations that the viscosity of suspensoids should be independent of the degree of dispersion of the colloid. He, however, experimentally found an approximately 50% greater viscosity with sulphur sols in which the particles had a diameter of 10μμ than with sols of diameter of 100μμ. This is certainly due to the greater amount of water adsorbed by the increased surface of the smaller sulphur particles.

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[1] J. Chem. Soc., **119**, 1369, 1374, 1669 (1921).

[2] Medd. K. Vetnsk. Nobel Inst. **4**, 41 (1920).

[3] Kolloid-Z. **20**, 20 (1917).

[4] Proc. Akad. Wet. Amsterdam. **18**, 170 (1915).

[5] Z. physik. Chem. **80**, 709 (1912).

Hatschek[1] has deduced that the thickness of water films round the sulphur particles is about 0.87$\mu\mu$ which corresponds to an increase in volume of about 62% for particles having a diameter of 10$\mu\mu$. Hence the greater hydration of the particles is associated with the increase in viscosity. Alexander[2] has shown with Karaya gum that the viscosity of emulsoids or hydrophile colloids increases as the dispersed phase becomes finer. This is also due to the greater amount of water adsorbed by the fine particles of the colloid.

Moreover, Miss Chick[3] has shown that 2.1, 3.8, and 5.8 cc of water are adsorbed per grm of protein with serum albumin, ψ globulin and euglobulin respectively at 25°. Hence by the withdrawal of water in any salting out process, the euglobulin requiring most water is the first, and the serum albumin is the last to be precipitated.

In the case of water-soluble colloids, the viscosity may increase enormously with the concentration of the colloid—a one percent solution of agar forms a solid jelly. The metal and the sulphide sols have only a very slight effect on the viscosity of water. The fact that the viscosity of many colloidal solutions changes more rapidly than the concentration is not in agreement with Einstein's formula[4] and Hatschek[5] has expressed the views that this is due to the formation of an envelope of the medium round each particle of the dispersed phase. Both Arrhenius[6] and Smoluchowski[7] are not in favour of this view of Hatschek's. Smoluchowski has also remarked that on various occasions it has been suggested that the increase in viscosity on coagulation of a colloid is directly opposed to Einstein's formula. Smoluchowski ascribes this increase to the formation of non-spherical aggregates. The same author finds greater difficulty in explaining such cases where the addition of a small quantity of an electrolyte results in the diminution of the viscosity of the sol; and he throws out the suggestion that the decrease of viscosity is due to the reduction of the volume of the dispersed phase. To my mind the origin of these difficulties of Smoluchowski lies in the assumption that the viscosity increases with the increase in the charge of the colloids. On the other hand, according to my view, that the unchanged particles are more hydrated and more viscous than the charged particles under identical conditions, seems to be more consistent with the experimental observations, and immediately solves the difficulties of Smoluchowski.

Moreover, Getman[8] has shown that in every case the viscosity concentration curve of some solutions of potassium salts having lower viscosity than that of the solvent passes through a minimum; it is suggested that this abnormal behaviour was due to the combined action of ions and the non-disso-

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[1] Kolloid-Z. **11**, 284 (1912); **12**, 238 (1913).

[2] J. Am. Chem. Soc., **43**, 434 (1921).

[3] Biochem. J. **8**, 261 (1914).

[4] Ann. Physik, (4), **19**, 289 (1906).

[5] Kolloid-Z. **11**, 284 (1912); **12**, 238 (1913).

[6] Medd. Nobel Inst. **1**, 16 (1916).

[7] Kolloid-Z. **18**, 190 (1916).

[8] J. Am. Chem. Soc. **30**, 721 (1908).

ciated molecules. The potassium ions appear to lower the viscosity of the solvent while the anions and undissociated molecules tend to increase it.

In this connection the following remarks of Bancroft[1] will be of interest. "If the suspended particles aggregate into chains, the viscosity will be increased very much. If the particles form larger spherical particles which are homogeneous, there will be a decrease in the viscosity, because of the decrease in the surface and consequently in the amount of the bound water. If however the particles simply agglomerate loosely into spherical masses, the viscosity will increase, because the water in the voids inside the spherical agglomerates no longer counts as free water. We shall therefore expect to get an increase of viscosity as a result of agglomeration, when the effect of agglomeration is not to increase the size of homogeneous drops. The important point is that the increase in viscosity does go hand in hand with an increase in agglomeration, which must mean that increase in agglomeration involves decrease in the amount of available free water. The phenomenon is apparently general, because Freundlich has made use of the increase in viscosity as a means of studying the rate of agglomeration of aluminium hydroxide sol".

Although there has been an immense amount of work done on the viscosity changes of the substances like gelatin, blood, etc., no very definite conclusion have yet been arrived at. Bancroft[2] has remarked that "with colloidal solutions of gelatin and other substances of the same type, the viscosity changes with the time, showing that there is a gradual change in structure. This is further confirmed by the fact that the viscosity of such solutions changes when they are shaken violently.

Where a film formation is possible, the surface viscosity will be quite different from that in the mass of the liquid. This is very striking in the case of colloidal solutions of saponin, peptone etc".

Gokun[3] has reported that the viscosity of 0.28% gelatin solution increases with time by 1.5 in 115 hours. The viscosity depends on the mechanical treatment to which the solution has been subjected. This points to the existence of structure in the solution.

Gunzburg[4] has shown that the viscosity of the muscular juice from a frog decreases on the addition of KCl, whilst it increases in the presence of uranium nitrate. It appears that the juice is negatively charged and becomes more stable and less viscous by the adsorption of Cl′ ions from KCl whilst the bivalent uranium ions reduces the charge and increases the viscosity of the juice. In the presence of a mixture of the two salts, the viscosity depends on the proportions of the two salts present.

Moreover, Rothlin[5] has divided hydrophile colloids into two groups, one of which follows Poiseuille's law, whilst the other does not. These deviations

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[1] Applied Colloid Chemistry", 192 (1921).

[2] "Applied Colloid Chemistry", 195 (1921).

[3] Kolloid-Z. 3, 84 (1908).

[4] Arch. néerl. Physiol. 4, 233 (1920).

[5] Biochem. Z. 98, 34 (1919).

are to be ascribed to the formation of larger aggregates in the sol through gelation; these aggregates according to the conditions of flow, can be broken down to different extents and so give rise to the observed irregularities. Bungenberg de Jong[1] concludes that for viscometric measurements to have any value, the system under examination must not only follow Poiseuille's law, but the dispersed phase must retain its stability. Consequently with some hydrophile colloids, the variation in the distribution in the shears in the liquid play an important part. Recently Freundlich and Schalek[2] have observed that certain inorganic colloids such as vanadium pentoxide, and $Fe(OH)_3$ etc., also do not follow Poiseuille's law.

It is not easy to explain all the viscosity experiments in presence of electrolytes with substances like gelatin, albumin blood, casein etc., from a single point of view. Two main workers in the field, Pauli and Loeb do not agree with each other's conclusions, as will be evident from the following quotations from Loeb's book[3]. "The idea that the viscosity of protein solution depends primarily upon the protein ions was accepted by Pauli, who made the additional hypothesis that each protein ion is hydrated, i.e. that each individual protein ion is surrounded by a considerable shell of water. Pauli worked with blood albumin which had been freed from salts by a dialysis continued for several weeks. When he added acid to water soluble alumin, the viscosity increased first from 1.0623 for the pure albumin solution to 1.2937 when the concentration of HCl added to the albumin solution was 0.017 N; when the HCl concentration was increased to .05 N the viscosity was only 1.1667. The following figures give the data according to Pauli.

Conc. HCl:	0.0N,	0.005N,	0.01N,	0.012N,	0.017N,	0.02N,	0.03N,	0.04N,	0.05N
Viscosity:	1.0623,	1.2555,	1.233,	1.274,	1.2937,	1.277,	1.224,	1.1822,	1.166

"Pauli assumed that the protein ions are surrounded by a jacket of water, while the non-ionised molecules of protein, he assumed not to be hydrated. Addition of a little HCl to isoelectric albumin would cause the transformation of non-ionised albumin into albumin chloride, which is highly ionised and hence assumed to be highly hydrated; the more acid is added the more albumin chloride and more hydrated albumin ions should be formed. Hence the viscosity should at first increase with the quantity of acid added, until a point is reached where the addition of more acid represses the degree of electrolytic dissociation of the albumin chloride on account of the high concentration of the Cl′ ion common to both protein chloride and HCl". On page 115 Loeb remarks: "We have shown that the curves for osmotic pressure, swelling and viscosity reach a maximum at pH value varying between 3.5 and 2.8 and that they then drop. Pauli assumes that the drop is due to a repression of the degrees of electrolytic dissociation of the gelatin chloride (or any protein acid salt), through the addition of more acid on account of the common anions.

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[1] Rec. Trav. Chim. 42, 1 (1923).

[2] Z. physik. Chem. 108, 153 (1924).

[3] "Proteins and the Theory of Colloidal Behavior", 18 (1922).

It would however be mentioned that Pauli, Manabe and Matula state that the maximum of the curves occurs not at pH between 3.5 or 2.8 but at pH 2.1 or 2,0

"The hydration hypothesis can be put to a direct test by determining the specific conductivity of solutions of protein salts, e.g. gelatin chloride, albumin chloride etc. Since according to the hydration hypothesis only the protein ion undergoes hydration, the variation in the osmotic pressure, swelling, and viscosity should be accompanied by a corresponding variation in the concentration of the protein ions in solution. If therefore the specific conductivity of gelatin chloride is measured at varying pH value but equal concentrations of originally isoelectric gelatin, the curves representing the values found for conductivity of the protein should run parallel with the curves for the osmotic pressure, swelling and viscosity; moreover, the curve for the conductivity of gelatin sulphate should be only about half as high as the curve for the specific conductivity of gelatin chloride; while the curves for the specific conductivity of gelatin oxalate should be almost but not quite as high as that of gelatin chloride. The experiments show that this is not the case".

"Figure 39 on page 118 shows that the same disagreement exists between the conductivity curve and the osmotic pressure curve for solutions of the chloride of crystalline egg albumin. These curves then do not support the hydration hypothesis.

"Pauli's hydration theory rests as stated above on an assumption made by Kohlrausch that the difference in the mobility of ions is due to molecules of water being dragged along with the migrating ion. Lorenz, Born and others have come to the conclusion that while Kohlrausch's idea is probably correct for monatomic ions, it cannot be correct for large polyatomic ions. This would exclude the assumption of a high degree of hydration of protein ions".

The results obtained by Pauli, Loeb and others can be explained qualitatively, in the following way. We assume that substances like gelatin, albumin, casein, etc., are slightly negatively charged. When HCl is added to these substances, at first preferential adsorption of hydrogen ions takes place and the charge on the substance decreases and consequently, according to our conception, hydration and along with it viscosity are increased. Now if more and more HCl is added the colloid may become completely neutral and at this stage would show maximum hydration and maximum viscosity. Now if more HCl is added, the neutralised particle will pass into a positively charged colloid by the adsorption of hydrogen ion and the viscosity will decrease. Hence we can explain the maximum in the viscosity curve as obtained by Pauli by the addition of HCl to albumin. Similarly Loeb has got a maximum in the viscosity curves when gelatin is treated with small quantities of different acids. When small quantities of alkalies are added to casein or gelatin, the negative charge is slightly decreased by the adsorption of sodium ions but in this case the negatively charged OH′ ions, because of their great affinity for albuminous substances, are appreciably adsorbed by gelatin, albumin etc., and consequently on the addition of alkali, charge neutralisation of the albuminous matter is far less complete than when acids are added to these substances. Consequently the experimental results on the viscosity of substances like gelatin, albumin, etc., in presence of alkalies do not show as much marked increase as on the addition of acids. When the addition of alkali is continued, the albuminous matter becomes again negatively charged by the preferential adsorption of OH′ ions and hence the viscosity again decreases on the adsorption of further quantities of OH′ ions.

The effect of neutral salts is not as marked as that of acids or alkalies, because ions of the neutral salts, are not as preferentially adsorbed by substances like gelatin, casein, albumin etc., as H˙ or OH′ ions.

Loeb on page 90 remarks: "The addition of neutral salts of a concentration below N/16 to isoelectric gelatin has no effect on osmotic pressure, swelling, viscosity etc". On the other hand, other workers[1] have observed increase in viscosity of gelatin when certain crystalloids are added to it.

It is well known that small quantities of salts of heavy metals like Cu, Co, Pb, etc., can readily coagulate albumin. This is because the negatively charged albumin has a marked chemical affinity and adsorbs preferentially these heavy positive ions. In this connection it will be interesting to note that negatively charged MnO_2 sol has a great affinity for heavy positive ions like Ag˙, Cu˙˙ etc., and is readily coagulated by these ions.

We can also explain the increased swelling of substances like gelatin, albumin etc., in presence of acids and alkalies. As we have already suggested both the acids and alkalies, in small quantities act in neutralising or decreasing the charge on these substances and consequently uncharged matter can take up water more readily and hence greater swelling is observed with gelatin and other substances with small quantities of acids and alkalis.

In fact that the viscosity of 5% solution of isoelectric gelatin increases rapidly at the temperature of 20° or below cannot possibly be explained on the basis of the hydration theory of Pauli, since isoelectric gelatin is not ionised. This fact can be satisfactorily explained because we have assumed, from our point of view, that the uncharged substance is more hydrated and more viscous than the charged particles under otherwise identical conditions. Consequently isoelectric gelatin which is very feebly charged becomes more and more hydrated and viscous by the adsorption of water.

There is another way of looking at the problem of the viscosity of hydrophile colloids and this viewpoint seems to be more satisfactory than the point of view already discussed. It is well known that colloids like $Fe(OH)_3$, arsenious sulphide, gold etc., do not appreciable affect the surface tension of water while some of the gelatinous colloids have a marked effect. Addition of soap decreases the surface tension of water to a great extent. The addition of small quantities of gelatin to water markedly decreases the surface tension of water.

We must emphasise therefore that the changes in a colloidal system need not always consist in the diminution of dispersion. Occasionally we find that

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[1] Compare Levites: Kolloid-Z. 2, 208 (1908).

the particles become smaller with lapse of time and this has hitherto been observed only in the case of hydrophile colloids e.g. glycogen, benzopurpurin, haemoglobin, lecithins, etc.

If we assume that the particles of a sol of gelatin or albumin, have a neutral tendency to disintegrate, we can satisfactorily explain the viscosity measurements of such substances. In the case of isoelectric gelatin, according to this point of view, the suspended particles are becoming smaller and smaller because of their natural tendency for disintegration and consequently these smaller particles will adsorb more water and the viscosity of the system will increase.

When HCl is added to isoelectric gelatin the gelatin becomes positively charged by the adsorption of hydrogen ions and the particles of gelatin containing more charge than the particles of isoelectric gelatin have a greater tendency for disintegration than the particles of isoelectric gelatin itself. Consequently, in presence of HCl the degree of dispersion of albumin will increase and along with it the hydration and viscosity will also increase. Now in presence of larger quantities of HCl the adsorption of negatively charged Cl' ion by the positively charged gelatin will become appreciable and consequently the charge on the gelatin will not rise proportionally and with the increase in the concentration of HCl and after a time the change will have a tendency to decrease due to the adsorption of Cl' ions. As soon as the charge on the gelatin is decreased, the degree of dispersion will also decrease and along with it the hydration and viscosity will also decrease. Hence we can explain the viscosity curves for gelatin, albumin etc., with a definite maximum on the addition of acids or alkalies.

From the disintegration point of view, the increase in viscosity on the addition of alkalies to albumin, gelatin etc., can also be readily explained in the following way: When small quantities of alkalies are added to gelatin or albumin, OH' ions are preferentially adsorbed and the charge on the albuminous matter is increased, consequently the disintegration tendency and the degree of dispersion of the particles of albuminous matter are increased. As soon as the degree of dispersion is increased, more of hydration of the substance takes place and the viscosity increases. Now, if more and more of alkali is added the adsorption of OH' ions will increase, but after a time, a limit will be reached, because at this stage the influence of the positive ion will be felt due to the adsorption of $Na^{\cdot}$, $Ca^{\cdot\cdot}$ ions etc., from the alkali. Along with the decrease in the charge, the degree of dispersion will decrease and subsequently the amount of hydration and viscosity will decrease. Loeb has shown that the viscosity of gelatin, albumin etc., increases much less in presence of H_2SO_4 than HCl of the same concentration. This is due to the fact that the increase in the charge due to the adsorption of $H^{\cdot}$ ions and consequent increase in disintegration of albuminous matter will be less pronounced with H_2SO_4 than with HCl, because of the more pronounced effect of the oppositely charged bivalent SO_4'' ions. Similarly from the experimental results of Loeb we find that increase in viscosity of casein, gelatin etc., is more pronounced when

KOH, NaOH etc., are added than with $Ca(OH)_2$, $Ba(OH)_2$ etc. This is also due to the fact that the increase in the charge due to the adsorption of OH ions and consequent increase in the degree of dispension will be less pronounced with $Ca(OH)_2$, $Ba(OH)_2$ etc. than with NaOH KOH etc., because of the more pronounced effect of the oppositely charged bivalent ions $Ba^{\cdot}$, $Ca^{\cdot\cdot}$ etc., in decreasing the charge.

From this point of view increased swelling in presence of acids or alkalies is due to the fact that in presence of them the degree of dispersion is increased and along with it the amount of hydration will also increase. It must be emphasised that this explanation of the increase in viscosity from the point of view of increased dispersion is only applicable to those hydrophile colloids, which show a decrease in surface tension of the solvent when these substances are added to the solvent.

This explanation of the viscosity changes on the addition of acids and alkalies to gelatin, albumin, casein etc., is more satisfactorily than the first explanation advanced in this paper. It must be emphasised that his disintegration point of view is only applicable to hydrophile colloids and not to hydrophobe colloids.

My best thanks are due to Messrs. K. C. Sen, and S. Ghosh for helping in writing this paper.

Summary and Conclusion

Experimental results of several workers on the viscosity determination of colloids, specially of the hydrophobe type, are in support of the following assumptions:

1. Other things being equal, the unchanged substance is more hydrated than the sol.

2. The greater the hydration of a substance the greater is its viscosity.

3. When a sol adsorbs an ion carrying the same charge as the sol because of chemical affinity, the charge on the sol is increased, and consequently to our view the viscosity of the sol should decrease.

4. Those sols, which behave abnormally towards dilution, towards a mixture of electrolytes, and show positive acclimatization, should also show more appreciable decrease of viscosity when small quantities of a coagulating electrolyte are added to them, than sols which are normal towards dilution, towards a mixture of electrolytes and show the phenomenon of negative acclimatization.

5. When the sol adsorbs more of the ion carrying the opposite charge than ion carrying the same charge, the charge on the sol is decreased and more of hydration will take place and the viscosity will be increased.

6. It is well known that substances like gelatine, albumin etc. markedly decrease the surface tension of the solvent. If we assume that the particles

of gelatine or albumin have a natural tendency to disintegrate we can satisfactorily explain the viscosity measurements of these substances. In the case of isoelectric gelatine the suspended particles are assumed to disintegrate and consequently the smaller particles will adsorb more water and the viscosity of the system will increase. When acids or alkalies are added the charge on the sol is increased by the preferential adsorption of H' or OH' ions and hence the tendency to disintegrate and hydration and viscosity are increased.

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April 30, 1925.

ON THE VISIBLE DECOMPOSITION OF SILVER HALIDE GRAINS BY LIGHT*

26-5

BY A. P. H. TRIVELLI AND S. E. SHEPPARD

The photochemical decomposition of the silver halides is a phenomenon of considerable complexity; the interpretation of its many aspects is by no means complete nor conclusive.

However, recent studies upon this subject have greatly increased our knowledge of the character of the decomposition, as a chemical reaction. The observations of Schwarz and Gross[1] on the decomposition of silver bromide and chloride in light have completely established the fact of the release of halogen as the result of the reaction, although showing that the rate of reaction (sensitivity) is greatly affected by the mode of preparation, the adsorption of salts, and the presence of moisture. Still more conclusive in some respects are the results of E. J. Hartung[2]. Using a sensitive micro-balance, this investigator has shown that the photochemical decomposition of silver bromide *in vacuo* in presence of bromide acceptors,[3] can cause the loss of over 90 per cent of the bromine. This, together with the continuity of the regain of bromine by silver on bromination, may be taken as quantitatively comfirming the conclusion that the products of the visible decomposition of the silver halides by light are metallic silver and halogen. The relation of this to the energy consumed in absorption of light is less definitely settled. J. Eggert and W. Noddack[4] have published results which they interpret as confirming the Einstein photochemical equivalence principle for the decomposition of silver bromide in gelatino-silver bromide emulsions. For every quantum of light $h\nu$ absorbed *by the silver bromide* for wave-lengths $365\mu\mu$, $405\mu\mu$ and $436\mu\mu$ they deduce that one atom of silver is produced,—by the reduction of one equivalent of silver bromide. F. Weigert[5] has severely criticized these results. It appears certain that the absorptions of the silver bromide were incorrectly calculated by Eggert and Noddack, aad that these results fall considerably short of confirming the Einstein photo-chemical equivalence. On the other hand, for the decomposition of a mixture of silver chloride and silver salt of an organic acid (silver citrate), Weigert[6] claims to have demonstrated that if the absorption of light is calculated for the *silver metal* formed (as photoproduct), on extrapolation to zero silver, the Einstein equivalence is confirmed. According to this, under these conditions a trace of colloid silver

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*Communication No. 235 from the Research Laboratory of the Eastman Kodak Company.

[1] Z. anorg. Chem., **133**, 389 (1924).

[2] J. Chem. Soc. **125**, 2198 (1924).

[3] In some cases, the glass walls of the reaction vessel.

[4] Sitzungsber. Akad. Berlin. **1923**, 116.

[5] Z. Physik, **18**, 232 (1923).

[6] Sitzungsber. Akad. Berlin., **1921**, p. 646.

(initially) is the true photochemical inductor, the organic silver salt being indirectly decomposed. Weigert's conclusion is disputed by Lüppo-Cramer[1] and by Eggert and Noddack[2].

Direct proof of the Einstein equivalence relation for the photolysis of silver salts is therefore not yet forthcoming. To this it may be added that by assuming the validity of this, Fajans and Frankenburger[3] have given a plausible explanation of their results on the influence of adsorbed silver ions, of bromide ions, and hydroxyl ions on the optical sensitivity of silver halides. Further, Toy and Egerton[4] regard their results in the relative spectral absorptions of silver bromide in relation to latent image formation as in good agreement with Eggert and Noddack's conclusions if supposed to hold for the formation of the latent developable image.

Microscopic Observations of the Decomposition of Individual Crystal Grains

The observations made in the course of the present investigation were partly qualitative, on special individual crystals, partly quantitative (statistical) on the grains of emulsions. They were made in the microscope, and in so far as possible, recorded by photomicrography. These observations lead to a tentative theory of the mode of photochemical decomposition of the silver halides which is not without interest for the theories of photographic sensitivity and image formation.

For the study of the decomposition in individual grains, regularly formed crystals of silver bromide were specially prepared from ammoniacal solution, as described in a monograph on the silver bromide grain[5]. As noted there, such crystals showed black dots of reduced silver scattered over the surface[6] unless prepared and photographed in red light. On continued exposure these scattered centers increased in number and size until the whole crystal was decomposed and deformed. Recently Lüppo-Cramer[7] has reported the same appearance of visibly isolated reduction centers, apparently haphazardly distributed, in the unusually large and regularly formed crystals of a specially prepared emulsion. But subsequent to the publication of the monograph, we have observed and described[8] a photochemical decomposition of a quite definitely vectorial character, although still disperse or discrete in nature. We have further amplified and confirmed these observations, and present here some illustrations of this interesting orientation of the photochemical effect in crystals. The crystals of silver bromide were exposed in the focus of the

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[1] Phot. Korrespondenz, "Festnummer", 1922, 49.

[2] Z. Physik. 18, 299 (1923).

[3] Z. Elektrochem., 28, 499 (1922).

[4] Phil. Mag., 48, 947 (1924).

[5] A. P. H. Trivelli and S. E. Sheppard: "The Silver Bromide Grain of Photographic Emulsions", (Monographs on the Theory of Photography, No. 1, Eastman Kodak Company, 1921).

[6] Ibid, p. 83.

[7] Camera, 3, 89 (1924).

[8] A. P. H. Trivelli and S. E. Sheppard: Phot. J., 63, 334 (1923).

microscope; the appearance of the decomposition was followed visually, as well as photographed at certain stages. As will be seen from the photomicrographs, the decomposition did not proceed according to chance, but in many cases in a definitely vectorial manner, following a pattern determined by the habit of the crystal.

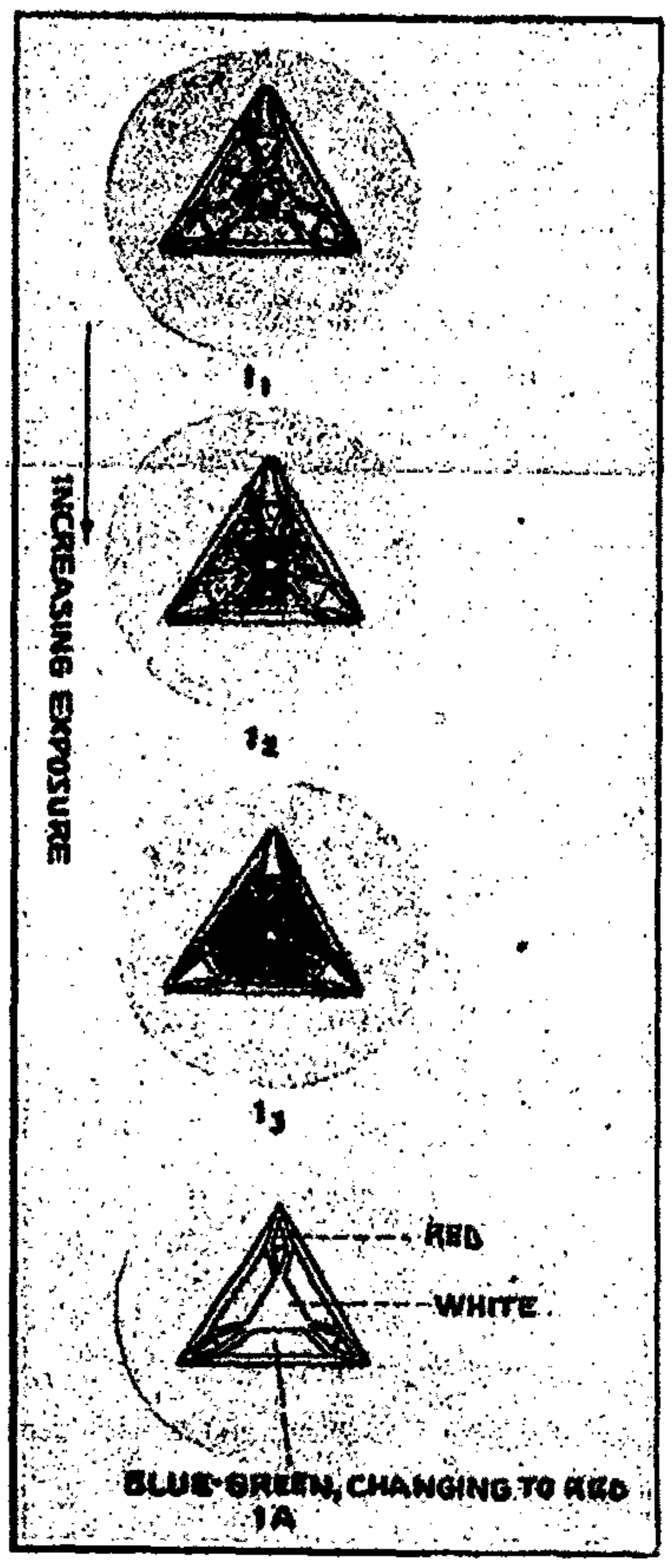

Fig. 1

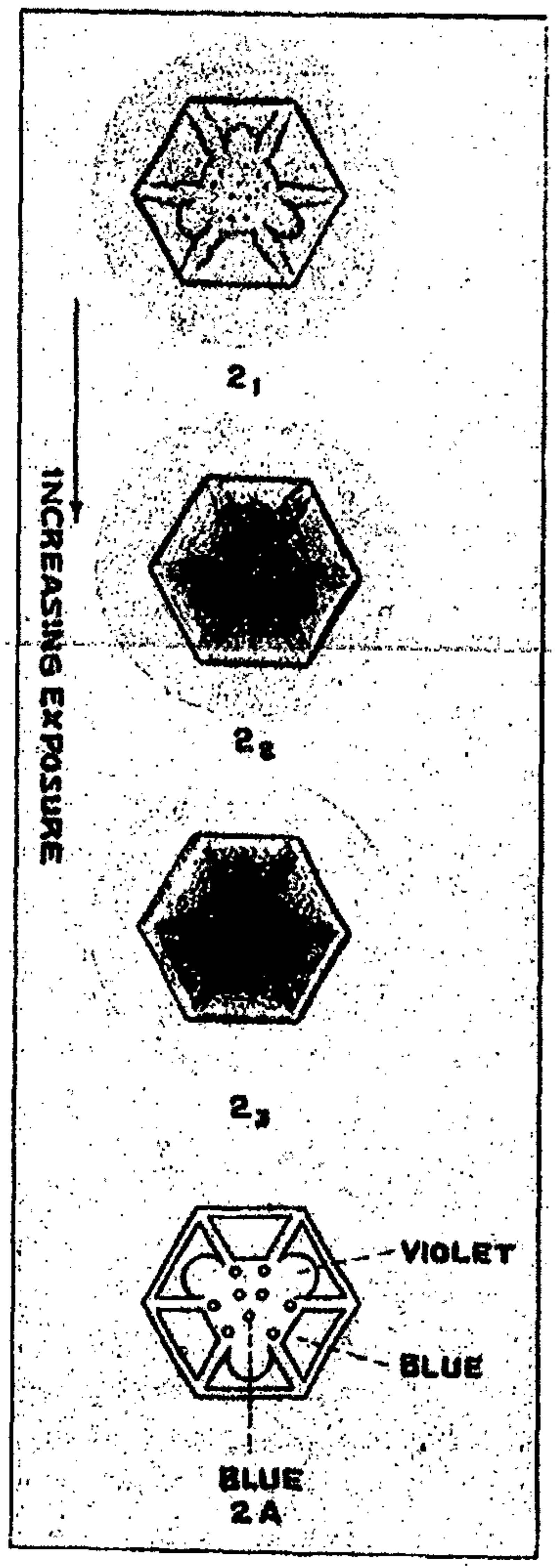

Fig. 2

In general, the decomposed silver is deposited or aggregated along the lines of most rapid growth, the edges of the crystal remaining markedly free from decomposition. Lamellar patterns on the faces of the crystals seem to have a definitely directive and specific influence on the decomposition. This extends not only to the coarser localization of the reduced silver, but also to the finer structure and inner dispersity of the colloid silver particles, as evidenced above all by their color. Thus in the diagrams *1A*, *2A*, *3A*, *4A*, the noteworthy polychromasy and pleochroism of the different areas has been partially indicated. (See figures) In one case the cluster of reduction centers in the central pattern was bluish-green from the beginning, while those in the corners turned from the red of highly disperse silver to the bluish-green of a lower dispersity.

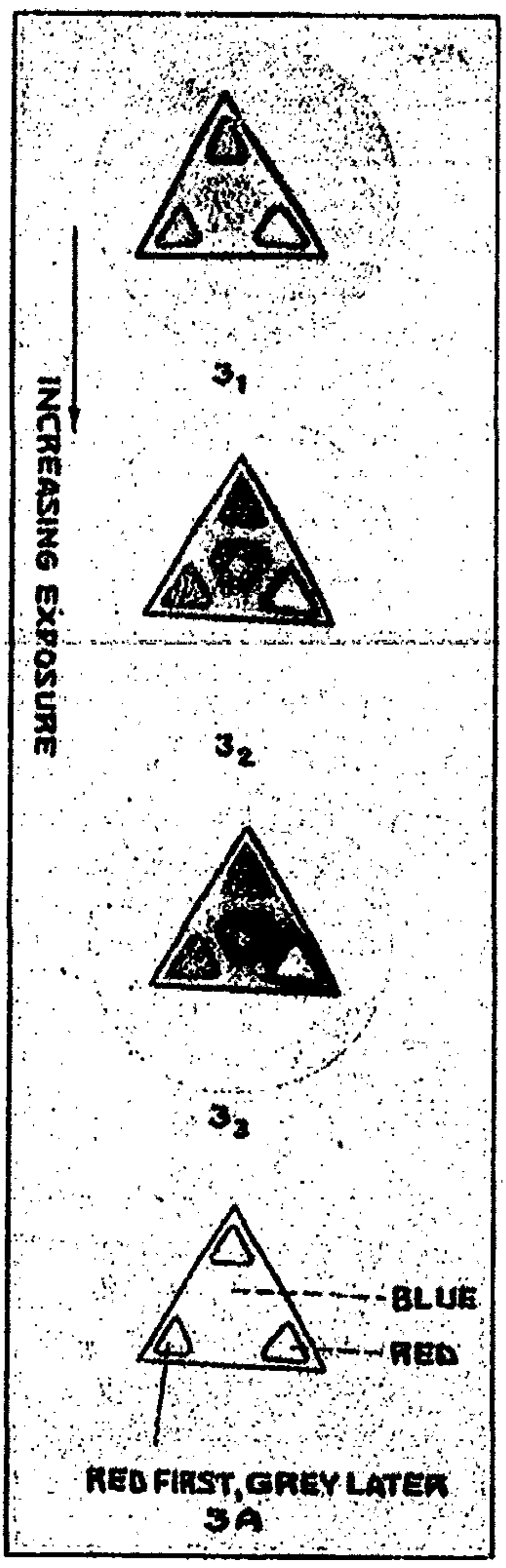

FIG. 3

As decomposition goes on the center hexagon appears blue.

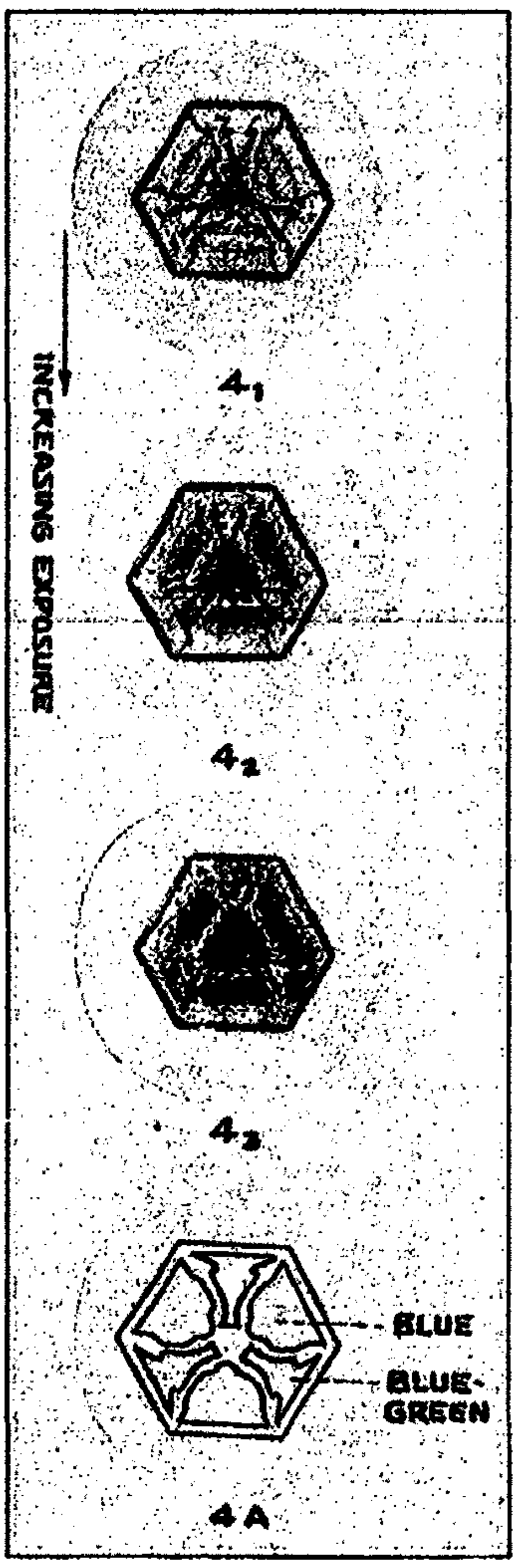

FIG. 4

The Silver Bromide Grains of Emulsions

These observations on specially crystallized silver bromide do not seem to be in accord with certain results on the initial exposure of the grains of emulsions and the distribution of the latent image. It has been shown that if development of exposed grains is stopped very early, grains shows a greater or less number of isolated "development centers"[1]. Svedberg gave evidence[2] that these centers were scattered wholly according to the laws of chance on the surface of (approximately) spherical grains; Toy[3] has reported further quantitative results confirming this haphazard distribution, but at the same time recorded the observation, considerably at variance with this result, that the "centers" tended to occur preferentially at the edges and corners of tabular, polyhedral grains.

Moreover no such regularity of the visible decomposition as was found in the special crystals was observed in the case of the grains of commercial emulsions. T. Brooksbank[4], who investigated this, describes the darkening of the grains as extremely patchy, being more complete in some grains than in others, and our observations are in agreement with his on this point. In some grains the darkening is so rapid that it occurs during focussing in white light. While in the case of the larger, more regular tablets decomposition may first be noted as a discontinuous ring inside the unaffected edge, or as dark blobs on the edge, usually the reduction patches are not resolved by the microscope into discrete centers. In any case, further decomposition proceeds in a very irregular manner. However, observation of an X-ray emulsion has furnished us with examples of a type of visible decomposition intermediate between the strongly vectorial, or regularly oriented decomposition of the specially prepared crystals, and the largely irregular and haphazard distribution of the latent image, or developable centers. This photograph in Fig. 5 was taken with the new Watson dark field condenser, which allows the full aperture of the objective to be used. Careful examination discloses discontinuities at the edges and corners of some of the crystals which appear upon exposure to the strong light of the microscope and cannot be explained as other than points or centers of photochemical decomposition. As will be noted later, the very slight tendency to regular orientation or vectorial distribution of these is to be expected from the consideration that the directions of growth in the crystals

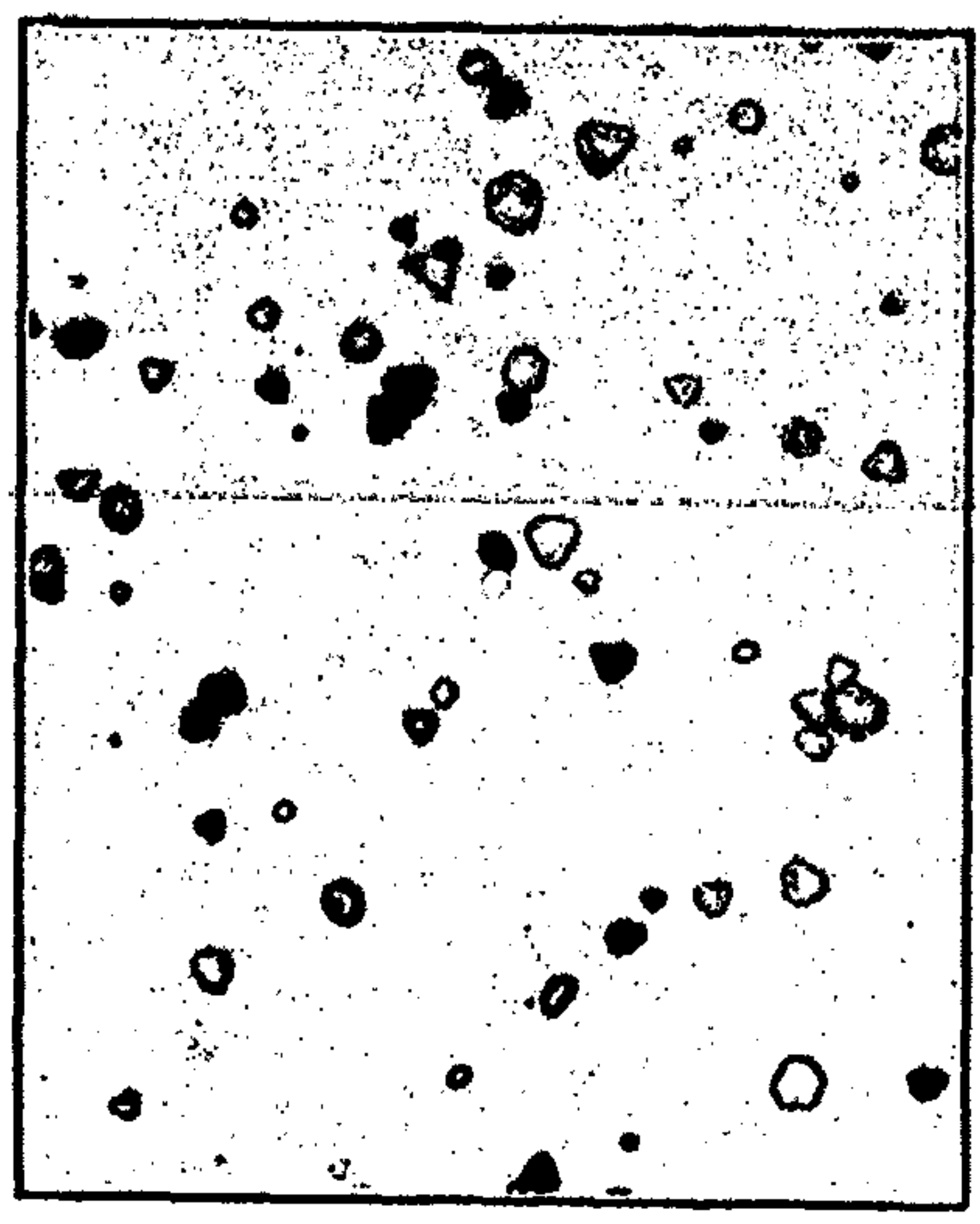

Fig. 5

Emulsion Grains showing Visible Centers.

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[1] M. B. Hodgson: Brit. J. Phot., 1917, 532.

[2] The Svedberg: Phot. J., 42, 186, 310 (1922).

[3] F. C. Toy: Phil. Mag., 44, 352 (1922).

[4] T. Brooksbank: Phot. J., 1921, 421.

from emulsions must be very irregularly distributed, frequently interrupted and reoriented.

A remarkable observation on the visible decomposition of a special emulsion may be mentioned here, which is figured in Fig. 6. As will be seen, the larger grains labelled "unexposed" already show beginnings of decomposition. Specially noteworthy, however, is the way in which spurs of silver have been thrust out from the grains, and the general expansion of the grains on prolonged exposure. If the great strength of dry gelatin, which has a tenacity of 1200 lbs. to sq. in., is borne in mind, it is evident that tremendous force has been exerted in extruding these jets of metal. As might be expected, photographs by polarized light showed very marked strains in the gelatin about these grains. Such effects were not observed with any other emulsion.

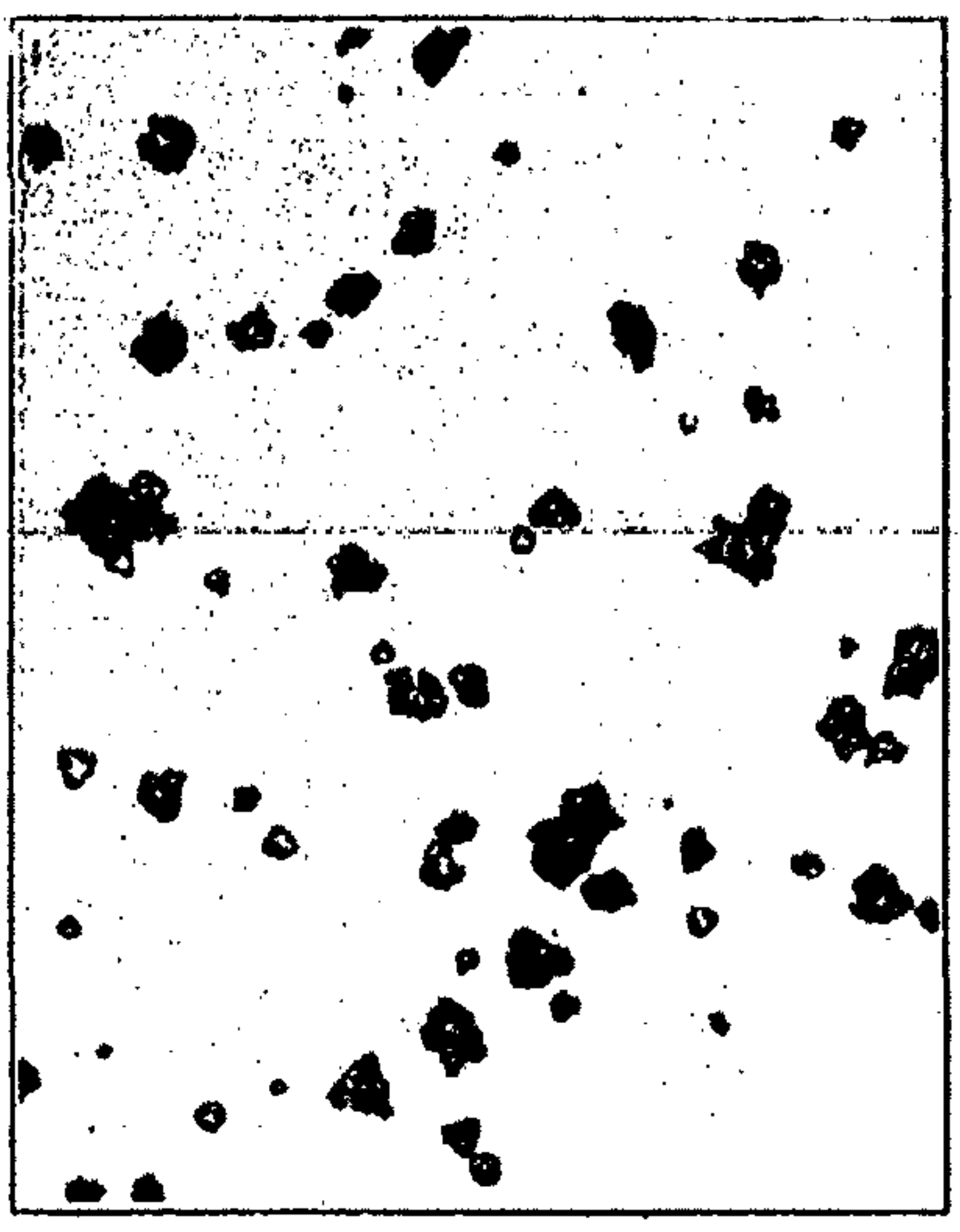

FIG. 6
Emulsion Grain showing Visible Distortion

Statistical Observations

Apart from the work of Brooksbank[1] very little microscopic study has been made of the factors in the visible photochemical decomposition of silver bromide grains. As already noted, the decomposition is accelerated by vacuum and the presence of bromine acceptors. Schwartz and Stock[2] found that many colloids accelerated the decomposition of precipitated silver halide. A factor of initial importance for photographic sensitivity (latent image formation) is grain-size. Concerning this Brooksbank remarks "Grains of all sizes in the emulsion appear to be capable of darkening, and in cases of grains of apparently the same size and shape the darkening does not take place at the same rate in each crystal". He investigated emulsions of various speeds and color sensitivity, and concluded that the visible darkening would not be directly associated with either of these two characteristics. Hence he considers that "Beside the well-known variation in grain-size and crystalline form there is yet another kind of heterogeneity among the grains of dry plates, having apparently no connection with grain size, shape, or initial sensitiveness to light".

Before we can definitely state the effect of such a factor as grain size, even in the same emulsion, when other factors may be regarded as at least uniform, it must be studied statistically, as for developable sensitivity, which is statistical in character. Observations on a few equal-sized and different-sized grains are insufficient. None the less, a quantitative statistical study of the

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[1] Phot. J., 62, 310 (1922).

[2] Z. wiss. Phot., 22, 26 (1922).

visible darkening encounters particular difficulty, as compared with the corresponding study of developable sensitivity. In contrast to developed grains, there is no sharp line of demarcation between the affected and unaffected grains. The difficulty is enhanced by the very irregular and individual modes of darkening of different grains. As will be seen from Fig. 7, beside the easily distinguished completely blackened grains, there are many of almost every intermediate stage. Sometimes it is the corners that are black, sometimes the edges, while again these may be the only unaffected parts. Often the black portion is an irregularly shaped patch or group of patches. To this must be added an equal number of variates of what have been termed "gray grains" in this Laboratory, that is, grains which appear to refuse to blacken entirely but become only grey, but with the same variety of localization of the effect. They are more evident in some emulsions than others, and some grains appear to consist of both "blackening" and "graying" material.

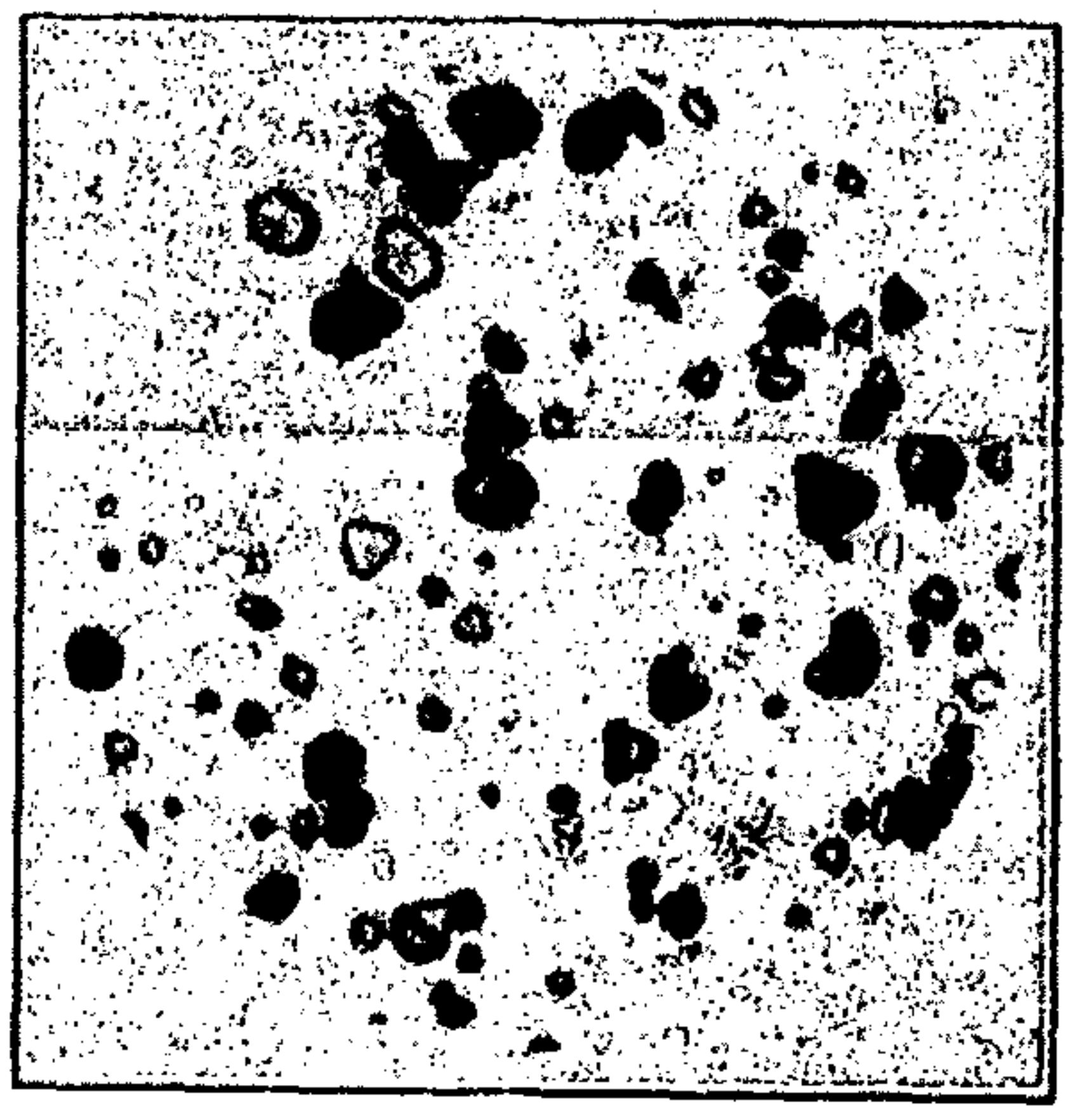

Fig. 7
Selective Visible Decomposition

In spite of these difficulties, a statistical study of the relationship between visible sensitivity and grain size was made. Microphotographs were taken at a magnification of 2500 diameters, after 5 minutes exposure of the grains to the unfiltered light of a tungsten ribbon filament lamp, run at 110 volts, 18 amperes. These were enlarged by projection to 10,000 diameters, and the grains classified according to their size. The only procedure possible was to sort them into three groups: unaffected, or negligibly so, darkened, and doubtful, and later to apportion the doubtful ones equally to the two definite classes. This procedure is, of course, very rough, and the results only of an approximate character. None the less, they appear to indicate a fairly definite relationship. From the graph in Fig. 8 it appears evident that, statistically, the visible sensitivity increases with grain-size. As a starting point we may regard the "darkening" as something distributed at random over the area of all the grains, but as insufficient to completely (uniformly) blacken the whole surface of all the grains. This may be put more definitely as follows. [Suppose q quotas of "blackening" (visibility) are scattered haphazardly over a number of grains of total surface S, then the probability that a grain of area a will get r quotas of "blackening" is

$$p_r = \frac{(a\,q)^r}{r!} \cdot e^{-\frac{aq}{S}}$$

it being understood that a grain getting one quota of "blackening" is classed as "blackened." Then the probability of a grain getting no quota, or remaining unblackened is

$$p = 1 - e^{-\frac{aq}{s}}$$

whence the percentage number of blackened grains of a given class-size *a* is given by the expression

$$p = 100 \left(1 - e^{-ca} \right)$$

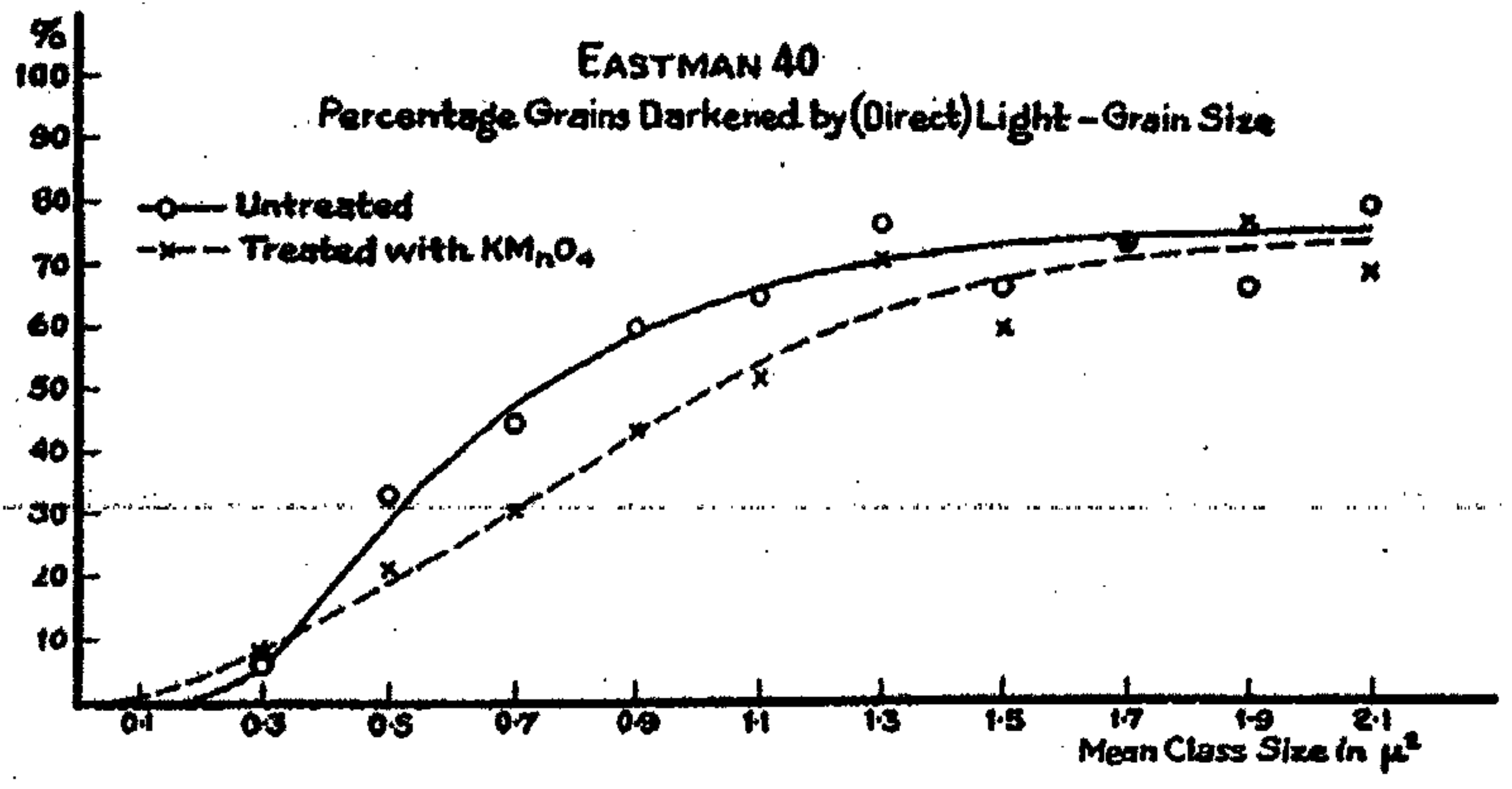

FIG. 8

where *a* is the class-size (area) of the grains, and *c* is a constant; evidently

$$c = \log \frac{100 - \log (100 - p)}{a}$$

This expression is found to represent the results of the classification over a considerable range:

TABLE

a Area in μ^2	*p* percentage blackened	*c*
$\cdot 3\mu^2$	5	.074
·5	30	·444
·7	45	·371
·9	57	·407
1.1	63	·392
1·3	69	·391
1·5	71	·360
2.1	76	·302

This relation is similar to one found to hold for the probability of spontaneous fogging (developability) of grains in an over-ripened emulsion[1]. The question as to a relation between these two phenomena will be noted later in discussing

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[1] Phot. J., March, (1925).

a tentative theory of the photochemical decomposition. Meanwhile it will suffice to point out that these results indicate that the photochemical (visible) sensitivity is discrete in character, limited in magnitude, and behaves to a considerable extent as though alloted to the grains in definite quotas, the chance of a grain securing a quota being proportional to its size.

The developable sensitivity of high speed emulsion is greatly reduced by treatment with oxidizing agents, such as chromic acid, permanganate, etc. The curves in Fig. 9, from a previous publication[1] show the great effect of this treatment. The statistical survey of visibly darkening grains was repeated with grains exposed after treatment with permanganate. It will be seen by comparison of Fig. 8 with Fig. 9 that the effect of desensitizing is very much less on the chance of visible darkening than it is on latent image formation. There is some tendency for the effect to be greater for the smaller grains than for the larger, but the experimental errors are too large to regard this as established for this visible decomposition. The results may be equally interpreted as increasing the tendency of the curve to show an inflexion.

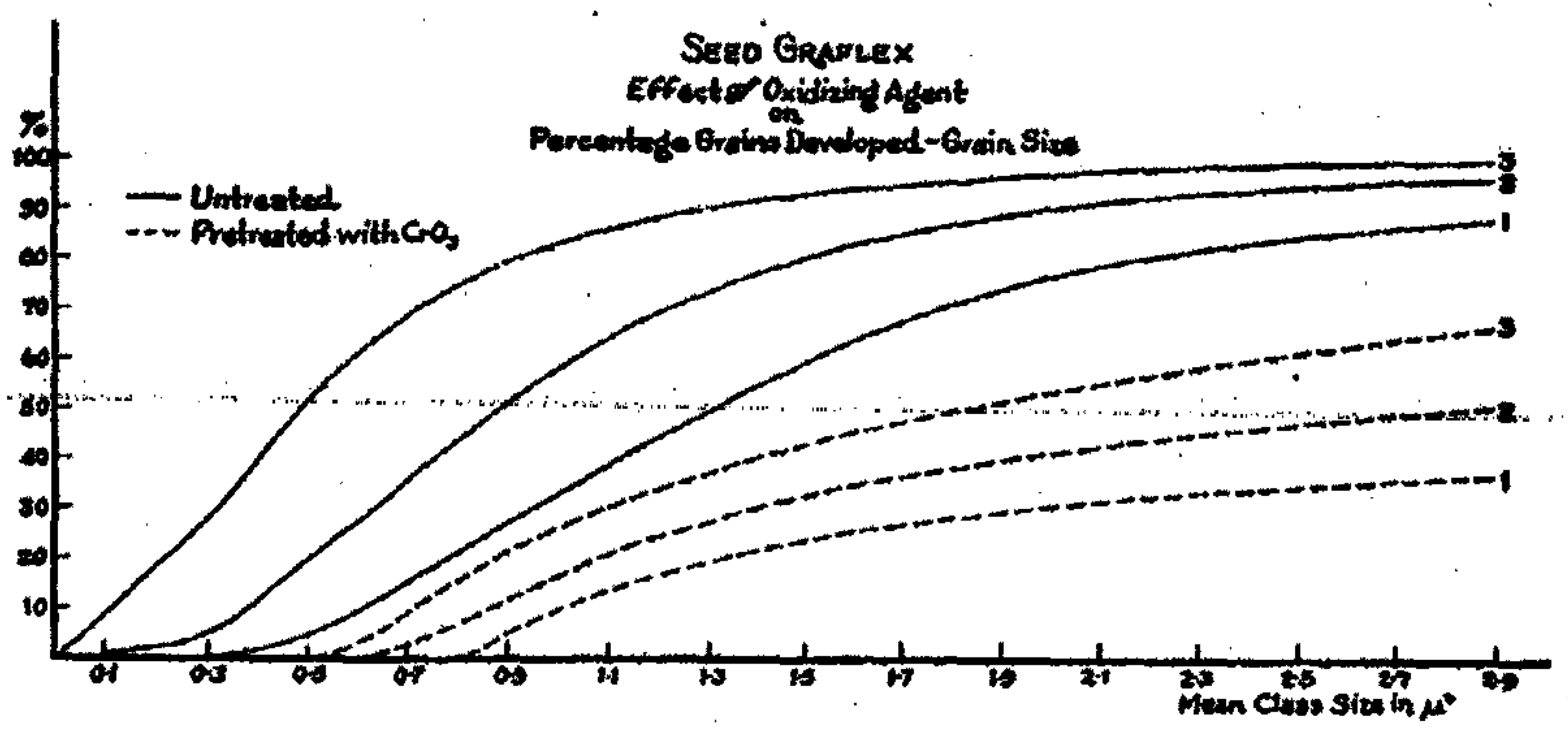

FIG. 9

A comparison of visible and developable sensitivity discloses a certain general parallelism with many particular deviations. In each case grain size appears to be a factor statistically increasing sensitivity, if this be defined as the chance of blackening, or developability, for a given exposure—naturally of entirely different magnitude in the two cases. Again this factor may be outweighed in either case by others, since emulsions may have every similar grain size but differ greatly in developable sensitivity and visible sensitivity. The relatively small effect of oxidizing desensitizers on visible sensitivity, compared with its effect on developable sensitivity, is a point of difference.

Brooksbank expresses disbelief in the existence of the inherently dark grains mentioned in the first Kodak monograph and remarks, "They (that is emulsion grains) are probably all transparent to the greater part of the visible spectrum in the unexposed plate, and it is only on exposure to light that some grains become visibly darkened." We cannot agree with this. While differ-

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[1] J. Franklin Inst., November and December (1923).

ential focusing makes the average grain either translucent or dark there are some that cannot be made translucent even though only deep red light has been used, which is the condition he employed for obtaining his pictures of "unexposed" grains. These grains are undoubtedly thicker, and hence have greater absorption or have surfaces producing total reflections. In either case, the exposure would be more photochemically efficient and we would expect them to be more sensitive.

A Tentative Theory of the Photochemical Decomposition

It appears to us that both the resemblances and the dissimilarities between the developable sensitivity (latent image) and the visible sensitivity of silver bromide grains can be explained by the following considerations. The decomposition by light of the crystal is at first only (auto) catalytically *oriented*, i.e., affected as to locus and distribution, not magnitude per energy incident and absorbed. The energy effective is that absorbed by the silver halide[1]. Later, as the period of latent image formation passes into that of visible image formation, the decomposition is not merely autocatalytically oriented but accelerated and intensified, to some extent by spectral (auto)-sensitization.

Furthermore, the initial orientation of the photolysis is dominated by the presence of "sensitizing nuclei"—those destroyed by oxidizing desensitizers; these have little effect (not necessarily *no* effect) on the subsequent stages, when the photolysis is becoming considerable and producing visible decomposition. In this stage, the progress of the photolysis is determined by two principal factors, *viz.* (a) the structure of the grain, in particular, the numbers and direction of lines of growth, and (b) the thereby regulated autocatalytic orientation and sensitizing by the photoproduct itself. There ensues a synergy or antagonism between the pure original structural influence of the silver halide crystal on the photolysis, and the derivative (autocatalytic) effect of the products, upon further decomposition. In very regular and symmetrically developed crystals, these factors harmonize, so to speak, leading to definitely vectorial decomposition patterns, (q.v.). But in less regularly developed crystals, when the directions of most rapid growth are deviated, multiplied, and repeatedly reoriented, the secondary autocatalysis becomes dominant, with the patchy and irregular effect observed in emulsion grains.

The effect of size in grain is probably complex also. In the case of developable sensitivity, we have suggested, in recent paper with Loveland[2] that the larger crystals contain, on an average, larger sensitizing nuclei, which therefore *initiate* the secondary condensation of photoproduct in a similar haphazard fashion. Reaching a size which induces developability earlier than smaller nuclei, (which have to concentrate a greater number of silver atoms about them) they therefore ensure greater apparent photo-sensitivity for

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[1] Cf. Toy and Egerton: Phil. Mag., 48, 947 (1925); Sheppard, Trivelli and Loveland: J. Franklin Inst., 200, 51 (1925).

[2] J. Franklin Inst., 200, 51 (1925).

development. However, the effect of *size* on *relative* sensitivity remains, if anything enhanced, when the nuclei are destroyed[1] by oxidizing desensitizers (cf. Fig. 9). To explain this, and other characteristics of latent image formation, we have proposed, in the paper referred to,[2] the hypothesis that not only the original foreign sensitizing nuclei, but also photolytically formed silver nuclei, *orient* the photodecomposition of the AgBr to occur immediately adjacent to them. Hence, a nucleus present, or formed, in a (large) grain has a greater chance of growing, by orienting decomposition about itself, according as the number of coherent silver bromide particles exposed to light is greater, i. e., as the superficial area of the crystal is greater.

According to this, it is not necessary to suppose that the sensitivity nuclei *increase* the amount of silver reduced by a given amount of light energy. It suffices if the energy decomposes silver bromide according to Einstein's photochemical equivalence principle, or at even lower efficiency. It is only necessary that they concentrate the reduced silver atoms in groups or aggregates more rapidly than would occur in their absence.

When we pass beyond the stage of latent image formation, where these aggregates or development centers may not number more than a few hundred silver atoms, to *visible* decomposition, the position may be changed. Here the *initial* effect of any foreign nuclei is less important—at least if they are small and few—and is rapidly overshadowed by that of the photoproduct itself. It is very possible that at this stage not only a catalysis of orientation, affecting the direction of the photolysis, but a true acceleration occurs. It is true that the sorting of blackened grains, as previously described, involves a large subjective factor of "visibility", whereby concentration of the photoproduct gives the impression of a greater blackening than the same amount of material more dispersed. But it is difficult not to conclude that a real and objective increase of blackening, i.e. decomposition, existed in the larger grains. Decision on this must await chemical analysis on centrifugally fractionated grains of different sizes. Such a true autocatalysis may well occur, however. In the first place consider the reverse action of the liberated halogen on the silver formed. When a number of silver atoms are reduced close together, the probability of escape of the halogen is greater, due to its greater concentration head. In some cases it may even tend to remove smaller aggregates of silver or single atoms by recombination. This holds also for halogen released *inside* the grain affecting the *surface* layers as it diffuses out. For the *visible* decomposition the interior of the grain is much more important than it is for the developable (latent) decomposition. Moreover, it is possible that the colloid silver formed can act as an *optical* sensitizer for the decomposition, i.e., lower the $h\nu$ limit effective in reducing a silver atom. This possibility has been discussed by one of us in relation to oriented autocatalysis in iodide treated silver bromide emulsion[3] and evidence for silver optical sensitizing exists. This effect is

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[1] At least, as far as ascertainable.

[2] J. Franklin Inst., Ibid.

[3] S. E. Sheppard: "The Action of Soluble Iodides and Cyanides on the Photographic Emulsion", Phot. J., 62, 88 (1922).

definite in the case of plates exposed first to X-rays, then to ordinary light, and may well occur in ordinary light[1]. We propose to investigate this spectro-sensitometrically, however, and regard it at present as uncertain for the point at issue.

If an orientation, eventually autocatalysed by the photoproduct itself, of the decomposition in silver halide grains exists, it evidently requires itself an explanation. That such an orientation does not exist appears certain from the results with the specially prepared silver bromide crystals, and one specifically related to the directions of most rapid growth. Equally the orienting influence of the photoproduct appears in the cases of deviation from the vectorial decomposition.

In explanation of this orientation, a modification and application of an idea suggested by F. Weigert seems worthy of thought. The application of Maupertuis' principle[2] to photochemical reactions had been made in very generalized form by Sheppard[3]. As Weigert justly points out, the fruitfulness of the application necessarily lies in the installation of specific hypotheses as to its mechanism. The specific hypotheses he proposed[4] was as follows: "On excitation of a system in which the electrons move in deformed orbits, by a frequency within the deformation interval, an alteration of the system takes place in the sense of most completely removing the deformation."

A deformed orbit we shall regard as synonymous with a perturbed orbit. Weigert considered the simplest response of a system to such an excitation to consist in a mutual repulsion of the parts from each other, in which connection he refers to Bohr's conception of light absorption by increase of the size of orbits. Weigert's interpretation of his idea in terms of a mechanical separation of neighboring particles "not yet aggregated to one molecule" may be regarded as less happy. In any case, it is very difficult to apply to atoms or ions forming part of a crystal, which may therefore be regarded as practically parts of one molecule. It may be equally argued that expansion of the orbit to infinity, i.e., transfer of the electron to a hyperbolic orbit, would "most completely eliminate the perturbation." This seems to us most consonant with both outer photoelectric effects and those inner photoelectric effects inferred in photochemical reaction.

In "ideal" reactions, the optical coupling, resulting in perturbed orbits, is a minimum. Weigert points out that in concentrated solutions, and gases under pressure, the number of optically coupled molecules must be very considerable, and even in dilute systems "fluctuations" lead to local concentration spots, indicated by deviations from Beer's law. "These complexes of optically coupled molecules are evidently in many cases the real seat of the photochemical reaction, for which the above mentioned specific application of the

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[1] Cf. Lüppo-Cramer: Phot. Ind., 1924, 982.

[2] Sometimes termed the LeChatelier-Braun-van't Hoff principle, but fundamentally the principle of least action.

[3] "Photochemistry". (1914).

[4] Z. Elektrochem., 23, 366 (1917).

LeChatelier principle holds. This implies the possibility of catalytic light-reactions."

It is evident that in the close packing of the crystalline state there exists the greatest possibility for the development of perturbed orbits. Although Weigert has subsequently considerably modified his views, and not continued to develop this hypothesis, there are many valuable features in it. The importance of perturbed orbits, and deformed ions, for reactivity has been recently extensively discussed by K. Fajans[1]. It is considered in regard to spectral emission and absorption, particularly with regard to the broadening of spectral lines, by Foote and Mohler[2]. "The quantum theory substitutes for impact damping the influence of the electrical fields of neighboring atoms upon the position and energy of an electron in a quantized orbit. Since the energy of any orbit is altered, the energy difference of two orbits between which an electron jump takes place may be changed, with a resulting modification of $h\nu$"

The photochemical reduction of silver halide may be regarded as consisting fundamentally in the transfer of a valency electron from a halide ion to a silver ion of the crystal lattice[3]. It is generally considered at present that the silver halides are distinctly polar, and that the lattices consist of silver ions and bromide ions held together by electrovalences[4]. The orbit whose perturbation would be of principle importance on this view is that of the valency electron of the bromide ion. Now it seems probable that in the case of crystals the orbital perturbations proper to the constituent atoms will be more or less symmetrically partitioned according to the homogeneity and symmetry of the crystal. In particular, there will be definite traces of the directions of most rapid growth, reflected also in differential densities of packing. The modified Weigert principle, that the photochemical reaction will be in the sense of completest elimination of the perturbed orbits, is therefore in good accord with the vectorial patterns of decomposition observed in special crystals. But a factor of equal, in some cases greater importance in this matter, than the growth structure of the crystals, is the presence of foreign inclusions in the crystal. The "foreigness" of these may vary from that of atoms capable of entering into the lattice, but having different volume, and altering the lattice interval[5] to that of substances very slightly if at all congruent with the lattice. Certain substances, notably metallic silver, will induce marked perturbation of the orbits of electrons of adjacent silver halide. *The nucleating effect of so-called "sensitivity centers", as also of photochemically reduced silver in the crystal is probably due to this effect.* In consequence of this, and helped by the much less symmetrical growth of the crystal grains of emulsions, we have in these latter photochemical decomposition much less affected by the vectorial

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[1] Naturwissenschaften, No. 10, March 9, (1923).

[2] "The Origin of Spectra", p. 92.

[3] Cf. S. E. Sheppard and A. P. H. Trivelli: "On the Relationship between Sensitiveness and Size of Grain in Photographic Emulsions" Phot. J., 61, 403 (1921). Independently proposed by K. Fajans: Z. Elektrochem, 28, 499 (1922).

[4] Cf. Wightman, Trivelli and Sheppard: Trans. Faraday Soc., **19**, Pt. 2, Oct., (1923).

[5] Cf. Iodide Effects in Silver Bromide. On the X-ray Patterns, R. B. Wilsey: Phil. Mag., **46**, 67 (1923).

character of the crystal, much more by the orienting effect of the photoproduct formed.

In sum, then, if a photochemical change can occur in a crystal, it is reasonable to suppose that this will occur preferentially at the boundary of foreign inclusions (particularly free metals and substances of high refractive index) eliminating the perturbed orbits adjacent to these boundaries. Taken in conjunction with the vectorial character of the crystal, this nucleation effect may well extend over a considerable region. In this way the greater sensitivity of larger silver bromide crystals is enhanced over and above that afforded by their greater chance of having larger original sensitivity nuclei present. This would remain effective, whether the light be incident in continuous waves or by quanta.[1]

It may be suggested that the pecularities of the distribution of visible blackening in silver halide crystals could be sufficiently explained by considering only the diffraction and internal reflection of light in the crystals. This might be assumed to produce local concentrations of energy, giving at least some of the effects observed. But, such an explanation, although having the merit of apparent simplicity, does not in our opinion satisfactorily account for the gradation of effects observable between specially prepared crystals and emulsion grains. Nor does it directly cohere with the explanation of the primary photochemical effect itself.

In a paper on "The Dispersity of Silver Halides in Relation to Their Photographic Characteristics"[2] one of the writers concluded, in discussing dispersity and sensitivity that "since the atom itself is now recognized to be a disperse system, we may have to follow through into the silver atom itself."

If the importance of perturbed electronic orbits for sensitivity is sustained, this conclusion is justified.

Summary

1. The photochemical darkening of specially prepared silver bromide crystals has been studied microscopically. It is shown that the decomposition occurs in definitely oriented patterns depending upon the growth and structure of the crystal.

2. The visible darkening of the silver bromide grains of emulsions was studied statistically. In contrast to the specially prepared crystals, the decomposition is largely irregular. The visible sensitivity is found to increase with the size of grain in the same emulsion. The lack of parallelism between the developable sensitivity and the visible sensitivity of different emulsions is due to the fact that the visible sensitivity is relatively independent of sensitivity nuclei.

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[1] Cf. J. Franklin Inst., loc. cit.

[2] S. E. Sheppard: "Colloid Symposium Monograph", 1, (1923).

3. A tentative theory is proposed. It is suggested that the photochemical decomposition is oriented in the crystal according to the gradients of ionic deformation, or perturbation of electron orbits following certain directions of growth. Since sensitivity nuclei, as also the reduced silver, will induce marked deformation in contiguous silver bromide, the decomposition becomes autocatalytically oriented. This explains the contrast in behavior between the special silver bromide crystals and emulsion grains, as well as the effect of size.

The writers wish to express their thanks to Mr. R. H. Loveland for assistance in the experimental work.

Rochester, N.Y.
March 20, 1926.

AN IMPROVED SALT BRIDGE*

BY HANS T. STERN

In the course of a number of various electrometric investigations, the author has developed an improvement in the form of the electrolytic connection tube usually used in these measurements. He believes that a short description of its construction and its main advantages may be useful to other investigators.

At present the type of salt bridge most used is the one devised by E. Müller, consisting of an H-shaped glass tube plugged at both lower ends with paper stoppers, the upper openings being connected by a rubber tube. The chief disadvantage of this construction is the presence of foreign porous material at the liquid junction. This may cause errors of several millivolts, as has been shown recently by R. Fricke.[1] E. Müller[2] therefore recommends having both ends of the electrolytic connection tube drawn out in capillary form with paper plugs placed immediately above the capillary constriction.

Apparatus permitting the use of free liquid junctions without a porous stopper have been devised for many types of routine pH determinations by W. M. Clark[3] and L. Michaelis[4] (Praktikum der physikalischen Chemie, 1922). The free liquid junction gives a rapid establishment of equilibrium while the results are at the same time reliable.

The same advantage can be attained by replacing the rubber tube in Müller's salt bridge by a stop-cock and in omitting one of the paper stoppers. At the same

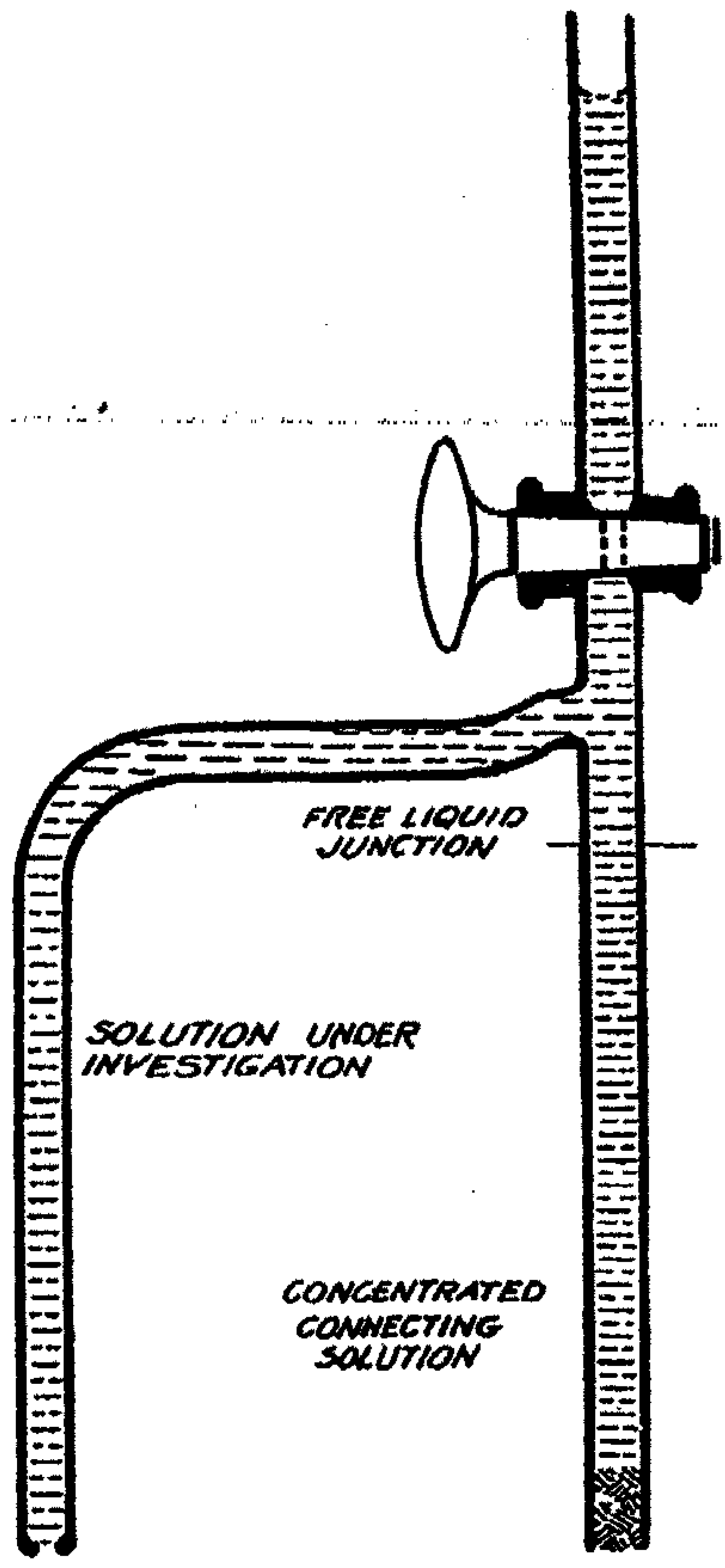

Fig. 1

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*Contribution from the Plant Research Laboratory of Lehn and Fink, Bloomfield, New Jersey.

[1] Z. Elektrochem, 30, 577 (1924).

[2] "Elektrochem. Praktikum" 4th edition (1924).

[3] "The Determination of Hydrogen Ions," (1923).

[4] "Praktikum der physikalischen Chemie", (1922); also L. E. Dawson: J. Am. Chem. Soc., 47, 2172 (1925).

time the salt which forms the bridge can be prevented entirely from diffusing to the electrode as will be shown. The tubing inside of the remaining plug is filled with the same solution into which it dips, (this usually being concentrated KCl solution). This leg of the tube can be most conveniently filled with a pipette drawn out to a capillary. If then the other part of the tube is filled by suction with the fluid with which it is to be brought into contact, a free liquid junction is established in the upper part of the tube.

This arrangement is suitable for a great variety of chains to be built up, and has been found very reliable, quick and easy to handle. The tubes once cleaned are usually kept in a beaker under distilled water and the paper plug rarely need be renewed.

This salt bridge provides a long path for the diffusion of bóth solutions into each other, and may, therefore, be left in connection for a very long time. The only precaution to be observed is to fill the more concentrated solution on the stoppered side. An additional advantage is that the solution cannot be pressed out or sucked in through the porous stoppers by changes of volume which always occur in handling rubber tubing.

For work with very dilute solutions, the glass tube is made wide to increase the conductivity. Only the open end is provided with a short and narrow tip.

ON THE INFLUENCE OF THIN SURFACE FILMS ON THE EVAPORATION OF WATER

ERIC K. RIDEAL

In a recent communication Hedestrand[1], as a result of a series of experiments, arrives at the conclusion that a unimolecular film of oil molecules on the surface of water is without influence on the rate of evaporation of the water from the surface. This conclusion being at variance with some experimental results obtained some time ago, it was considered of interest to repeat and enlarge upon these preliminary experiments.

As a result it may be definitely stated that the rate of evaporation of water from a surface is very considerably diminished by the presence of a unimolecular film of fatty acid upon the surface and that this diminution in rate is materially affected by the compression or surface concentration of the film.

Hedestrand has noticed that, in the air-streaming method employed by him, a stagnant layer of air and vapour may be assumed to exist in close proximity to the liquid surface, through which layer the water vapour has to diffuse before removal by the air current. He assumes in addition, however, that the concentration gradient of water vapour in this stagnant layer is always sufficiently small so that any real change in the rate of evaporation of the water from the liquid surface would be detected by a change in the rate at which water vapour would be swept from the surface of the stagnant layer by the air stream. A simple calculation, however, indicates that this is by no means the case.

When equilibrium between a water surface and the vapour above it has been established, the rates of evaporation and condensation are equal. On the assumption that there is no reflection of water molecules striking the surface from the gas phase the rate of condensation, and thus the rate of evaporation may readily be calculated from the effusion equation of Herz and Knudsen.

$$\mu = \frac{K.P}{\sqrt{MT}}$$

where μ is rate of evaporation in gm. mols. per sq. cm. per second. P the vapour pressure, M the molecular weight and T the absolute temperature.

Hedestrand employed a water surface of 18.25 sq. cm. at a temperature of 20°C. We should thus anticipate, according to the above considerations, an evaporation rate of no less than 4.032 gms. per second; his observed maximum rate at which the water was swept from the quiescent layer never exceeded 0.331 gm. per hour or 0.0023% of the true rate of evaporation. Evidently the number of molecules of water vapour swept away from the stagnant layer per

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[1] J. Phys. Chem. 38, 1244 (1924).

second by the air is negligibly small compared to the rapid rate of evaporation and condensation occurring in the stagnant layer itself and Hedestrand's results are thus readily interpreted.

We should anticipate that if the rate of removal of the water vapour from the neighbourhood of the water surface could be increased so that the ratio between the rate of removal and true rate of evaporation were increased, any effects due to the presence of a unimolecular film of fatty acid on the water surface would become apparent.

The apparatus employed consisted essentially of a closed inverted U tube each limb being one sq. cm. in internal cross-section; the two vertical limbs being connected by a relatively wide tube 3 cms. in diameter. Now one limb of the tube was filled with water and the system was then evacuated. Maintaining the limb containing the water at any desired temperature, say, 25°C or 35°C and cooling the other limb, the rate of distillation could readily be determined by the rate of condensation in the cooled limb. It was found that the condenser could be maintained at 0°C by means of broken ice without violent boiling of the water in the other limb occurring. The rate of stripping of the water surface could not be accelerated beyond limits set by these temperature gradients and size of evaporating surfaces without turbulent boiling occurring.

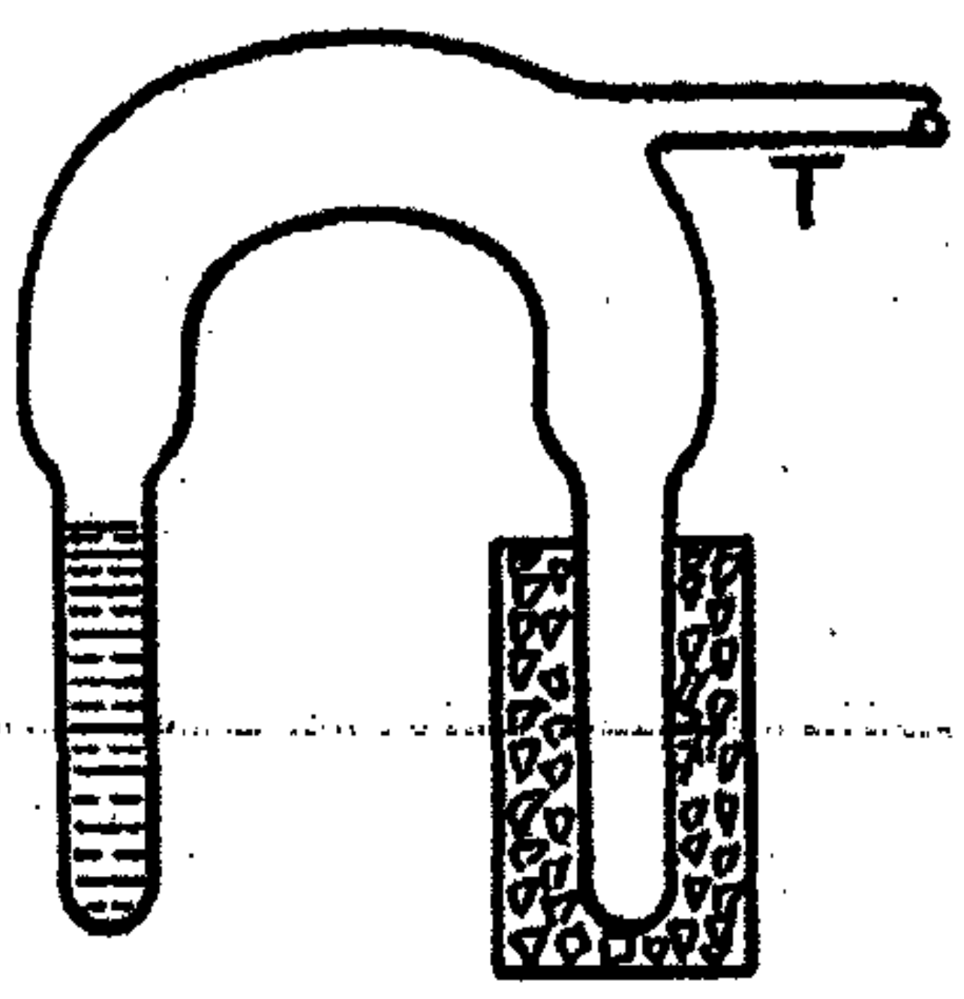

Fig. 1

The data are given in Table I

TABLE I

Temperature of Cold Limb 0°C.

Temperature of hot limb	Rate of condensation mgm. per minute	Maximum rate of evaporation possible gms. per minute	Maximum rate of evaporation less condensation from cold limb	Percentage of maximum possible rate obtained
25°C	62.5	17.82	17.82 − 3.13 = 14.69	0.42
35°C	88.3	26.91	26.91 − 3.13 = 23.78	0.37

Although the observed rates of evaporation are but a small fraction of the maximum rates theoretically possible it is to be anticipated that if unimolecular films do in reality cover most of the surface a difference in the rate of evaporation should be observed; these rates are some two hundred times greater than those obtained by Hedestrand.

If a small lens of a liquid fatty acid or a minute crystal of a solid fatty acid be placed upon the surface of water surface evaporation will take place and the acid will spread over the surface of the water in a molecular film until the pressure of the film (defined as F = σ (water) − σ (liquid)) rises to a constant value determined by the temperature of the water and the nature of the fatty acid. These equilibrium pressures for a number of fatty acids were determined by the ring method of measuring surface tension and the values of F the superficial pressures of the films calculated by means of the equation

$$F = \sigma(H_2O) - \sigma\ (H_2O \text{ with lens})$$

The rates of evaporation were determined in the manner indicated above after a minute crystal if solid or small lens if liquid of the acid had been placed upon the surface of the water in one limb and equilibrium between crystal or lens and film had been attained by allowing the liquid to stand at the desired temperature for a few hours.

As typical of the data obtained those in Table II may be cited.

Table II

Lens	Temperature	Minutes per c.c.
Lauric acid	25°C	24.5
		25.5
		28.5
		24.5
	35°C	16.5
		17.5
Oleic acid	25°C	32
		35
	35°C	23
		22.5

The variation in rates of evaporation through the films is undoubtedly due to local film rupture when incipient boiling of the water occurs. It will be noted, however, that the average values for the rates of evaporation of water protected by films are different for the acids employed and are very considerably less than the rate for a clean water surface.

The data obtained are summarised in the following table where the rates of evaporation in mgm. per sq. cm. per minute for water surfaces covered with oil films at various pressures are given. From these data the apparent reductions in the rate of evaporation are calculated. The percentage reduction in rate of evaporation so determined is necessarily a minimum value for, as we have noted, the maximum rate of evaporation actually observed for a clean water surface is much less than the rate theoretically possible. The rates observed with the film protected water surfaces are distinctly smaller and thus probably represent a very large fraction of the true rate of evaporation of the water through the film than in the former case. It is even possible that the rates observed with the film protected surface do represent a very large fraction of the maximum possible rates of evaporation from such surfaces which would indicate that the rate of egress of water molecules through the unimolecular film and fatty acid is in reality extremely slow.

TABLE III

Temperature 25°C.

Acid	Surface compression dynes per cm.	Rate of evaporation in mgm. per minute per sq. cm.	% reduction effected.
None	0	62.5	—
Stearic	5	44.9	28.1
Lauric	26.3	36.0	42.4
Oleic	29.1	29.7	52.5

Temperature 35°C.

Acid	Surface compression dynes per cm.	Rate of evaporation in mgm. per minute per sq. cm.	% reduction effected.
None	0	88.3	—
Stearic	9.27	69.9	20.8
Lauric	28.35	59.7	32.7
Oleic	28.8	43.9	50.3

It is interesting to note that unimolecular films both in the condensed and expanded states exert a similar retarding influence on the rates of evaporation, a result not to be anticipated if expanded films consist in reality of isolated molecules in kinetic equilibrium with one another.

Summary

The rates of evaporation of water and of water covered with unimolecular films of various fatty acids have been determined. The rates of evaporation from the film protected water surfaces are found to be much slower than from a clean water surface. An increase in surface concentration or film pressure retards the rate of evaporation, whilst both condensed and expanded films exhibit this characteristic to similar extents.

Department of Physical Chemistry,
Cambridge.
March 9, 1925.

NEW BOOKS

Atombau und Spektrallinien. *By Arnold Sommerfeld. Fourth revised edition. pp. xii + 862. Braunschweig: F. Vieweg and Son. Price: paper 22 marks; bound 25 marks.* Weighty witness to the rate at which investigations on matters of atomic structure are being prosecuted is afforded by the new edition of Sommerfeld's celebrated book. The book, of which the preface is dated October 1924, now contains 862 closely printed pages, an increase of 100 pages on the preceding—third—edition and of more than 300 pages on the first edition of five years ago. The recent increase in bulk has taken place in spite of the fact that a certain amount of the material of the third edition has been left out, the chief omission being some sixteen pages of introduction to the theory of relativity which are now judged superfluous. Furthermore, when we take up this considerable volume, we must remember that, as the title indicates, only one aspect of atomic structure, the radiation aspect, is fully considered, although, of course, there are references to the work of the Cambridge School led by Rutherford.

The bulk of the new matter may be classed under two heads, firstly that which deals with Bohr's theory of the periodic properties, and secondly that which deals with the complex structure of spectra, by which is to be understood the doublet, triplet, and, in general, multiplet series which have now been ordered for so many elements, and the abnormal Zeeman effect. At about the time when the last edition was appearing, Bohr was putting forward his method of considering the structure of the general atom in terms of the so-called n_k orbits, n being the total quantum number, and k, which is equal to or less than n, the azimuthal quantum number. The value of n is 1, 2, 3, 4,—for successive periods in the periodic table. There is therefore one class of orbit for the period consisting of hydrogen and helium; two classes of orbit, 2_1 and 2_2, for the period beginning with lithium; three classes of orbit, 3_1, 3_2, and 3_3 for the period beginning with sodium; four classes for the period beginning with potassium; and so on. From the chemical point of view the essence of the theory is that—in contrast with the older view, on which the electron system representing a period, when once the period was completed, remained unchanged as a feature of all heavier atoms—in the long periods, after one or two electrons have been placed in orbits of the highest possible total quantum number to represent the first one or two elements of the period, subsequent electrons, added to represent the succeeding heavier elements, go into orbits of lower quantum number, until these groups of orbits are built up to a symmetrical completeness. Thus, for example, the sodium period is formed by adding four 3_1 orbits and four 3_2 orbits to the neon arrangement: for potassium and calcium one and two electrons respectively are added in 4_1 orbits, but for the group scandium to nickel the electrons go into 3_1, 3_2, and 3_3 orbits until the inner system is built up to its completed state, with six electrons in each class of orbit. After this the period is completed by adding electrons in various orbits of total quantum number 4. It is in this way that Bohr accounts for the "interpolated" elements in the long periods. For the period of thirty-two, where the total quantum number is 6, there are two groups of interpolated elements, one being the rare earths. This theory is fully discussed in the book, especially the evidence afforded by the spectra as to the allotment of the electrons to their orbits. The theory is, of course, not yet fully worked out mathematically, but, as Sommerfeld says "*intuitiv erfasst*", a fact not always realised. The importance of this hypothesis of the building up of inner structures which were not fully completed when the preceding periods were completed needs scarcely to be emphasized. We may term it, for convenience, the two-quantum-number theory of atomic structure.

Whereas two quantum numbers suffice for explaining spectra and chemical behaviour in broad outline, to account for the multiplet series and the abnormal Zeeman effect a third quantum number must be introduced, the so-called inner quantum number. By assuming sub-divisions of the n energy levels, and allotting to each sub-division an inner quantum number, the possibilities of combination between these levels being governed by a selection principle, the number, position, and intensity of the lines in multiplets and the general

Zeeman effect has been beautifully described. The interpretation of the inner quantum number in terms of the mechanical model is, however, less satisfactory, especially since, to account for the Zeeman effect, half-quantum numbers have to be introduced, and Sommerfeld does not pay much attention to this aspect of the subject. The arithmetical character of the quantum theory is, however, very finely illustrated by the work.

We may say, in short, that the original, or one-quantum-number theory, has been mathematically worked out, and, the fundamental hypothesis once granted, the results follow naturally, in excellent agreement with such experiments as bear on this simple case. The two-quantum-number theory can be stated in terms of the model: when, as in the case of the fine structure of spectral lines of the hydrogen, or hydrogen-like, atom, the results have been mathematically worked out, the agreement is good, but for the general case detailed calculation is not possible so far. The three-quantum-number theory is, at present, a purely empirical way of representing conveniently and suggestively some of the finer features of spectroscopic observation. The exact meaning of the inner quantum number is still to seek, and only the roughest outline of a mechanical theory has been sketched.

Professor Sommerfeld shows his accustomed skill and clearness for exposition, and the book, in its new form, is assured of the same warm welcome which previous editions have received. It is a pity that Millikan and Bowen's results on the optical spectra of stripped atoms, which are of such importance for the grave problems presented by the abnormal Röntgen doublets, appeared too recently for discussion in this book.

E. N. da C. Andrade

Grundzüge der physikalischen Chemie in ihrer Beziehung zur Biologie. *By S. G. Hedin. Second edition. 25 × 17 cm., pp. vi + 189. München: J. F. Bergmann, 1924. Price 7.50 marks.* The conceptions and methods of physical chemistry have now become a prominent feature of modern works on biology and physiology, and it is recognised that students of these sciences must familiarise themselves with the point of view of the physical chemist. In the volume under review Professor Hedin sets out in five chapters those portions of physical chemistry which he considers significant for biology, covering respectively osmotic pressure, colloids, velocity of reaction and catalysis, enzymes, and the action of ions and salts.

The first, second, and fourth chapters together constitute about seven-eighths of the volume, and the reviewer feels that the ideas and methods of electrochemistry have received too little attention. Thus, for example, no real attempt is made to explain the measurement and significance of the conductivity of salt solutions, while the reference to hydrogen electrodes and their use in the determination of hydrogen ion concentration is too brief to be of much value to the beginner. However excellent Professor Hedin's work may be in other respects, no book which aims at presenting the point of view of the physical chemist can afford to omit adequate treatment of the topics just mentioned.

J. C. Philip

Food Products. *By Henry C. Sherman. Second edition. 20 × 14 cm., pp. xii + 687. New York: The Macmillan Company, 1924. Price: $2.75.* The second edition of this book has been carefully revised to include the large amount of new information that has accumulated in the ten years since the first edition appeared. The extent of this revision in respect to vitamins may be judged from the indexes. In the first edition one line suffices, while in the second edition nearly a column is required to enumerate the entries in the text dealing with vitamins.

The book is well arranged, well written and quite free from typographical and other errors. The many new facts regarding the nutritive functions of foods have been treated in a conservative manner and probably not unduly emphasized. The numerous references at the end of each chapter add much to the value of the work.

A chapter dealing with the causes of food spoilage, the recognition of such spoilage, and the conditions necessary to prevent it would be a valuable addition to the book.

F. R. Georgia

The Nature of Enzyme Action. *By Sir W. M. Bayliss. Fifth edition. 24 + 15 cm; pp. 200. New York and London: Longmans, Green and Co., 1925. Price: $3.25.* The first edition was reviewed in 1909 (**13**, 348). This latest, and unfortunately the last, edition is more than twice as long as the first one; but there has been no change in the number or the headings of the chapters.

"Attention must be called to one more point before passing on to the consideration of the special class of catalysts known as "enzymes". In view of certain theories as to the nature of enzymes, according to which catalytic properties may be conferred on any substance by appropriate means, it is important to notice that all the catalysts mentioned in this chapter are definite chemical individuals of known composition and properties. As yet this statement cannot be made of any enzyme. We are not, however, warranted in denying definite chemical constitution to this latter class of bodies, until it has been shown that bodies of known constitution may at one time possess the properties of enzymes and at another time, without any change in their chemical nature, be devoid of such properties," p. 10.

"Enzymes then are colloids and have the property of carrying down with them, by adsorption, constituents of the solutions from which they are precipitated. It is not therefore to be wondered at that amylase or invertase, as obtained in the usual way, gives carbohydrate reactions, and that pepsin or trypsin gives protein reactions. It is found, however, that the more the bodies are purified, the fewer characteristic reactions of any kind do they show. By appropriate methods, their activity, weight for weight, can be enormously increased, as shown by Willstätter. Invertase, for example, was increased in activity 1600 times. It appears that the chemical properties are due to impurities and one preparation may give slight protein reactions but none of carbohydrates, while another, equally active may be devoid of protein but contain traces of carbohydrate. Finally a product is obtained of intense activity but in very small amounts; in this respect enzymes behave like hormones and vitamins. They sometimes lose in activity when the accidental impurities are removed and this may, probably, in some cases, be due to the removal of bodies necessary for the full activity of the enzyme, such as electrolytes, co-enzymes, and so forth. Amylase is inactive without neutral salts, the lipase of liver without bile-salts, pepsin without acid, etc. When this fact is known, it can, of course, be allowed for by the addition of the necessary co-enzyme, etc., after the process of purification has been performed," p. 35.

On p. 117 the author notes that Armstrong and Hilditch hold that the most satisfactory explanation of the catalytic action of nickel in their work is the formation of "a very loose unstable intermediate system." Bayliss adds that "it is rather difficult to see how this differs from adsorption, although the authors prefer to regard it as chemical."

"A somewhat trivial illustration of the phenomena of heterogeneous catalysis may be of service in understanding the process. Take the "reaction" between a strawberry and a number of snails in its neighbourhood. As soon as a snail, in its wanderings, becomes sensible of the presence of food, it proceeds towards it. This is the first, preliminary, stage of diffusion. The next stage, that of adsorption, may be represented by the attachment of the animal to the strawberry. This takes place rapidly, as soon as proximity is achieved. So long as nothing more happens, no chemical change results. The final stage is the devouring of the fruit and its consequent hydrolysis, etc. This final stage is obviously dependent, as far as its rate goes, upon the number of snails "adsorbed." It will also be noted that it will not be in linear proportion to the number of snails at work. The more there are, the more they interfere with one another, and, when the fruit is completely covered by them, the advent of more will not further accelerate the disappearance of the food, since the newcomers will not be able to get at it," p. 118. *Wilder D. Bancroft*

Physico-Chemical Evolution. *By C. E. Guye. Translated by J. R. Clarke. 19 × 14 cm; pp. xii+172. New York: E. P. Dutton and Company. Price: $2.40.* "It is well known that since the investigations of Gibbs and Boltzmann, the principle of Carnot has assumed a new and unexpected significance, in the sense that the physico-chemical evolution of a system takes place towards states of greatest probability, equilibrium occurring when this probability is a maximum in the analytical sense of the term. The change of entropy which, in the language of thermodynamics, characterizes this evolution, will be proportional to the difference between the logarithms of the probabilities of the initial and final states.

"Thus this new conception has introduced, with a particularly strong intensity, into the domain of physical chemistry the idea of the "statistical law," with all the consequences which it involves from the scientific and philosophical point of view.

"By virtue of these conceptions the determinism of physico-chemical evolution appears, therefore, as a larger statistical determinism, in which the apparently inevitable exactness is only due to the law of large numbers. In fact, this determinism permits the occurrence of other very rare possibilities, or fluctuations, particularly when the law of large numbers is no longer entirely satisfied.

"For this reason, the question of absolute determinism is transferred into the domain of the individual actions between molecules, atoms, or electrons, which still evade our direct experimental investigations almost completely. This seems to be a philosophical consequence of considerable importance," p. 9.

The volume consists of three essays entitled: Einstein's Principle of Relativity in the Classification of the Sciences; The Evolution of Physico-chemical Phenomena and Calculus of Probabilities; Carnot's Principle and the Physico-chemical Evolution of Living Organisms.

Arithmetic involves number; geometry number and space; kinematics number, space and time; mechanics, physics, chemistry and astronomy involve number, space, time, and matter; biology number, space, time, matter, and life; and psychology number, space, time, matter, life, and thought, p. 9. The author asks, p. 8, whether the conceptions of number, space, time, matter, life, and thought are really irreducible and whether they will some day throw light on one another. He suggests that they may perhaps be derived from one and the same principle which we cannot at present perceive.

"Statistical laws, which for a long time seemed to apply exclusively to the biological, social, economic, and kindred sciences—precisely on account of the extreme complexity of the phenomena in these sciences, and because of the impossibility generally experienced of discerning the causes which produced them and made them vary—have been extended, little by little, by means of the calculus of probabilities to what are usually termed the "exact sciences." It seems as though these latter sciences, and particularly physical chemistry, only owe their title of exact sciences to the law of large numbers, which usually renders the effects of fluctations inappreciable.

"In recent years these statistical laws have been introduced with particular intensity into physical chemistry, following the conception of the granular structure of matter and the generalization of the kinetic theories. Thus even the study of fluctuations and of their consequences has given to these theoretical conceptions a reality which may be termed experimental," p. 115.

"To the philosophers of India, struck by the eternal return of events, the appearance of life must be regarded as an unfortunate accident, the source of innumerable sufferings. It is therefore necessary to desire that eventually the chaos of statistical phenomena shall end by reabsorbing it; life and conscience will then be annihilated in the *nirwana*. Such a philosophy can be considered as the expression of the pessimism and the discouragement inherent in a civilization which is more or less crystallized and the evolution of which is actually paralyzed.

"But a civilization in the process of evolution and of progress would be right in adopting a diametrically opposite point of view and in supposing that in its evolution life will always succeed in producing superior organizations; that these powerful organisms will end by dominating completely the chaos of physical-chemical phenomena; that they will perhaps succeed in vanquishing even death, which, from the point of view that we have adopted, is only the triumph of the chaos of non-organized energies over organized energies; and that finally, guided by a superior morality, these organisms will ultimately attain happiness, the final goal toward which appear to be directed the more or less conscious or unconscious efforts of individuals or societies," p. 169. *Wilder D. Bancroft*

Ions, Electrons and Ionizing Radiations. *By J. A. Crowther. Fourth edition. 21 × 14 cm; pp. xii+328. New York and London: Longmans, Green and Co.; Edward Arnold and Co., 1924. Price: $4.00.* That this book has gone into four editions in five years seems to prove that it meets a need. The subject is presented under the headings: introduction; the passage of a current through an ionized gas; the properties of the gaseous ions; the charge on an ion; ionization by collison—the spark discharge; the phenomena of the discharge tube; cathode rays and positive rays; emission of electricity by hot bodies; photoelectricity; X-rays; the alpha rays; the beta and gamma radiations; radio-active changes; radium and its products; some problems in radio-activity; the electron theory of matter.

"The number of collisions per second between uncharged molecules of oxygen is known from kinetic theory to be $1.25 \times 10^{-10}n^2$ where n is the number of molecules per c.c. The number of recombinations occurring between oppositely charged ions in oxygen as determined above is $1.6\ 10\times^{-6}n^2$. The number of collisions producing recombinations between the ions is thus about 10000 times the total number of collisions which would occur in the same time between uncharged molecules of the gas. This must be due to the strong electrical attraction between the oppositely charged ions, which draws them together when otherwise they would never have met," p. 35.

"No connection can be traced between photo-electricity and fluorescence, many fluorescent compounds being quite inactive. On the other hand, phosphorescent substances always shew a well-marked photo-electric effect. Thus calcium sulphide with a trace of powdered bismuth and a flux of sodium borate yields a very actively phosphorescent substance. On testing this it was found to be exceedingly photo-electric also, giving a photo-electric effect nearly as large as brightly polished magnesium. The three substances taken separately and also in pairs were found to be neither phosphorescent nor markedly photo-electric. By using absorbing screens it could also be shown that light which did not produce phosphorescence did not produce a photo-electric effect. The two effects, therefore, seemed to run parallel to each other," p. 151.

Wilder D. Bancroft

The "Chemical Age", Chemical Dictionary, Chemical Terms. *25 × 19 cm; pp. 158. New York: D. Van Nostrand Company, 1924. Price: $4.50.* This dictionary gives the meanings of many chemical terms met with in organic, inorganic, physical, and analytical chemistry, and biochemistry. So far as the reviewer can judge, the work has been done pretty well. It was new to him, under chromoisomerism, p. 36, that the silver salt of violuric acid is white, green, brown, or pink, according to circumstances. Of course there are things that one would have liked to see worded differently. The test for adsorption, p. 12, is not that the isotherm can be represented by the Freundlich equation. There is no reason to suppose, p. 33, that there is only one type of contact catalysis. No really intelligent person believes that one always has the formation of definite intermediate compounds or that one always deals with adsorption.

The reviewer noticed one misprint, p. 34, the statement that a cation is a negative ion. The context clears the thing up. He doubts whether anybody really believes that the properties of nascent hydrogen, p. 107, are those of very minute bubbles of molecular hydrogen. Under photochemical action, p. 121, one would have liked to have seen the statement that only the light which is absorbed can be chemically active.

These are not essential things, however, and the book will prove valuable to many people. One especially good feature is the listing of Blagden's Law, Henry's Law, Raoult's Law, etc., under the names of the originators.

Wilder D. Bancroft

Artists' Pigments. *By F. W. Weber. 23 × 16 cm; pp. vii+223. New York: D. Van Nostrand Company, 1923. Price: $2.50.* The book is based on lectures given by the author. The subject is treated under the headings: pigments; nomenclature of colors; technique employed in testing; artists' pigments; color theory; elementary color chemistry. The information is not always very definite or accurate. We are told, p. 29, that cadmium yellow can vary from light yellow to fiery orange; but not the causes for these differences. On p. 46 the author says that "optically cobalt blue reflects a considerable amount of green and violet light," whereas it really transmits these rays in addition to the blue. It is not accurate to say, p. 74, that "a true theoretical lake pigment is best represented by a compound of which the natural or artificial organic coloring principle is united in equivalent proportions with a metallic inert base to form an insoluble, transparent, unalterable pigment." Basic and acid dyes are not subdivisions under the general heading of substantive dyes, p. 77.

The reviewer questions the propriety of advertising the author's Permalba in just the way he has adopted, p. 99. The book may be good enough for art students but it can scarcely be commended to chemists, although the reviewer did learn from it, p. 31, that cadmium red contains cadmium selenide.

Wilder D. Bancroft

ERRATA

In the footnote to Mr. Adam's paper, p. 97, the word 'if' has been omitted from the first sentence, which should read: "Dr. Langmuir has pointed out to me that if the expanded films consist of molecules oriented vertically and projecting from the surface, these molecules will have a high potential energy, and may tend to lie down flat on the water surface."

In the paper by Messrs. Bangham and Burt the following corrections are to be made. On page 113 line 5 for S^m read s^m. On p. 116, Fig. 3 A_1 should be directly under A'_1. On p. 117, 7th distribution read 0.875 for 1.875. On p. 118 line 6 read 60 for 20. On p. 118 line 30 read $s^{m/2}$ for $s^{2/m}$. On p. 120, footnote read 'covered' for 'correct'. On p. 121, last column of Table IV read p_t for P_t. On p. 131, line 31 read 'in the previous experiment' instead of 'than the previous experiment.' On p. 125, footnote read 50 cmm. instead of 50 cc. On p. 128 lines 11, 12 read ζ instead of ξ. On p. 128 line 20 delete the parenthesis after 'time-range one.' On p. 129, lines 16, 17 read p^2t and p^5t instead of p_t^2 and p_t^5.

In the paper by Messrs. Patrick and Eberman the equation on p. 225, line 4 should read $K = \frac{.2}{2^{.767}}$ instead of $K = \frac{.2}{2.767}$.

In the paper by Mr. Weiser, on p. 964 second paragraph, change 'more' to 'less', so that the sentence reads: "Further, the results in Table VI furnish almost conclusive proof that the univalent ions are adsorbed less strongly than bivalent barium.

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